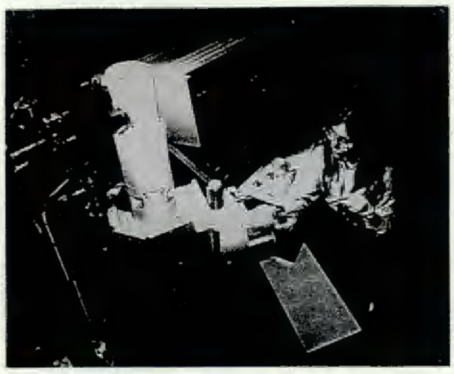
Number Three 1986

Oak Ridge National Laboratory review

Getting Down to the Basics: The Physical Sciences at ORNL

Oak Ridge National Laboratory
review

VOLUME 19 **NUMBER THREE 1986**



THE COVER: *Nicole Heibots changes samples in a scanning electron microscope at ORNL's Surface Modification and Characterization Collaborative Research Center. The microscope is being used to examine the roughness of germanium layers ion-beam-deposited at 600°C on silicon. See article on "Surface Modification Using Ion Beams and Lasers" on page 18. This research is one of many ORNL projects in the physical sciences described in this special issue of the* Review.

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The *Review* is published quarterly and distributed to employees and others associated with the Oak Ridge National Laboratory. The address of the editorial office is: Building 4500-North, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, TN 37831. Telephone: Internal 4-7183, Commercial (615) 574-7183, or FTS 624-7183.

ISSN 0048-1262

OAK RIDGE NATIONAL LABORATORY
operated by Martin Marietta Energy Systems, Inc.
for the Department of Energy

EDITORIAL: PHYSICAL SCIENCES FLOURISH AT ORNL

By ALEX ZUCKER

Basic research is both old and young at ORNL. Old in the sense that it played an important role early in the Laboratory's history, a key role in the development of reactors and in extracting plutonium from irradiated fuel. Young because now, perhaps more than ever before, it is full of promise for the future. Science has never been better, more interesting, or more pregnant with new discoveries and the practical benefits that are sure to follow. What are the roles of quarks and gluons in nuclear matter? Why is a metal ductile or a ceramic tough? Can we make a Wigner solid? How can you make a machine learn from experience? Can we tailor-make surfaces with implanted ions? Can we design molecules for specific separations? How do you program 1000 parallel computers? These and many equally fascinating questions are being studied at ORNL. Read on in this issue of the *Review*, and you will find some answers emerging, at first seemingly answering one puzzle with another, but here and there the answers solidify, take shape, and enrich our vision of the world.

But there is more to the physical research program at the Laboratory than a string of isolated research projects. The advantages of working at a large laboratory are apparent in many visible and invisible ways. For example, the ion-source expertise developed for nuclear-physics accelerators turns out to be invaluable to the surface modification group in their ion beam deposition experiments. Then, in turn, the ion implantation facilities prove to be useful in studying such disparate topics as corrosion and ceramics. Many projects depend critically on the Laboratory's strength in instrumentation, on the engineers from the central staff of Martin Marietta Energy Systems, Inc., and most importantly on the builders and operators of large facilities, research reactors, and accelerators.

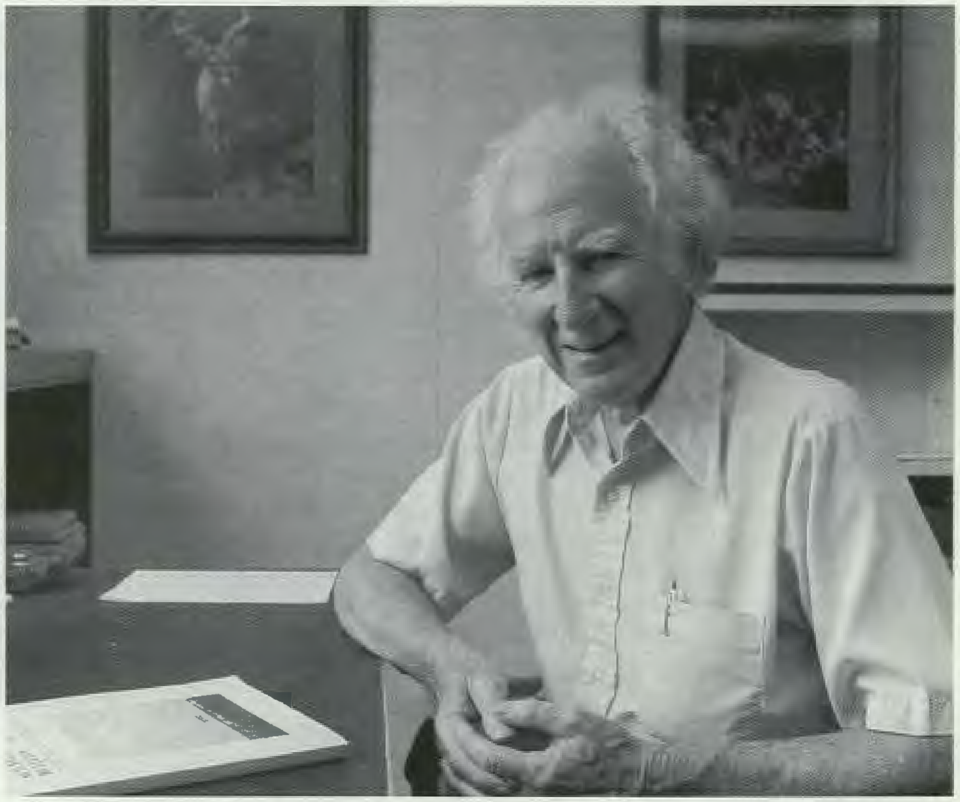
Theoretical research has special roles to play. Theorists help interpret results and draw from them new insights which in turn expand our fundamental understanding. In some cases, rare ones to be sure, a theoretical prediction is proved to be true by a new experiment. What a triumph that is!

We do many things at ORNL, and the question naturally poses itself: how do we decide what research we will do, what we will emphasize, and where we will decline involvement? The first criterion is that the research must somehow be connected with energy. The connection need not be short term, indeed in basic research it cannot be short term, but somewhere there must be a plausible view that what we do will improve some form of energy production or consumption or waste handling. A second criterion has to do with large facilities. The Department of Energy is the builder par excellence of large research facilities. The Atomic Energy Commission gave the world research reactors and accelerators, and DOE as its successor carries on this trust. We at ORNL carry on this tradition. We exploit our large facilities in nuclear and atomic physics, in condensed-matter research, and, finally, in the study of the large machines themselves. A third and emerging criterion is that our facilities be made available to the academic and industrial communities. This requires a partnership between our scientists and the many hundreds of users who come to ORNL each year to work, to take advantage of our instrumentation, and to draw on the help of our experienced and excellent staff.

Physical research at ORNL is varied, lively, and above all intellectually exciting, as reflected in this issue of the *Review*.

The* Review *staff gratefully acknowledges Ellison Taylor and Lydia Corrill for their many hours of invaluable editorial assistance. Special thanks are also due Dick Hahn of the Chemistry Division, Lou Mansur of the Metals and Ceramics Division, and Karl Erb, formerly of the Physics Division (and now with the National Science Foundation), for their help in planning and soliciting articles for this special issue. We also thank the many contributors for eloquently describing ORNL's interesting projects in the basic physical sciences.

Arthur H. Snell, a nuclear and atomic physicist, has been a consultant to ORNL since 1973. Before then, he was an ORNL associate director (1970–1973), an ORNL assistant director (1957–1970), director of the Thermonuclear Division (1958–1967), and director of the Physics Division (1948–1957). Snell came to ORNL in 1944 from the Metallurgical Laboratory (Manhattan Project) of the University of Chicago, where he was chief of the Cyclotron Section. He holds a Ph.D. degree from McGill University in Montreal. From 1954 through 1961 he served as chairman of the Subcommittee on Instruments and Techniques of the Committee on Nuclear Science of the National Academy of Sciences–National Research Council. He is a Life Fellow of the Royal Society of Arts and a Fellow of the American Physical Society and American Association for the Advancement of Science.



The Origins of Physics Research at ORNL

By ARTHUR H. SNELL

The first physics research at Oak Ridge National Laboratory (then the Clinton Laboratories) was stimulated by the presence of the Graphite Reactor, which started operating in November 1943, slightly less than a year after the original nuclear chain reaction had been achieved in the CP-1 experiment in Chicago. Locally known as "the Pile," the air-cooled Oak Ridge reactor was the first to operate at power. As such, it not only served as a base for a crucial development in reactor engineering, but also (like the heavy-water CP-3 reactor at the Argonne Forest Preserve, outside Chicago) offered wonderful new opportunities for basic science.

The advance in reactor engineering resulted from the "water-lattice" experiments at Oak Ridge. Previously, natural water had not been considered as a neutron moderator in a reactor in spite of the evident simplicity of having a single material serve as both moderator and coolant, because its light hydrogen would capture too many neutrons. However, light hydrogen is the most efficient substance for slowing the fast neutrons produced in fission. Thus, it was later believed that uranium fuel elements in water could be spaced much more closely than they were in the graphite reactors and still provide enough moderation.

Experiments in massive uranium at Chicago and Oak Ridge had shown that fast-neutron fission could be an important source of neutrons in a reactor in which the fuel-rod spacing was closer than in the air-cooled graphite reactors. The question was, Could these neutrons from fast fission make up for the losses of slow neutrons captured in a light-water reactor? Alvin Weinberg (who became ORNL director in 1955) had been examining the question, and his results, along with the measurements in massive uranium, suggested that a light-water reactor might indeed be possible.

Thus, in 1944, a team of experimentalists, including Bernard Feld, Henry Newson, Louis Slotin, Seymour Bernstein, and Haydn Jones quantified the situation in a series of measurements of uranium rods in various arrangements and spacings in a tank of water on top of the Pile. In all, 17 different water lattices were examined. The Oak Ridge researchers concluded that light-water cooling would be possible if the natural uranium were slightly enriched in its fissile isotope uranium-235.

Eugene Wigner, a Nobel Prize-winning physicist who served as research director of ORNL in 1946, guided reactor development at the Laboratory. He and Alvin Weinberg coauthored a book on the theory of reactors, a copy of which he is holding.

In the years that immediately followed, physicists, chemists, and engineers jumped into the development of this attractive reactor concept. Eugene Wigner, a Nobel Prize-winning physicist who was research director of the Laboratory in 1946, made suggestions of fundamental importance to reactor development. Many experimental physicists divided their time between basic physics and the measurements required for reactor development: the pertinent neutron cross sections (the target area for interaction with various nuclei) measurements of neutron diffusion in different materials, neutron-reflection measurements, and shielding studies. But for the theorists, as I recall, reactor development was dominant. In fact, the only basic theoretical physics of those times that comes to mind is Maury Rose's computation of atomic K-shell internal conversion coefficients using the vacuum-tube computers that were available at Harvard University and elsewhere. The fruits of the reactor work are well known: the Materials Testing Reactor in Idaho, the Low Intensity Test Reactor at Oak Ridge, and, more generally, the civilian and the naval power reactors that were developed in the United States.

Neutron Diffraction at the Pile

In the history of basic physics experimentation at Oak Ridge, the field of neutron diffraction has a dominant position. Slow neutrons had been known to undergo X-ray-like diffraction by crystals. When the steady, intense neutron beams became available at the Oak Ridge pile and at the CP-3 reactor, spectrometers were immediately set up. Ernie Wollan, who was experienced in X-ray diffraction, was the leader in the local effort, which involved adapting an X-ray spectrometer to neutron use. Various crystals that were tested as monochromators included gypsum, calcite, rock salt, and bent quartz (all of which later were replaced by metallic crystals and still later by graphite). The single-crystal reflections contained monoenergetic neutrons that were smoothly adjustable in energy by varying the angle of reflection. One of the first experiments using single-crystal reflections obtained a measurement of the well-known absorption resonance in cadmium; the cross section was found to be 6750 barns at a neutron energy of 0.176 eV.

In 1946 Wollan brought a second X-ray spectrometer from Chicago and modified it also for neutron use. Coupled with the first, it gave a "two-axis" assembly in which the structure of a crystal mounted on the second axis could be studied by its diffraction of energy-selected neutrons from the first crystal. Techniques improved in sundry ways, and a big break came when it was found that, as with X rays, powdered crystal samples could be

The history of physics at ORNL begins with reactor development. Many early physics experiments, especially those in neutron diffraction, were performed at the Graphite Reactor. Later, ORNL physicists turned to new instruments (some of which they had developed) and new accelerators for their experiments. An early experiment at ORNL that had a profound effect on reactor development was the water-lattice experiment. Experiments that advanced nuclear physics included demonstrations of the spontaneous decay of the neutron, the relationship between Coulomb excitation and the shapes of nuclei, and the rich possibilities of heavy-ion interactions.

used for structure studies—big single crystals were not needed. The feasibility of powdered crystals allowed ORNL researchers to obtain in 1948 the first Laue diffraction pattern using neutrons. Another triumph followed when Wollan, Cliff Shull, and W. L. Davidson determined the locations of the hydrogen atoms in ice and settled a controversy over which theoretical suggestion about atomic positions was correct. Similar work followed on the hydrides and carbides of heavy elements.

The group gathered strength with the arrival of Wally Koehler and Mike Wilkinson around 1950. By then attention had switched largely to magnetic structures in solids. The monoenergetic neutron beams could be made of neutrons whose magnetic moments were polarized mostly into a common direction either by passage through magnetized iron or (better) by reflection from a magnetized "first axis" crystal. In 1949 Shull and Jim Smart had observed the formation of the first antiferromagnetic lattice as manganese oxide was cooled below 80 K. In 1951, after further technological advances, another high mark was reached with the discovery that a single crystal of iron oxide (Fe_3O_4) in a magnetic field could be made to yield a monoenergetic reflected beam that is almost 100% polarized. In all, these developments initiated an expanding field in solid-state science.

Other Experiments at the Pile

In addition to the neutron diffractometer, Wollan's associates John Dabbs, Charlie Moak, Lou Pardue, Harvey Willard, and Merle Burgy set up two cloud chambers in 1945. They were used to measure (1) the energies of the gamma rays emitted during neutron capture in samples placed in a neutron beam and (2) the energies of delayed neutrons in fissile samples that emerged from the pile in the "fast rabbit." They also observed the "long-range alpha particles" that occasionally accompany fission, although more definitive work was to follow using an ionization chamber. (The long-range alphas are droplets of nuclear matter left behind as the two big fragments separate; they are shot out equatorially by electrostatic repulsion.) Dave Saxon, Erwin Shrader, and I set up an apparatus to look for the radioactive decay of the free neutron (see sidebar on page 6).

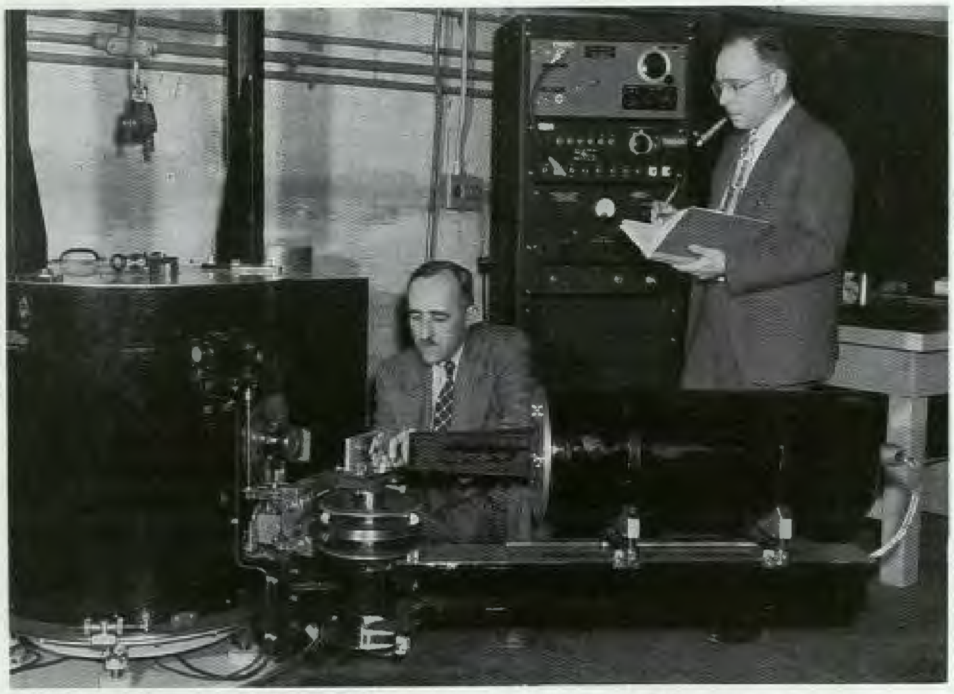
A carbon-14 factory was circulating ammonium nitrate solution in and out of the pile in a production process that may have been chemically naîve but gave rapid yields, some of which were of high specific activity. With this product, Dewey Norris and Mark Inghram obtained the first reasonably accurate value for the half-life of carbon-14—6100 years. (Previous estimates varied between 2000 and 25,000 years. The modern value is 5600 years.) In 1950, a magnetic resonance experiment by Norman Ramsey of Harvard University and ORNL's Jim Smith showed that if the neutron should happen to possess an electric dipole moment, the separation between its +e and −e charges must be less than 3×10^{-19} cm.

Away from the Pile

In the surrounding laboratories and offices at ORNL, many other physics investigations were devoted to the products of the pile. Paul Levy's magnetic beta-ray spectrometer measured the internal conversion lines of several heavy-element isotopes (e.g., gold-198 and iridium-192). Photoneutron sources that were evaluated involved pile-produced radioisotopes, such as sodium-24, gallium-72, and lanthanum-140, which emit gamma rays sufficiently energetic to knock neutrons out of beryllium or deuterium. In the evaluation, a typical radioactive source of known gamma-ray strength was centered in a 10-cm-diameter sphere of beryllium or deuterium oxide and the neutron output of the assembly was compared with that of a neutron source of known strength. The derived (γ, n) cross sections for beryllium and deuterium were found to lie in the range of 10^{-28} to 10^{-27} cm^2.

The Nuclear Data Group was established in 1946 at ORNL by Katherine Way, who had performed a valuable service of collecting and evaluating data in Chicago during the war. The group systematized and summarized the increasing worldwide flood of experimental nuclear information.

The field of instrumentation deserves special mention. During the war, our nuclear counting equipment, although the best available, was nevertheless uncertain and had to be watched—from its rectifiers to its amplifiers and the scales-of-64 that registered on clunking mechanical counters. Then in 1946, P. R. Bell and Walt Jordan came to ORNL from the wartime Radiation Laboratory at the Massachusetts Institute of Technology. They developed the A-1 Amplifier, which offered tremendous improvements in versatility and reliability. The A-1 became an accepted workhorse at ORNL and other nuclear laboratories. With it came refinements in the pulse-height selector circuits; the rise-time of a pulse was sharpened, and the tail of its fall was cut off, to reduce pile-up. (A welcomed improvement in scalers also came from Willie Higinbotham, then at Los Alamos.) Another innovation used at ORNL and elsewhere were the scintillation detectors, which replaced the slow and often inefficient beta- and gamma-ray counters and the cloud chambers. Appropriate scintillators had to be found; anthracene and stilbene were used, to be followed



Ernie Wollan (left) and Cliff Shull work at the old neutron diffractometer at the Graphite Reactor in the 1940s.

by thallium-activated sodium iodide. Some readers also will recall the light pipes and the 1P21 and the 5819 photomultiplier tubes used back then. Multichannel analyzers followed, locally under the leadership of P. R. Bell and George Kelley. Kelley's 20-channel analyzer, for example, enabled ORNL scientists to measure a pulse-height spectrum 20 times faster than previously, and his subsequent 100-channel analyzer offered even greater measurement speed.

One example of the impact of instrumental developments on early physics research in Oak Ridge was the search for short-lived nuclear isomeric states. Sergio de Benedetti and Francis McGowan in 1947 used two Geiger counters in a common tube with a radioactive source between them. A beta particle entering one counter would produce a pulse, but it would be followed by a dead time in that counter. If an isomeric state had been produced, a conversion electron from its decay in the source would have to enter the other counter to be registered, whereupon the lifetime of the isomeric state could be measured by the method of delayed coincidences between the first and second counter pulses. Using this equipment, the physicists found four isomers out of about 60 radionuclides examined; the half-lives of these isomers range from 20 μs in tantalum-181 to 0.65 μs in rhenium-187. Three years later, using new electronic devices and two anthracene or stilbene crystals with the source sandwiched between them, both the efficiency and the sharpness of the pulses were so improved that McGowan found an additional group of isomers having half-lives ranging from 130 ns (lutetium-177) to 0.8 ns (osmium-186). The improved instrumentation had increased the sensitivity of the experiments by a factor of 1000.

The Standard Pile

To permit interlaboratory comparisons, some slow-neutron measurements had to be stated against a common standard. To make this possible, a "standard pile" was built at ORNL. It was a stack of graphite, 1.2 × 1.2 × 2.4 m (4 × 4 × 8 ft) high, in which a 1-g radium-beryllium neutron source was placed. The sensitivity of any slow-neutron detector, be it a counter or an indium foil, could be determined by exposing it at a given distance from the source and measuring its counting rate or induced radioactivity; conversely, neutron source strengths could be interrelated. The pile was calibrated against a similar pile at the National Bureau of Standards in Washington, D. C.

Fast-Neutron Spectrometry and Accelerators

From 1948 through 1952 physics research at ORNL became diversified. One reason for this trend was the requirement for more complete sets of fast-neutron cross section data for materials expected to be used in future power-reactor development. The slow-neutron energy range (up to a few eV) had already been widely researched. The next energy range, into the tens of keV, was under study mainly by using neutron beam choppers with time-of-flight equipment. The original choppers had been used with cyclotrons; the first chopper at the ORNL pile, built by Gerry Pawlicki and Ed Smith, had a 10-m flight path and came into operation in 1952. It was largely patterned after one that had been in service at Brookhaven National Laboratory.

However, the hundred-keV and MeV-neutron energy ranges became subjects of concern. Reactors that would generate plutonium-239 faster than they consume uranium-235 ("breeders") would be fast-neutron, not slow-neutron, reactors. Thus, a new energy range of neutron capture, scattering, and fission had to be explored. The widely used procedure for generating the necessary monokinetic neutrons involved bombarding a thin lithium target

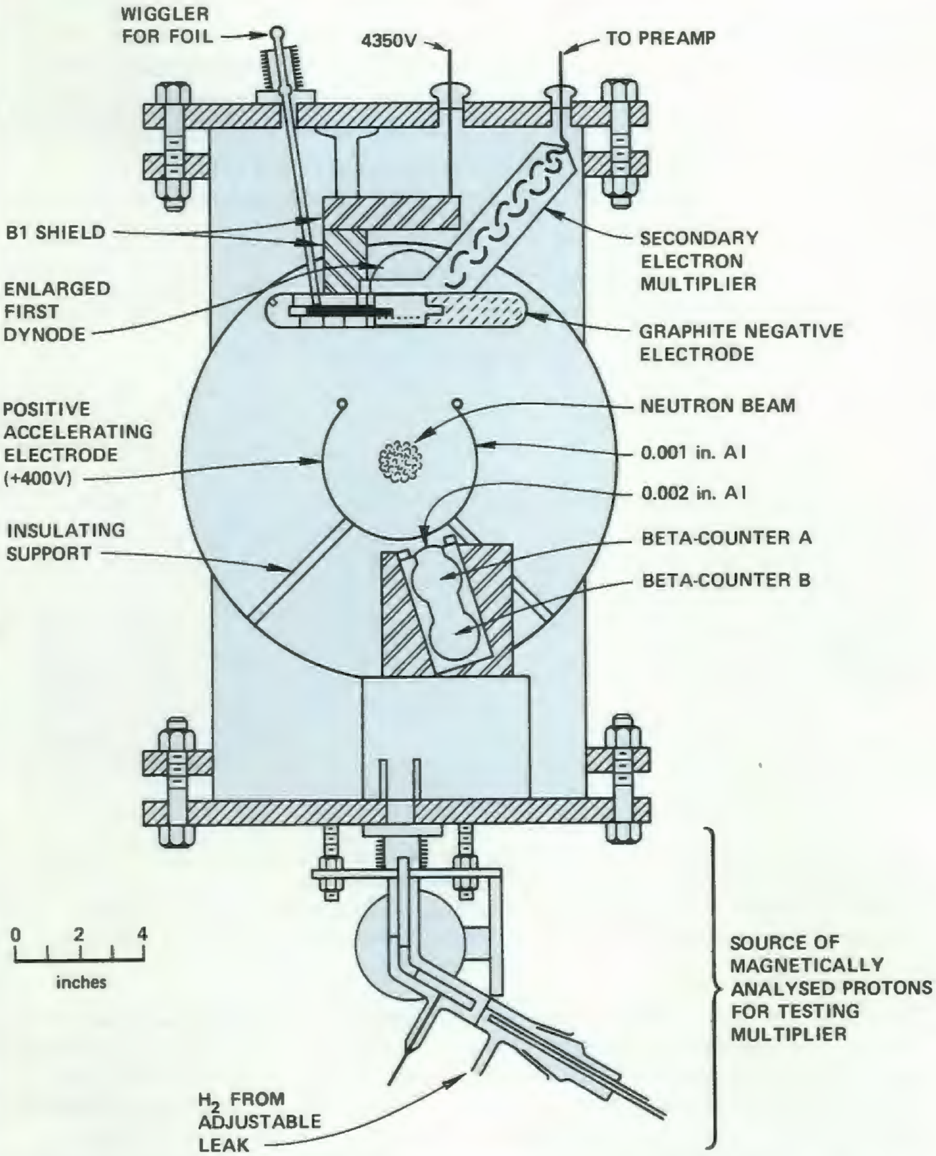
The Spontaneous Decay of the Neutron

The neutron was discovered in 1932, and three years later it was found to be appreciably heavier than the proton. The immediate suggestion was that it is probably radioactive, and like many other known radioactivities, emits a beta particle and a neutrino to transform itself into its more stable partner—the proton. The measured mass difference between the nuclear partners showed that the neutron's beta particles would probably have energies up to 750 kilo electron volts (keV) and that their emission would probably cause the protons to recoil with energies up to 760 eV. These numbers prompted the prediction that the half-life of the neutron is on the order of minutes.

The concept was intriguing at the time; it was the first suggestion that an elementary particle might spontaneously transform itself into other elementary particles. Deeper implications resulted from the fact that it was the only case of pure beta interactions, the influence of other nuclear effects being absent because of the lack of neighboring nucleons.

An early response to the experimental challenge was that of Luis Alvarez and Cornelius Tobias at the University of California at Berkeley, but their work was interrupted by the war. In 1946, using one of the steady, slow-neutron beams available from the Oak Ridge Graphite Reactor, Erwin Shrader, David Saxon, and I started looking for the neutron's radioactivity. We sent a collimated, horizontal neutron beam lengthwise through an evacuated tank, entering and leaving through aluminum-foil end windows. In the midsection of the tank, we had an electrostatic collection system that would pull the sought-for protons sideways out of the neutron beam and focus them on the first dynode of an electron multiplier—a

Art Snell at the neutron decay apparatus on the north balcony of the Graphite Reactor, around 1947.



Cross-sectional diagram of the neutron decay apparatus. The neutron beam (center) is perpendicular to the paper.

high-vacuum device that amplified an initial pulse resulting from the impact of a positive ion. Many background pulses resulted, but subsidiary tests, such as interrupting the neutron beam before it could enter the vacuum tank, left a component of counts that might well be the result of protons produced by neutron decay.

Leonard Miller and I increased the stringency of the tests, and in 1948 at a meeting of the American Physical Society, I explained that about one-third of our multiplier counts could be caused by neutron decay and that we were proceeding to look for coincidences between these positive-ion counts and beta-particle emission. After my talk, Luis Alvarez came forward from the audience and said, "You've got it!"

Frances (Tony) Pleasonton, Reuben McCord, and I performed the coincidence work using a specially designed apparatus. In this arrangement, to be registered as a neutron decay event a count would have to satisfy three conditions: (1) a beta particle would have to pass through the foil of the focusing electrode, pass through the window foil of counter A, and produce a coincidence between counters A and B; (2) a positive-ion pulse would have to be registered on the multiplier; and (3) because it would take 0.25 μs for a proton to be accelerated onto the multiplier, the AB coincidence pulse would have to be delayed before being put into coincidence with the multiplier pulse. Walter Jordan arranged a coincidence circuit for us that embodied the 0.25-μs delay line; it identified the positive ion as a proton because any likely impurity ion would take longer to be accelerated; in other words, the protons were identified by time of flight.

With this arrangement, we found about 0.7 delayed coincidences per minute that survived corroborative tests as to their origin in the neutron beam and not in residual hydrogen in the vacuum tank. We were satisfied that we were seeing the radioactive decay of the neutron, and we estimated its half-life to be in the range of 10 to 30 min.

While we were making this cautious progress, John Robson had written to us that he planned to undertake a similar experiment at the Chalk River Laboratory in Canada. He had access to a much stronger neutron source there—the NRX reactor, which was producing neutron beams about 40 times as intense as those from our Graphite Reactor. He added a magnetic lens spectrometer for proton identification. So he caught up with us, and we published our results simultaneously in 1951. However, there is little doubt that the decay of the neutron was first observed at ORNL. Our getting there first was later recognized by the science museum of the Smithsonian Institution in Washington, which invited us to send our apparatus there as an exhibit. Unfortunately, it had already been scrapped.—*A.H.S.*

with protons from a Van de Graaff accelerator, resulting in the ^{7}Li(p,n)^{7}Be reaction (lithium absorbs a proton and, upon transmutation to beryllium, emits a neutron). With the smooth control of the proton energy and variation of the angle at which the neutrons emerged from the lithium (relative to the proton beam), the bumps and resonances of a sample's scattering and absorption cross sections could be surveyed in an energy-continuous manner.

ORNL's first accelerator was a 200-kV Cockcroft-Walton set, locally assembled in 1949. It was built in the abandoned heating plant building below what is now the cafeteria. Its transformers, capacitors, and rectifiers were mounted on a structural frame of wooden four-by-fours that had been soaked in paraffin. While pigeons fluttered about the ceiling high above the accelerator, Bill Good, Walt Kunz, and others studied

Coulomb Excitation and the Shapes of Nuclei

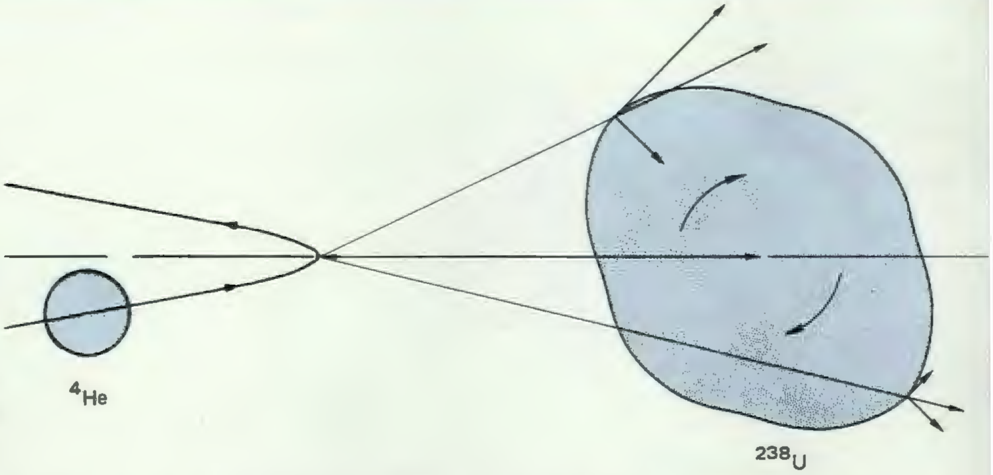


Fig. 1. An incident alpha particle approaches an ellipsoidal nucleus and is scattered aside by the electrostatic repulsion of their positive charges. The repulsion can lead to a tumbling rotation of the nucleus and a slight loss of the alpha particle's incident kinetic energy. The nucleus loses its resulting rotational energy by gamma-ray emission.

When a light positive ion such as an alpha particle approaches a nucleus, the mutual Coulomb repulsion between the two positively charged particles causes a scattering of the path of the ion and a gentle recoil of the heavier nucleus; this phenomenon, in fact, had led to the concept of the nucleus in 1911. As techniques and understanding developed through the years, much more detail has developed concerning the sizes and shapes of nuclei. One fruitful source of information has come from the study of "Coulomb excitation" of the target nuclei.

Despite the elementary concept of the nucleus as a tiny, dense, positive dot in the middle of a cloud of atomic electrons, nuclear physicists have found that many, if not most, nuclei are not true spheres. Consider, then, the situation pictured in Fig. 1. Here an alpha particle approaches a heavy nucleus that is ellipsoidal in shape. Because the Coulomb force is long-range, the repulsion can bounce the alpha particle aside or even mostly backward before a collision with the nuclear surface occurs. The recoil of the nucleus, however, can take the form largely of a rotation of the ellipsoid. The nucleus would then emit one or more gamma rays as its rotation stops, and the associated quanta would belong to the "rotational band" independently known in the gamma-ray spectrum of that nucleus. The intensity of the gamma rays has further implications because their excitation can be related through the theory of nuclear structure to the shape of the original target nucleus.

ORNL's Coulomb excitation studies, which had been pursued in the High Voltage Laboratory since the early 1950s, culminated in the 1970 work on the actinide series of elements. The measurements were made by Curt Bemis, Francis McGowan, Jim Ford, Bill Milner, Paul Stelson, and Russell Robinson of the Physics Division. They did not use gamma-ray spectroscopy, but instead made accurate measurements of the energy loss undergone by the scattered particles in starting the rotation of the target nuclei. Using 16- and 17-MeV alpha particles from the tandem accelerator, they bombarded small, thin targets of isotopically separated samples of 12 actinides that had even atomic numbers and weights from thorium-230 to curium-248, and performed magnetic analyses of the alpha particles scattered backward at an angle of 150° from the direction of incidence.

The pertinent results in the case of plutonium-240 (^{240}Pu) are shown in Fig. 2. The highest peak is the result of elastic scattering, no rotation being promoted in the Pu nucleus. But a second peak 42.8 keV to the left of the elastic peak corresponds to a transition in the ^{240}Pu from the spinless ground state to the first excited state in the rotational spectrum. This is a quadrupole ("E2") transition, and the intensity of this peak relative to the elastic peak is interpretable in terms of the degree of ellipsoidal departure from a sphere.

light-element nuclear reactions in detail, and George Evans, Paul Stier, and Clarence Barnett made early studies of the "ionization contours" of heavy ions as they slowed and stopped in various gases. The apparatus served also as a center for developing ion sources and detectors.

Meanwhile, Dick Lamphere converted a 2-MV Van de Graaff machine in the Chemistry Division from electron acceleration to positive-ion acceleration. In 1951 the 5-MV Van de Graaff accelerator that had been in use at the Y-12 Plant was transferred to X-10, as were its knowledgeable supervisors, Joe Bair and Conway Snyder. The High Voltage Laboratory (Building 5500), which was ready in 1952, became the home for these accelerators and the commercially built 600-keV Cockcroft-Walton accelerator. Thus, in the early 1950s, the ORNL physics group was well-equipped for fast-neutron

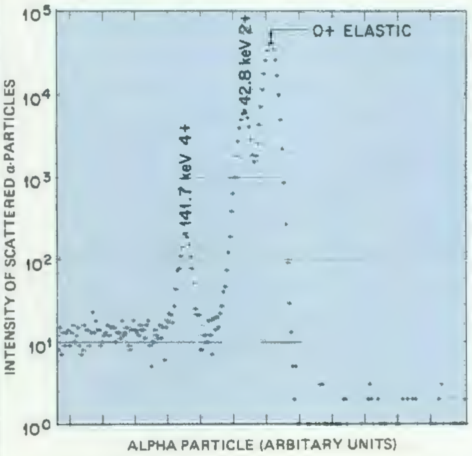


Fig. 2. Energy spectrum of 17-MeV alpha particles scattered through an angle of 150° from a thin target of ^{240}Pu. The high peak is the result of elastic scattering (no rotation induced in the target nucleus). The smaller peaks show energy losses respectively of 42.8 and 141.7 keV as a result of induced rotation. The relative intensities of the three peaks are interpretable in terms of the shape of the ^{240}Pu nucleus.

However, a third peak also appears at an energy loss of 141.7 keV in the scattered alphas. The intensity of this peak indicates the presence of a direct transition from the ground state to the second excited state—an "E4" or hexadecapole (16-polar) transition. In terms of nuclear shape, this peak indicates an equatorial bulge in addition to the pure ellipsoid. The relative intensities of the E2 and E4 peaks indicate the extent of this bulge; in fact, the ground-state shape of the nucleus is quite accurately derivable.

Fig. 3. Model of the ^{234}U nucleus as derived from scattering data qualitatively similar to that of Fig. 2. The elongated shape is supplemented by an equatorial bulge. The nucleus is 2×10^{-12} cm long and 1.5×10^{-12} cm in equatorial diameter.

In the early 1970s the ORNL physicists found that in the actinide group, the ground-state bulge is most prominent in the lighter members. Their scaled-up model of the uranium-234 nucleus is shown in Fig. 3. The nucleus is 2×10^{-12} cm long, and its equatorial diameter is 1.5×10^{-12} cm. The ORNL investigators also found that *as the nuclei of actinides get heavier, the size of the equatorial bulge* decreases and that ^{244}Pu, ^{244}Cm, ^{246}Cm, and ^{248}Cm nuclei are purely ellipsoidal. However, the lighter, closed-shell lead-208 nucleus is a sphere. Previous work at other laboratories had shown a similar tendency in the shapes of nuclei in the rare-earth *elements.—Arthur H. Snell and Paul H. Stelson, Physics Division.*

cross-section measurements and for many other activities. Technical improvements at ORNL, such as Charlie Moak's radiofrequency ion source, were partly responsible for continuing success.

Interest in basic theoretical physics gained strength in another aspect of the diversification. Some of this interest was related to the experiments that were in progress. Examples included the consideration by Maury Rose and Larry Biedenharn of the angular correlations between emissions from nuclei and George Trammell's work concerning neutron scattering in the paramagnetic lattices of rare-earth elements. Other parts of the ORNL effort were more purely theoretical, like Ted Welton's probing into relativistic quantum electrodynamics, or more calculational, like Rose's continued computation of internal conversion coefficients and its extension toward the probabilities of Auger transitions.

In the Electronuclear Division at the Y-12 Plant (Bob Livingston, director) cyclotrons were under development. The 86-in. cyclotron, which came into operation there in 1951, provided a beam of 23-MeV protons that slammed 30 kW of power into its (well-cooled) target. It was used first for isotope production, but subsequently its beam was extracted for use by Bernie Cohen's group of experimenters. The 63-in. cyclotron followed; built into one of the calutron racetracks, it accelerated nitrogen ions. Using this device, Alex Zucker, Harry Reynolds, and others were able not only to quiet fears that the explosion of a hydrogen bomb might ignite the world's atmosphere, but also to learn that interactions between heavy nuclei promised to be a fruitful field of nuclear investigation.

Further Activities of the Early 1950s

Other activities and achievements in the physics community at ORNL from 1950 through 1955 are listed below along with the names of the scientists involved in the work.

- In neutron diffraction the study of magnetic lattices continued, particularly in the family of perovskite compounds (e.g., $LaMnO_3$). Shifts were observed between paramagnetic and antiferromagnetic lattices as the temperature was varied. (Shull, Wollan, Koehler, Wilkinson, et al.).
- Coulomb excitation (see sidebar on page 8) and the energy levels of the target nuclei were revealed by gamma-ray spectroscopy (Stelson et al.).
- Work on short-lived isomers continued (McGowan).
- In atomic physics, studies of the ionization states of heavy ions in target gases extended to the higher energies available from the newer accelerators and the 63-in. cyclotron (Stier, Zucker, Reynolds, Barnett, et al.).
- Many details about specific nuclear reactions, including particle and gamma-ray emission, coincidences, angular correlations, and comparisons with theory, were obtained by many researchers.
- Nuclear recoil following neutrino emission was measured. The measured energy (9.6 eV) of recoiling chlorine-37 atoms following electron capture in argon-37 showed that a single neutrino is emitted at an energy predictable for the formation reaction $^{37}Cl(p,n)^{37}Ar$. Observation of seven different charges of the recoiling atoms stimulated further interest in the consequences of forming an atomic inner-shell vacancy (Pleasonton, Snell).
- Nuclear alignment in magnetic fields was achieved at the extremely low temperature of 0.035 K, a record at the time (Louis Roberts, Dabbs, et al.).
- The 5-MV Van de Graaff accelerator was adapted for time-of-flight measurements of fast-neutron cross sections using the $^7Li(p,n)^7Be$ reaction having nanosecond beam pulses and a 5-m flight path (High Voltage group).
- Fast-neutron fission cross sections were measured for several heavy nuclides (e.g., uranium-234 and uranium-238) up to 6-MeV neutron energy, giving thresholds, resonances, etc. (Lamphere).
- Gamma-ray emission accompanying fission was found to be continuous in energy (Jack Francis and R. L. Gamble; Fred Maienschein and Bob Peelle).
- Several physics groups shared in the development of liquid scintillation particle detectors and europium-activated lithium iodide detectors.
- The Oak Ridge Automatic Computing and Logical Engine (ORACLE) was installed at ORNL in 1952. A leading computer of its time, it had been built as a collaboration between Argonne and ORNL. ORACLE strengthened all branches of science at ORNL (Alston Householder).

I realize that this brief account of the first decade of physics research may not have cited or adequately covered the work of the many talented researchers in ORNL's physics community. The spirit of the times can perhaps be judged by perusing the 1955 Semiannual Progress Reports of the Physics Division and the former Electronuclear Division, which list more than 50 different activities in basic physics research; results of these activities were described in 25 scientific papers published in a six-month period and in 40 papers presented at scientific meetings. Basic physics at ORNL was in step with the times. ornl

The Origins of Chemical Research at ORNL

By ELLISON H. TAYLOR

The chemists who came to Clinton Laboratories (later Oak Ridge National Laboratory) in 1943 had a straightforward mission—to extract the plutonium from the uranium fuel slugs of the graphite pile then being built on the site. Only trace amounts had been available when the separation process for the Hanford plutonium production plant was being developed, so a test with weighable amounts of plutonium and a realistic mixture of fission products was urgent. How this original program in chemical science evolved during the formative years of the Laboratory (1945–1955) is the subject of this article.

In the Beginning

In the early, practical work, four themes can be distinguished: chemical separations, fundamental chemistry of new or little known elements, radiochemistry, and radiation chemistry. In practice, the first three were often involved at once, and the possible effects of intense radiation always had to be considered in planning or drawing conclusions from experiments in these areas.

For example, a typical request might ask for the determination of

Ellison Taylor, former director of ORNL's Chemistry Division and now an ORNL consultant, is a native of Kalamazoo, Michigan. He received his education from Cornell and Princeton universities. For two years he taught physical chemistry and thermodynamics at the University of Utah, where his students included current and former ORNL staff members George Adamson, Charles Coleman, and Jerry Kielholtz. He returned to Cornell to teach chemical engineering but left in the spring of 1942 to conduct war research at Columbia University, taking a leave of absence for six months. The work turned out to be part of the Manhattan Project so he remained at Columbia until the end of the war. Taylor came to the Chemistry Division of Clinton Laboratories in October 1945 to work on the forerunner of the Homogeneous Reactor. In 1946 he was appointed assistant director of the division by J. R. Coe; soon after he became acting director when the latter contracted tuberculosis. Subsequently, he served as group leader and as associate director of the division and, for three years, as Assistant Laboratory Director. From 1954 to 1978 he was director of the Chemistry Division, from 1974 to 1978 he was a senior staff member of the division, and since his retirement in 1978, he has been a consultant. During a leave of absence in 1965, he was a visiting professor of chemistry at Cornell. With several colleagues, including at various times Max Bredig, Sheldon Datz, Harold Kohn, Ralph Livingston, Bob Minturn, George Moore, Cole Waggener, John Wethington, and Henry Zeldes, Taylor conducted research on the use of molecular beams for studying chemical reactions, the use of ionizing radiation for the study of heterogeneous catalysis, the identification of the hydrogen atom in irradiated frozen solids, the measurement of forces in adsorption, and the denunciation of polywater. Here, Taylor adjusts an apparatus for studying the bending of a thin, bimetallic ribbon by preferential adsorption of a gas (e.g., oxygen) on one side.

the fission yield of a particular ruthenium isotope, which would require learning (or discovering) something about its chemistry, working out a satisfactory separation method, and, finally, making the desired radiochemical measurement. The urgency of the mission required all this work to be focused closely on the practical goals, but the materials concerned (new isotopes and unusual elements) and the conditions encountered (intense radiation and minute amounts of material) gave it many of the characteristics of research.

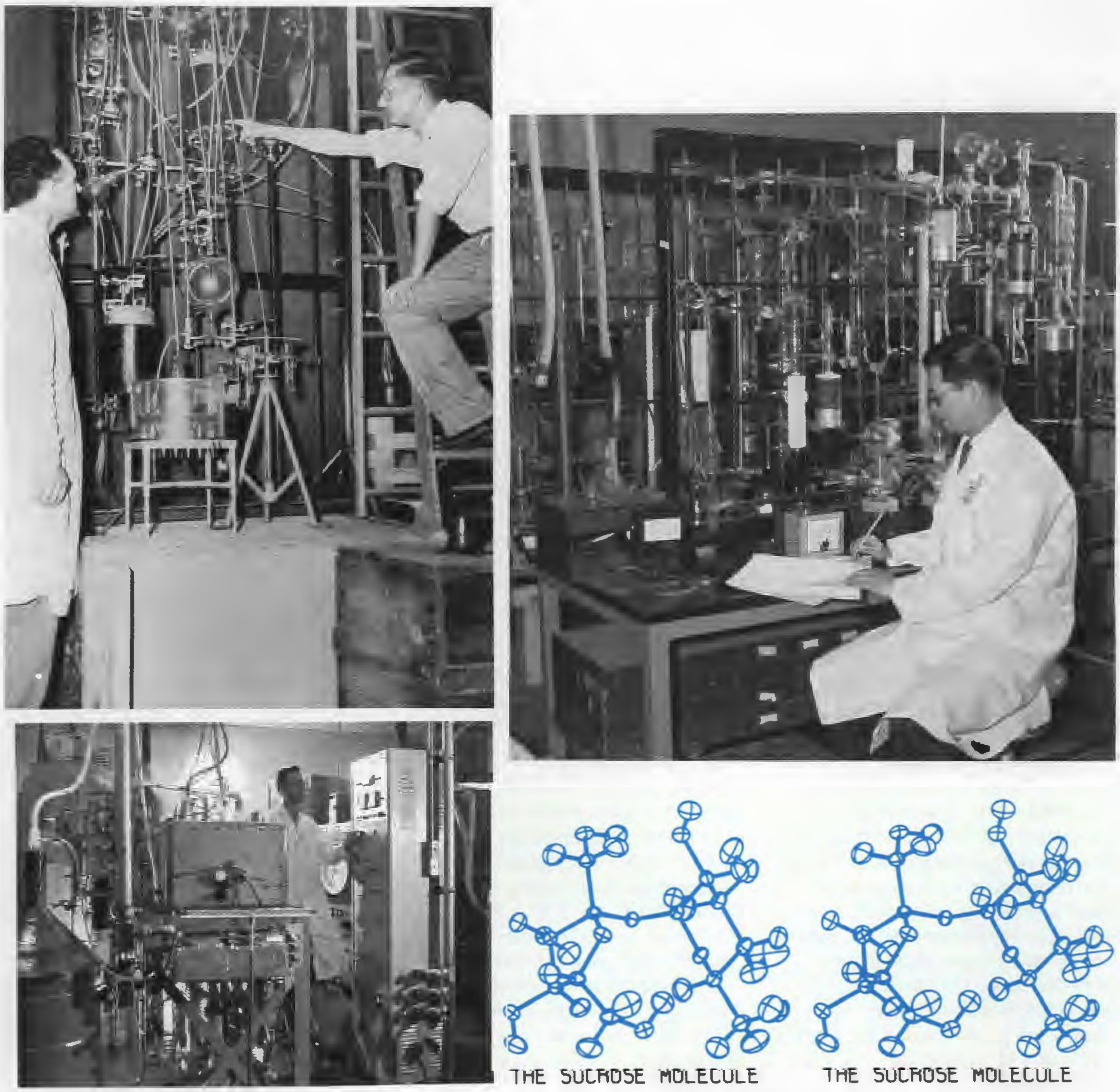
Evolving Laboratory Goals

In the ten years following the end of the war, ORNL underwent its most fundamental change, from a temporary satellite of a temporary project to a permanent national laboratory. What was chemistry like after those ten years? First, the enterprise of which it was a part had evolved. The Laboratory now had multiple goals: building new kinds of reactors (no longer just a pile of uranium and graphite); developing new processes for separating uranium from spent fuel; separating radioisotopes for distribution; and conducting a broad program of research in physics, chemistry, engineering, and biology. Second, part of the Laboratory's mission was to advance general scientific understanding of fields that were considered relevant to nuclear technology. Third, some kinds of research were encouraged not because of their perceived relevance to technology but because some feature of the Laboratory made them especially or even uniquely feasible here. Research requiring short-lived, reactor-produced radioisotopes is a good example.

> ***Chemistry at ORNL from 1945 to 1955 evolved from separating plutonium from uranium fuel slugs in the Graphite Reactor to supporting the multiple goals of a permanent national laboratory: building new kinds of reactors; developing new processes for separating uranium from spent fuel; separating radioisotopes for distribution; and advancing general scientific understanding of fields that were considered relevant to nuclear technology.***

Variations on Old Themes

In spite of the new emphasis on research not tied directly to practical ends, a large amount of the chemistry at the Laboratory continued to focus on immediately practical problems. These efforts included, among others, development of improved separation processes for plutonium, uranium, and fission products from irradiated elements (including a new element—promethium—first produced and discovered at ORNL in 1945); separation of individual fission products and other radioisotopes for distribution to universities and industry; separation of zirconium from hafnium to allow the former to be used as a reactor material; and the development of methods and instruments for chemical analysis of radioactive materials. These activities, which were spread among at least half a dozen divisions, occupied probably 80% of the chemists and chemical engineers at the Laboratory. Although most of this work was focused on practical ends, some opportunities existed for exploring the underlying science. Thus, for



Some examples of chemical research at different stages of the evolution of the Laboratory. Top left: *An early setup at the pile (Graphite Reactor) for conducting simple chemistry under difficult conditions. Here, Robert Garber (right) shows Waldo Cohn features of a chemical separation unit for preparing pure fission products.* Top right: *A homemade glass vacuum system from a slightly later period. Hiroshi Sakurai, one of the early visiting scientists in the Chemistry Division, conducts a gas analysis to measure the yield of (probably) hydrogen in a radiation decomposition experiment.* Bottom left: *Bob Minturn at a second-generation apparatus for studying reactions between crossed molecular beams.* Bottom right: *An example of the capabilities that have been developed in structure determination by neutron diffraction. This drawing of the sucrose (cane sugar) molecule shows the thermal motion of the atoms as ellipsoids centered at the atomic positions.*

example, both the Analytical Chemistry Division and the Operations Division (in its radioisotope program) amassed considerable basic information about radioactive decay schemes.

Much of the nonapplied work in chemical science could still be related to one or another of the original four themes: separations, inorganic and physical chemistry (of particular elements), radiochemistry, and radiation chemistry. A new program in electrochemistry arose because of the need to understand mechanisms of corrosion in the aqueous homogeneous reactor. Certain special opportunities gave rise to work in organic chemistry and to some programs grouped together under chemical physics.

Although bismuth phosphate precipitation, the process chosen for separating plutonium at Hanford, was the focus of separations chemists in the beginning, the relatively new technique of ion exchange was later used extensively in separating fission products and as the basis of an alternative process for Hanford. Noteworthy developments stemming from this early work were rare-earth separations at the Ames Laboratory and the application of ion exchange to biochemical separations at ORNL. Most of the later work in separations at ORNL was done using ion exchange, the most interesting being with anion exchange applied to complex ions of almost all the elements of the periodic table. This work contributed heavily to our knowledge of inorganic chemistry and had wide industrial applications.

Solution Chemistry

Most inorganic chemistry is carried out in aqueous solution, as was the case with most of the practical work at the Laboratory from the beginning. It was, therefore, natural that a good many areas of solution chemistry appeared useful and interesting to explore. Among these were the equilibria and reaction rates between the valence states of uranium and plutonium in various media studied by electrochemical and other techniques and the constitution of various complex ions in solution studied by anion exchange, light scattering, and ultracentrifugation.

The growing interest of the Laboratory in an aqueous homogeneous reactor gave a new direction to some of the basic work on solution chemistry—studies at high temperatures. Little was known about the chemistry of solutions above about 60°C. An extensive program p. 15 examined solutes ranging from uranyl sulfate, because it was the homogeneous reactor fuel, to alkali halides, because they were simple and had been widely studied at room temperature. Measurements included electromotive force, vapor pressure, and solubility, often up to the critical temperature of water (374°C). Both the large amount of data arising from this research and the local availability of excellent computing facilities stimulated the development of new computational techniques for efficient reduction of the thermodynamic data to activity coefficients for compilation and comparison with theory. Incidentally, the Water Research Program, the Laboratory's first major foray into nonnuclear technology, was launched mainly because of the large amount of experience and expertise at ORNL in aqueous solution chemistry.

Research in another kind of solution chemistry began to be supported during the 1950s by reactor interests. Laboratory-wide projects to build, first, an aircraft reactor and then a stationary power reactor that would use molten-salt fuel and coolant led to a massive effort in molten-salt chemistry, embracing work from pure research to fuel preparation and in-pile corrosion testing.

The study of radioactivity had naturally been a particular interest of the Laboratory. In the beginning, chemists were concerned mainly with isolating the nuclides to be studied and performing the simplest measurements, primarily to determine the amount of radioactivity present. With experience, however, they began to encroach more and more on the domain of nuclear physics, making more subtle measurements and concerning themselves with nuclear theory. These newer activities for chemists, now referred to as nuclear chemistry, can be illustrated by the painstaking, precise measurement of the angular distribution of electrons from the decay of phosphorus-32. This work was carried out to define quantitatively the violation of parity conservation, which had recently been discovered and had led to quantum electrodynamics. The new measurements, the most extensive and precise yet made, allowed comparison with fine details of the new theory.

The possible deleterious effects of high-intensity nuclear radiation on materials of construction had been recognized from the start of the Manhattan Project. Many kinds of materials had been tested, first in accelerators and then in the Clinton Pile. Growing interest in water as a reactor moderator or as a fuel solvent prompted chemists to turn their attention to its behavior upon irradiation. Furthermore, water's ubiquity in living matter and as the commonest solvent in chemical operations made understanding the mechanisms for its behavior under various kinds of radiation a central problem. Water studies were pursued at all the national laboratories. At ORNL the early work was done using pile radiation and then progressed to sources that were simpler to use and that delivered less complicated radiation. A Van de Graaff accelerator for electrons and a cobalt-60 source for gamma rays were in service by 1955.

New Directions

Corrosion of metals is largely electrochemical, that is, it involves transfer of electrons between the metal surface and the corroding liquid. Motivated by corrosion problems with the aqueous homogeneous reactor, ORNL set up a program devoted to the fundamental electrochemistry of corrosion before 1950. It elucidated mechanisms for corrosion for metals of practical interest (iron, titanium, zirconium) and provided assistance to the groups concerned with specific corrosion problems in reactors.

A number of chemists who had worked on the Manhattan Project had training and experience in areas other than those relevant to nuclear technology. As special feasibility rather than nuclear relevance became an acceptable justification for research, some of these chemists began to attack problems that combined their former interests and capabilities with the special opportunities available at the Laboratory.

One example involved organic chemists who had originally developed high-yield synthetic methods for organic intermediates labeled with carbon-14 so that the distribution by the Laboratory would be in a form that could be used efficiently by outside researchers. They began a small program to use some of these materials in their own research on organic mechanisms. This research was based on their extensive experience in using isotopic substitution in synthesis and in doing precise counting of organic compounds containing carbon-14. The program was highly successful in the study of mechanisms but was perhaps more important in training visitors in the techniques of radiocarbon organic chemistry.

Chemical Physics

Three more programs, probably best classified as chemical physics, arose from efforts to exploit the Laboratory's capabilities in other directions. The most obvious of these was neutron diffraction, which employed the wave nature of neutrons as a tool for structural research. Neutrons complement X rays very usefully because they are strongly scattered by hydrogen nuclei; thus, the resulting diffraction pattern gives information about the location of hydrogen. X rays are scattered only very weakly by the hydrogen atom's sole electron; X rays, therefore, are almost useless for locating this important element. The ORNL group using neutrons in this way made major contributions to crystallography, including not only the working out of particular structures but also the development of computational methods (because the Laboratory possessed advanced computers very early) and of automated diffraction equipment (also used for X rays) that is now a commercial product.

ORNL collaboration with a university physicist to measure spins and moments of radioactive nuclei by microwave rotational spectroscopy led to an independent program using microwave and radiofrequency techniques. Among the program's accomplishments are (1) the first and most extensive chemical work on pure quadrupole spectroscopy in this country, (2) the first direct identification of a free radical (the hydrogen atom) in an irradiated solid by electron spin resonance, and (3) a long and fruitful program applying electron spin resonance to problems in radiation chemistry, photochemistry, and more recently, coal chemistry.

Finally, chemists at the Laboratory achieved a long-sought goal of chemical kinetics, the study of a chemical reaction between crossed molecular beams. Measurement of the minute amounts of product from such reactions had been the obstacle, and the rationale for trying it at ORNL was the possibility of using neutron activation as part of the detection scheme. As it turned out, a less tedious method was discovered that was applicable to many reactions of the alkali metals with such molecules as the hydrogen halides. Because these reactions could be used effectively to discover general features of bimolecular reactions, the technique was widely used. With new developments in sensitive detectors and in tunable lasers, the goal of studying reactions in the most elementary fashion possible, that is, between molecules in single-energy states, can now essentially be realized.

So there's a rough outline of how chemical science evolved at the Laboratory between about 1943 and 1955. Today, thirty years later, it is still evolving. ornl

These members of ORNL's Chemistry Division photographed in January 1949 worked in Building 706A (background) along with members of the Analytical Chemistry and Chemical Technology divisions. The building is now designated 3550. From left in front are Jane Snow Johnson, Frank Neely, John Loy, Betty Lou Colwell, Joyce Gresham, Dorothy Inman, Peggy Carter, Essie Blair, Dorothy Clark, Edna Hennessee, Georgie Gibson, Lucille Raulston, Arnold Harrod; from left in second row, Cas Borkowski, Quentin Larson, Milton Feldman, Max Bredig, Fred Sweeton, Henri Levy, John Boyle, Al Smith, Henry Zeldes, Glen Jenks; from left in third row, Simon Freed, Clancy Hochanadel, Mike Silverman, Ralph Livingston, John Ghormley, John Ruth, Willis Baldwin, Howard Heller; from left in fourth row, Bruce Ketelle, Edward Fairstein, Ellison Taylor, Bernard Zemel, Don Richardson, Phil Chastagner, John McBride, Tony Skraba, and Gus Ropp.

List of Research Projects and Contributors

Here's a list of a few research projects from that period to bring this account a little more to life. It is, of course, only a sampling of what was done, and the inclusion or exclusion of specific names reflects only the author's casual memory. In particular, the monumental chemical efforts associated directly with the Aqueous Homogeneous Reactor and the Molten Salt Reactor are omitted.

1943–1945

Discovery of the new element promethium (Charles Coryell, Larry Glendenin, and Jacob Marinsky).

Separation of rare earths by ion exchange (George Boyd, Waldo Cohn, Ed Tompkins, and Paul Tompkins).

1945–1955

Comprehensive study of aqueous solutions at high temperatures (Milt Lietzke, Bill Marshall, Charles Secoy, Ray Stoughton).

Comprehensive study of complex metal ions by anion exchange (Kurt Kraus, Fred Nelson).

Discovery of the extraordinary inhibition of corrosion by pertechnetate ions (Groves Cartledge).

Characterization of metal solutions in molten salts (Max Bredig, Harry Bronstein, and Art Dworkin).

Chemical developments needed for measurement of the neutron capture cross section of xenon-135, the notorious reactor poison (Ralph Brosi, Simon Freed, Bruce Ketelle, George Parker, and Henry Zeldes).

Precise measurement of asymmetry in beta decay of phosphorus-32 (Ralph Brosi, Bruce Ketelle, and Harvey Willard).

Precise measurement of numerous yields in radiation chemistry of aqueous solutions (John Boyle, John Ghormley, and Clancy Hochanadel).

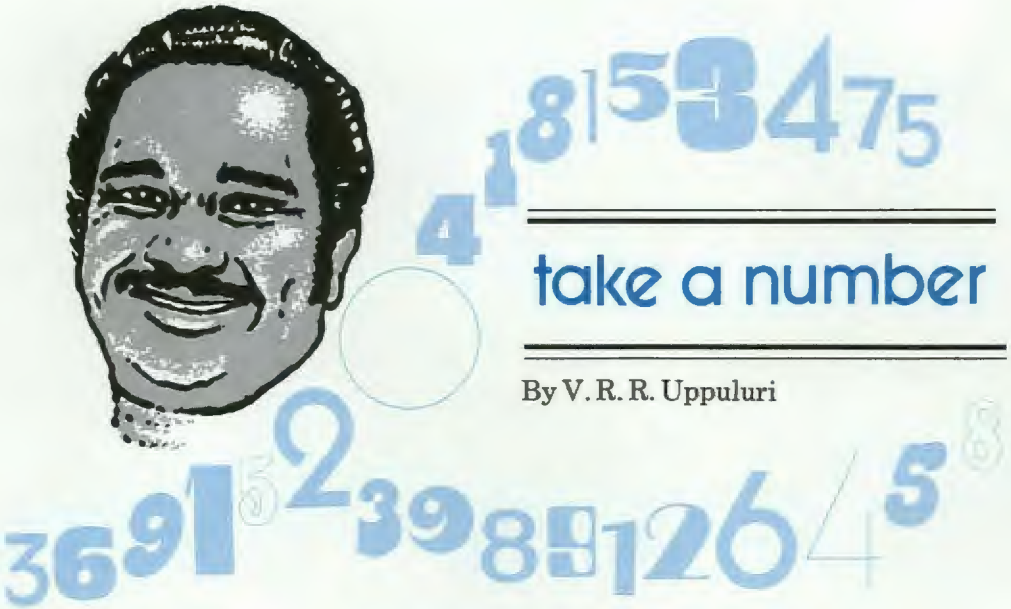
Separation of stable isotopes of light elements by chemical exchange (George Begun, Lloyd Brown, John Drury, and Al Palko).

Use of carbon-14 in the study of organic reaction mechanisms (Ben Benjamin, Clair Collins, and Vernon Raaen).

Neutron diffraction as a structural tool for crystals and liquids (Bill Busing, Henri Levy, and Selmer Peterson).

Microwave absorption, pure quadrupole resonance, and electron spin resonance spectroscopies in structural and reaction chemistry (Ralph Livingston and Henry Zeldes).

Use of molecular beams for the study of chemical reaction mechanisms (Sheldon Datz and Ellison Taylor)



take a number

By V. R. R. Uppuluri

Powers of Numbers and Divisibility

In terms of their powers and divisibility, numbers have predictable relationships. Consider 7 as the sum of 4 and 3. Cube these numbers and take the sum: $4^3 + 3^3 = 64 + 27 = 91$. Interestingly, 91 is divisible by 7. Similarly, the sum of 4^5 and 3^5 ($1024 + 243 = 1267$) is also divisible by 7. As a matter of fact, 7 divides $4^3 + 3^3$, $4^5 + 3^5$, $4^7 + 3^7$, $4^9 + 3^9$, . . ., $4^{2n+1} + 3^{2n+1}$, . . .

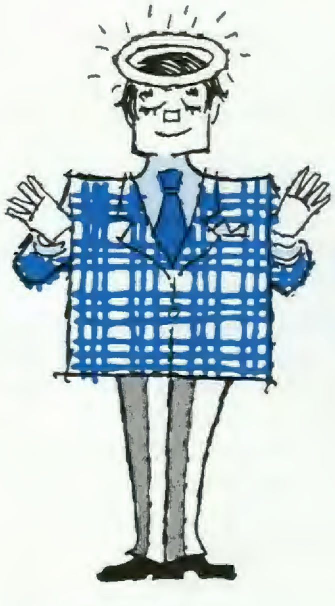
More generally, if a and b are arbitrary numbers, $a^{2n+1} + b^{2n+1}$ is divisible by $a + b$ for $n = 1, 2, \ldots$ In the special case in which $a = 4$ and $b = 3$, $a^2 + b^2 = 16 + 9 = 25$ is not divisible by $a + b$ or 7, suggesting that, in general, $a + b$ does not divide $a^2 + b^2$.

Similarly, in general, $a + b$ does not divide $a^4 + b^4$, $a^6 + b^6$, . . ., $a^{2n} + b^{2n}$, . . . In contrast, $a - b$ always divides $a^2 - b^2$, $a^3 - b^3$, $a^4 - b^4$, $a^5 - b^5$,

It is also interesting that 7 divides every member of the sequence $3 + 2^2 = 7$, $3^3 + 2^3 = 35$ (7×5), $3^5 + 2^4 = 259$ (7×37), $3^7 + 2^5 = 2219$ (7×317), $3^{2n+1} + 2^{n+2}$, . . . This statement can be proved using the theory of residues in number theory.

Rarities among the Plentiful

For $n = 40$, $2n + 1$ ($2 \times 40 + 1 = 81 = 9^2$) is a perfect square, as is $3n + 1$ ($3 \times 40 + 1 = 121 = 11^2$). It can be shown that there is an infinite number of positive integers n such that simultaneously $2n + 1$ and $3n + 1$ are perfect squares and that each n is a multiple of 20. For instance, for $n = 3960$, which is divisible by 20, $2n + 1$ ($= 7921 = 89^2$) and $3n + 1$ ($= 11881 = 109^2$) are perfect squares; the next number that has this property is 388,080.



Perfect Square

From left are B. R. Appleton, C. W. White, and O. E. Schow III.

Surface Modification Using Ion Beams and Lasers

By BILL R. APPLETON

It is a common challenge to those of us in basic research to explain to colleagues, relatives, friends, and sponsors why we have chosen to work on particular projects. Often we begin work on a phenomenon simply because it interests us or because it is not well understood, but if the project runs for any appreciable length of time, we are usually asked, or ask ourselves, about the relevance or potential worth of our efforts. When applied in moderation this questioning can be a beneficial exercise because it forces us to put priorities on our creative energies and focus our future research.

So, why study ion-beam and laser processing of solids? I believe there are several good reasons. First, because the rapid changes produced by these means break the solid out of the usual equilibrium constraints, they provide access to a wealth of new solid-state physics phenomena that could not be studied without them. We can now study for the first time rapid solidification in times much shorter than are required for the fundamental interactions that normally control them (see Fig. 1). Second, as a result of these nonequilibrium interactions, ion-beam and laser processing leads to

Bill R. Appleton is director of ORNL's Solid State Division. Before assuming this position in April 1986, he served as group leader, section head, and director of the Surface Modification and Characterization Collaborative Research Center in the Solid State Division. He received a B.S. degree from the University of Missouri and M.S. and Ph.D. degrees from Rutgers University in solid-state physics. He subsequently worked two years at Bell Laboratories in Murray Hill, New Jersey, in the areas of ion implantation and ion-beam analysis before joining the Solid State Division at ORNL in 1967. Appleton's research interests at ORNL have concentrated on fundamental research in the use of ion-beam and laser-processing techniques for surface modification of solids and on the study and use of ion-solid interactions for materials analysis. He has received several awards for his research, including the 1980 Department of Energy Award for Outstanding Sustained Research, an I-R 100 Award for his work in developing supersaturated substitutional semiconductor alloys, and the 1985 DOE Materials Research Award for Significant New Technologies. He has co-edited three books and is on the editorial boards of several scientific journals, including *Radiation Effects*, *Materials Letters*, *Nuclear Instruments and Methods in Physics Research*, and *Nuclear Science Applications*. He has served as chairman or organizer of numerous international conferences. In addition, Appleton is a member of the Solid State Sciences Committee of the National Academy of Sciences and of the Material Sciences Panel on Advanced Processing of Electronic Materials, which is a state-of-the-art assessment panel of the National Materials Advisory Board. In 1983 he was vice-president of the Materials Research Society, in which he is currently serving as councillor. He is a Fellow of the American Physical Society.

ORNL researchers have found that using beams of ions and laser light to process solids permits studies of rapid solidification phenomena; leads to a variety of new materials, new properties, and even a new state of matter; and modifies surfaces, including those requiring submicron patterning for use in very small electronic devices.

a variety of new materials and new properties (e.g., new metastable phases, supersaturated alloys, and extended solid solutions). With femtosecond laser pulses it is even possible to achieve a new state of matter by heating a solid far above its melting temperature without allowing it to melt or even evaporate! Finally, these techniques have become invaluable practical tools for modifying surfaces. In particular, for the fabrication of micro integrated-circuit semiconductor devices, ion-beam and laser-assisted techniques appear to be the only methods capable of the submicron patterning necessary for future device structures.

Laser-Solid Interactions and Materials Properties

Most of the laser processing work at Oak Ridge National Laboratory has involved very short-pulse lasers because the extremely short interaction times and the resulting rapid heating and cooling rates are the most likely source of new phenomena and new properties in materials. Nevertheless, the techniques that have come into use in recent years in this area include, in addition to pulsed lasers, continuous-wave lasers and electron beams, scanned lasers and electron beams, and rapid thermal annealing in conventional ovens. This array of annealing tools has made it possible for the first time to study heating, cooling, solidification, precipitation, segregation, solute trapping, and crystallization phenomena over a range of processing times as long as days and as short as femtoseconds (10^{-15} s).

At the one extreme, crystal growth from the melt proceeds at growth rates typically on the order of 10^{-5} to 10^{-7} m/s, and for years it was believed that defect-free crystal growth required these slow, near-equilibrium conditions. At the other extreme, pulsed-laser annealing research in the last few years, much of which has been pioneered and performed at ORNL, has shown that silicon (Si) can melt and recrystallize epitaxially at speeds as high as 12 m/s and still be completely free of extended defects in the regrown region. (Epitaxy is the growth on a crystalline substrate of a crystalline substance that mimics the orientation of the substrate.) This rather surprising result has opened a new era in studies of rapid solidification and crystallization. For example, by combining conventional techniques with laser and electron beam processing, it is now possible to study the solidification behavior of Si over more than 12 decades of growth rate or solidification velocity, as shown in Fig. 2. (Solidification velocity is the speed at which the interfacial region between the solid and liquid progresses as the liquid solidifies).

These extremely short processing times and the laser-solid interactions that are governed by these short times are also the cause of the nonequilibrium nature of the laser-processing technique and the new properties that result in processed materials. The pulsed lasers used at ORNL have primarily been ruby, Nd:YAG, or excimer

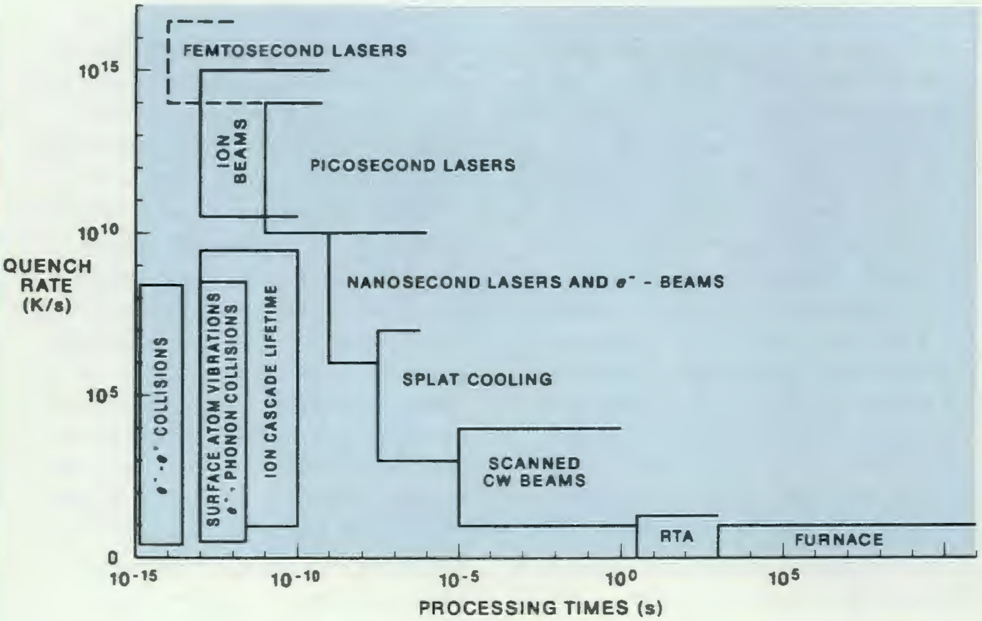


Fig. 1. Conceptualization of the tremendous extension of the range of processing times made available with recent ion-beam, laser, and electron-beam techniques and a comparison of the relative quenching rates accessible with the various techniques. Included for reference are some fundamental interaction times that mediate energy transfer in solids. Clearly, these transient processing techniques offer quenching rates much greater than those available with most conventional methods, and the processing times can rival or surpass fundamental transfer mechanisms. These features are the origin of the new and unusual materials properties that result.

lasers, which have photon frequencies in the visible to ultraviolet range and pulse durations of 10 to 50 nanoseconds (ns), or 10^{-9} s. In the case of Si, which is an indirect band gap material, the photon absorption process for such lasers involves only the electronic system—that is, the electrons rather than the nuclei of constituent atoms. Photons from the laser excite valence electrons, which then jump across the band gap into the conduction band; free carriers already in the conduction band are excited directly by the photons. This absorbed energy becomes rapidly thermalized (distributed) among the excited electrons through electron-electron interactions in times less than 10^{-14} s. Thus, at this point in the process, all the absorbed energy resides in the electronic system of the solid and the carrier temperature (i.e., temperature of electrons and holes) exceeds the lattice temperature (i.e., the temperature of the atomic nuclei that make up the structure of the solid). Because alterations in materials induced by laser annealing require *structural* changes in the material, the transfer of this energy from the electronic system to the atoms in the lattice is the crucial, controlling step.

After several years of intensive research and controversy, it is now agreed that the excited electrons transfer their energy to the lattice atoms in the form of heat via electron-phonon interactions that take place within a few picoseconds (10^{-12} s) after absorption. (A phonon is a quantum of vibrational energy used in mathematical models to calculate thermal properties of solids.) Because this transferred heat can melt the solid in the near-surface region, this process has been termed the "thermal model" of laser annealing.

Following publication of the thermal model, groups at IBM and elsewhere proposed an alternative "plasma model" of laser annealing in which they postulated that the absorbed energy remained in the electron-hole plasma for times of 100 ns or longer and that structural alterations resulted from ionization-induced instabilities as a result of this "plasma-fluid." Early experiments in ORNL's Solid State Division in 1978 by Woody White, Jagdish Narayan, Rosa Young, Peter Pronko, Syd Wilson, and me showed that the laser annealing process could be interpreted solely in terms of thermal melting; Jim Wang, Dick Wood, and Pronko provided thermal modeling calculations that accounted for these observations in detail by invoking only thermal melting. Although this work sparked a controversy that raged for several years, prompting hundreds of sophisticated measurements and calculations from around the world, the thermal model is now accepted as correct. This is but one of many examples from laser annealing research that highlights its contribution in understanding fundamental materials interactions. In this case it became necessary to devise experiments and verify calculations that could distinguish between interactions occurring in the extremely short processing times of pulsed-laser annealing. As later examples will show, much of this work was done at ORNL.

The advent of even shorter pulse lasers with processing times in the femtosecond regime promises an even more exotic probe of the solid state in the near future. Experiments by Nobel Laureate Nicolaas Bloembergen and his collaborators at Harvard University, as well as several groups around the world, have shown that solids can be "heated" far above their melting and vaporization temperatures without causing them to melt or evaporate. Because these processing times are short compared with the

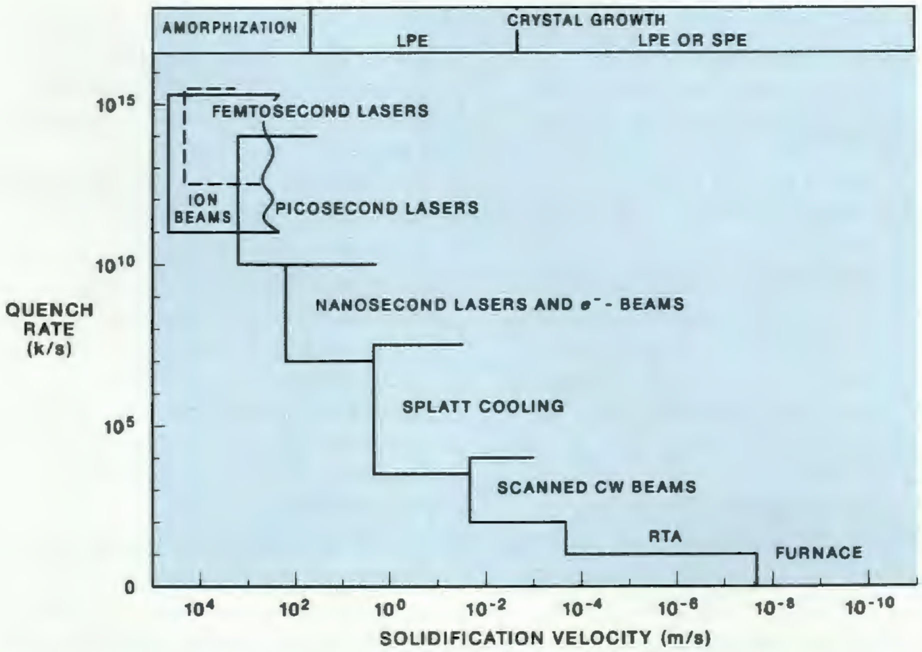


Fig. 2. This schematic shows that ion, laser, and electron-beam processing can induce solidification velocities in both the solid and liquid phase that span more than 12 decades. The bar plot at the top of the figure indicates that these techniques have made it possible for the first time to study crystal growth and amorphization in silicon over this whole range.

fundamental interaction times normally required to transfer energy in solids, this rapid heating leads to a new state of matter that is not yet totally understood. These processing times are more rapid than electron-phonon collisions (10^{-12} s), which are responsible for transferring the heat from the electronic system to the lattice in the example we discussed above for nanosecond laser annealing, so this avenue of energy transfer cannot lead to melting. Because these processing times are also shorter than surface-atom vibration times (10^{-12} to 10^{-13} s), the solid lacks time to expand or evaporate. Rapid heating thus leads to a solid structure that is in some high-temperature phase, the structure of which is not known.

Creating new states of matter by rapid processing is exciting, but how can we study them when the entire process is over in a very small fraction of a second? In the case of nanosecond laser annealing of a Si single crystal, for example, the near-surface region melts to a depth of about 10^{-6} m and then recrystallizes by liquid-phase epitaxial growth onto the underlying crystal substrate—a process that is complete in little more than 10^{-7} s. This rapid annealing is an amazing feat, but if we are to understand the highly nonequilibrium conditions under which it occurred, we must be able to follow the changes in properties during annealing of the solid by using techniques that have subnanosecond resolution.

Studying the results of laser processing of solids in real time is another area in which ORNL researchers were pioneers. Ben Larson, Woody White, and Tom Noggle of the Solid State Division along with Denny Mills from Cornell University exploited the pulsed nature of synchrotron radiation by developing an X-ray analysis technique capable of real-time structural characterization of solids having the required subnanosecond resolution. Their experiments provided some of the most definitive data in resolving the thermal melting controversy mentioned earlier. Since then, Larson, Jon Tischler (also of ORNL), and Mills have performed experiments that have successfully measured for the first time the overheating and undercooling of Si and germanium (Ge) interfaces during pulsed-laser melting (see sidebar on page 28).

Other analysis methods that have been developed for time-resolved characterization include optical reflectivity using a probe laser, particle emission measurements, transient electrical conductance, and electron diffraction techniques. This is a good example of the synergism that occurs often in basic research; in this case, the need to understand new phenomena has led to the extension of a variety of analytical techniques that will be useful in many areas of materials science.

Another crucial aspect in the use of laser processing for altering materials is the rapid quenching that arises from pulsed-laser annealing. During pulsed-nanosecond-laser annealing of Si, the heating pulse lasts only a few nanoseconds. At sufficiently high laser power, the absorbed energy melts the surface. As the heat is conducted away to the underlying substrate, the molten surface layer can solidify at extremely high melt front velocities. The solidification rate is determined by many factors, such as the laser pulse duration, the wavelength of laser light used, the sample reflectivity, absorption coefficient, thermal conductivity, and temperature gradients, but these parameters can be exploited to span a range of solidification velocities up to tens or hundreds of meters per second. This rapid melting and resolidification constitutes a rapid quench that can be as fast as 10^{14} K/s, placing extreme boundary conditions on material interactions occurring in the near-surface region and inducing a variety of properties that are new and often unique to the laser annealing process. In the case of Si, the molten layer recrystallizes into a defect-free crystal by liquid-phase epitaxy as long as the velocity of the liquid-solid interface is 12 m/s or less. If the quenching rate is increased, the velocity of the liquid-solid interface increases, and above about 12 m/s the interface is moving so rapidly that the atoms there no longer have time to arrange themselves into an ordered crystal structure. Thus, the surface layer solidifies into an amorphous structure resembling that of a liquid. It is not yet fully understood whether the amorphous phase nucleates separately at the liquid-solid interface or grows from a continuing accumulation of crystal defects at these rapid velocities. What is clear is that this question will most likely be answered by time-resolved measurements. Because of this tremendous control over the interface velocities, it is now possible to actually probe the kinetics that govern crystallization at the interface.

Some of the new properties of materials that can result from the use of laser annealing have been described in my article in the Fall 1983 issue of the ORNL *Review*. The article also discussed the fabrication of supersaturated substitutional alloys of Si. This new class of materials occurs when laser-annealed Si recrystallizes defect free at such rapid velocities that ion-implanted dopants such as boron, phosphorus, arsenic, antimony, and bismuth are trapped into substitutional sites at concentrations that can exceed equilibrium solid-solubility limits by more than a factor of 1000. These alloys also have unique one-dimensionally strained lattice structures in the ion implanted, laser annealed surface region and unique electronic properties.

A more recent example of the fundamental studies that can be made of the kinetics of such rapidly moving interfaces is the work of Mike Aziz and White in the Solid State Division along with collaborators from Sandia National Laboratory and Cornell University. The process by which dopants become trapped into substitutional sites during recrystallization is called solute trapping, but the exact mechanisms that control this process at the rapidly moving liquid-solid interface have been the subject of theoretical calculations and speculation for many years. Combining high-resolution ion scattering measurements of impurity profiles with real-time transient conductance measurements of the solidification velocity, these researchers modeled the solute trapping process and made sufficiently accurate measurements to specify the nature of these interface interactions.

Ion-Beam Processing of Solids

The study of ion-solid interactions is one of the older fields in physics. It has its roots in the pioneering works of legendary figures such as Niels Bohr and Ernest Rutherford and bridges the fields of atomic, nuclear, and solid-state physics. Although early work concentrated on fundamental ion-solid interactions such as scattering, energy loss, charge exchange, and nuclear reactions, the nuclear age brought the realization that energetic ions and neutrons can drastically alter the structure and properties of solids. Out of this marriage of disciplines has emerged the field of ion-beam processing, which uses the effects of ion bombardment to selectively alter the properties of solids.

One such process is ion-implantation doping. Ions of virtually any species can be produced in an ion source, extracted, analyzed for mass and energy, and accelerated to produce a beam of isotopically pure, monoenergetic ions. When directed onto a solid, these ions penetrate the near-surface region and become embedded there. The depth of penetration is accurately controlled by regulating the energy of the ion beam; lateral uniformity is achieved by beam scanning; and the implanted dose (concentration) is accurately controlled by measuring the accumulated charge.

Often in materials science small amounts of the "right" impurity can alter the properties of a solid or create a dominant property, and implantation doping provides an accurate, pure, and reproducible means of introducing any impurity into any solid. These attributes have made implantation one of the premier fabrication processes in the semiconductor industry. A present-day very large-scale integrated circuit, for example, may have from 6 to 12 implantation steps in its fabrication.

A companion ion-beam processing technique is ion-beam mixing. In this process a thin film of one material is deposited onto the surface of a substrate material and the composite is bombarded with a beam of energetic ions. When the ions penetrate the interfacial region separating the two solids, a variety of ion-induced interactions "mix" the atoms of the two materials together and induce unusual interactions, thus the name ion-beam mixing. Both ion implantation doping and ion-beam mixing are nonequilibrium processing techniques and, as a consequence, they often result in material properties that are very different from properties achieved using conventional equilibrium methods. In the case of ion implantation doping, because the ions are forcibly injected into the solid at depths determined solely by the ion energies and at concentrations determined only by the selected dose, normal processing constraints such as thermal diffusion and solid solubility limits are no longer limiting factors. It is instructive to consider the consequences of some of the ion-solid interactions that occur during these processes because they provide insights into the mechanisms responsible for the nonequilibrium nature of the resulting material interactions.

One such mechanism, called ballistic mixing, depends only on the dynamics of the collision process. Each energetic ion collides with many atoms as it penetrates into the solid, and each of these displaced atoms displaces other atoms in turn. This series of collisions results in thousands of displaced atoms along the track of the ion, forming a collision cascade. These ballistic collisions mix atoms of the two materials at their interface independently of, or if you will, in spite of, any thermodynamic or chemical driving forces that usually cause interactions in materials. Such interface mixing has many practical benefits. It is possible to create compositionally graded interfaces with increased resistance to thermal stress, to greatly improve adhesion of deposited films, and to "dilute" interface impurities.

In addition to ballistic mixing, many other ion-induced interactions can greatly accelerate mixing and induce unique materials interactions. Within each collision cascade, many defects are created by the energetic ions. These defects are vacancies (lattice sites vacated by displaced atoms) and interstitials (atoms displaced from their original sites). Normal thermal diffusion occurs when atoms work their way into the solid by jumping from defect site to defect site; the defects and atom motion are usually caused by heat (atom vibrations). The large excess of defects caused by each energetic ion can greatly accelerate diffusion without the introduction of heat. This process, called radiation-enhanced diffusion, can accelerate mixing by orders of magnitude over normal diffusion. Furthermore, huge amounts of energy are dumped into the lattice by collisions initiated along the track of the ion. The energy deposited in this ion cascade is shared among many atoms and yet dissipates in times of only 10^{-10} to 10^{-13} s. This time is equivalent to an extremely rapid quench of the affected region of the solid, suggesting one reason why ion bombardment is capable of inducing new metastable phases, extended solid solutions, amorphous alloys, and numerous other new material properties. The rapid quench resulting from ion bombardment may explain why this technique leads to the formation of amorphous, or highly disordered, regions in solids. Many of these effects were discussed in the Fall 1983 issue of the ORNL *Review.*

Very recently John Budai and Mike Aziz of the Solid State Division decided to see if some of the constraints placed on materials interactions by ion-beam and laser processing could be used to shed more light on the properties of a new alloy phase of aluminum-manganese (Al-Mn) that had been produced by rapid-quenching techniques and that exhibited metastable quasicrystalline order (so-called icosahedral phase of Al-Mn). The scientific interest in this unusual structure arose because it exhibited diffraction behavior that was inconsistent with current understanding.

Although several groups had produced and studied the unusual structure, no one had been able to establish the location of the atoms in the quasicrystal structure. Budai and Aziz found that implantation of Mn into Al single crystals formed quasicrystal precipitates that were highly ordered relative to the Al matrix. This allowed them to establish a unique orientation relationship between the symmetry axes of the icosahedral phase and the crystallographic directions of the Al matrix. The temperature dependence of the phase formation, along with what is known about ion collision cascades, also allowed them to obtain information on the formation mechanisms of the icosahedral phase.

Ion implantation produced an amorphous phase at room temperature, the icosahedral phase at 150°C, and the stable Al_6Mn structure at 275°C. The ORNL researchers reasoned that (1) if the icosahedral phase were created as a direct result of the collision cascade during implantation, they would also expect the phase at room temperature and (2) if it were created by precipitation from an intermediate amorphous phase, then no ordering should prevail relative to the Al crystal. Thus, they concluded that the icosahedral phase forms in the 150°C samples by solid-phase precipitation when many mobile defects are present after the collision cascade is finished. Similarly, by carefully controlling the conditions of pulsed-laser annealing of ion-implanted samples, they could control the temperature, composition profiles, quenching rates, and duration times and could calculate interface velocities during solidification. Using these constraints they were able to extract valuable information on the thermodynamics and formation kinetics, to determine the rapid growth direction of the icosahedral phase from the melt and to differentiate between models proposed to explain these novel structures.

Ion Beam Deposition

In 1984 we had the desire, and perceived the need, to get involved in the area of artificially structured materials. Thin films made using molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) had shown that a wealth of interesting new solid-state phenomena were accessible using these techniques for fabricating thin-film composite structures. Because many laboratories were already heavily involved and more experienced in MBE and CVD, we looked for a technique that would not only capitalize on our equipment and expertise in ion beam processing but also would be a truly new approach. We hit upon the idea of direct ion beam deposition (IBD). Instead of implanting energetic ions from an accelerator deep beneath the surface of a solid, the idea was to decelerate the ions to very low energies in an ultrahigh vacuum (UHV) environment and deposit them directly onto the surface of the solid and form thin-film structures one atom at a time. The concept itself was not a new one. Nuclear physicists had used this technique to make thin-film isotopic targets in the 1950s and 1960s. Indeed, isotope separation had become a field of science long before that (e.g., uranium isotopes were separated during World War II at the Oak Ridge Y-12 plant using calutron accelerators). Although the concept of IBD offered many attractive features for fundamental studies and had considerable potential for practical applications, it also presented some difficult problems that had to be solved before it could ever be used for fabricating materials. Fortunately, the ORNL Exploratory Studies Program provided the seed money, and the pool of diverse expertise at ORNL made it possible to start to solve these problems.

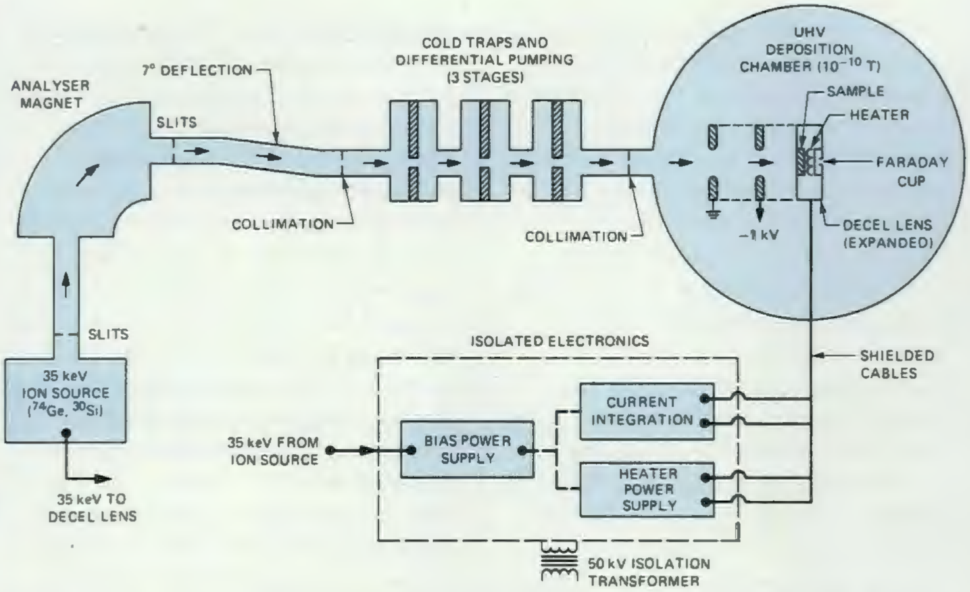


Fig. 3. Deceleration scheme used to convert an ion-implantation accelerator into an ion-beam deposition system.

Early in 1984 Jim Roberto of the Solid State Division and I initiated a Seed Money project in collaboration with Gerald Alton of the Physics Division. We designed, built, and installed a deceleration lens system in an existing UHV chamber on our ion-implantation accelerator. When Roberto temporarily left the division to become technical assistant for Alex Zucker, Associate Director for Physical Sciences, we quickly interested Tom Noggle, who had just returned from a one-year guest assignment in Germany, and Ray Zuhr in the project. Nicole Herbots also joined us later, fresh from her thesis research in Belgium. With this team in the Solid State Division, we began IBD research.

The IBD concept uses ion beams from an ion-implantation accelerator. The ions are produced in an ion source and extracted and accelerated to 35,000 electron volts (eV), then mass-and-energy analyzed in a magnet system to select a single isotope of the chosen ion. The ions are then deflected 7° to eliminate any neutral atoms, transported through three stages of differential pumping, and injected into a UHV (10^{-10} Torr) chamber that contains the deceleration lens system and the solid target (see Fig. 3). This approach ensures extreme purity and accurate control of uniformity, thickness, deposition rate, and energy of deposition and can result in the deposition of thin films of virtually any isotope of any element on any substrate. Initial experiments using IBD are beginning to show the promise and capabilities of this technique.

Much of the interest in artificially structured materials has arisen because the fabrication of layered structures of select materials with atomic dimensions can alter some of the fundamental solid-state interactions that occur. An example is the fractional quantum Hall effect, which exists in certain semiconductor quasi-two-dimensional structures; work in this area, incidentally, was awarded the 1985 Nobel Prize in physics.

One of our first tasks has been to determine whether IBD could deposit large-area, uniform, thin-film structures that have atomically sharp interfaces. By extracting isotopic beams of ^{30}Si and ^{74}Ge, we deposited a four-layer heterostructure composed of alternate thin films of Si and Ge, each a few tens of nanometers thick. The films were analyzed at the Solid State Division using a

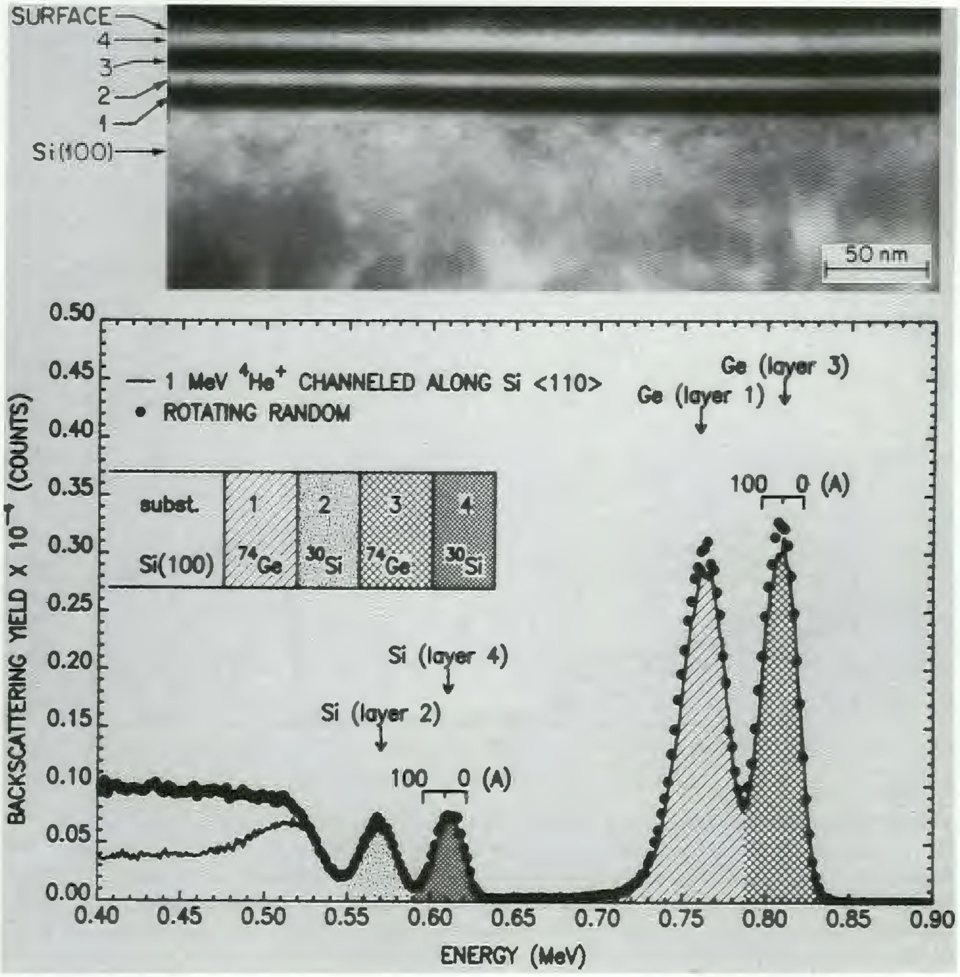


Fig. 4. This combined cross-sectional electron microscopy (top micrograph) and ion-scattering analysis (spectra at bottom) of an isotopic heterostructure made by ion beam deposition shows that alternate layers of germanium (^{74}Ge) and silicon (^{30}Si) can be deposited over large areas with uniform thickness, bulk densities, and atomically sharp interfaces.

variety of techniques: ion scattering-channeling measurements were made at the Surface Modification and Characterization facility; Steve Pennycook provided us with detailed cross-sectional electron microscopy of the layered structures; Tischler and Jim Lewis contributed X-ray scattering analysis; and Dave Zehner performed Auger electron, depth-profiling, impurity analyses. These measurements showed that at room temperature, we could fabricate amorphous, isotopic heterostructures of ^{30}Si and ^{74}Ge that were uniform in thickness over large areas, had atomically sharp interfaces to less than 1 nm (the limit of our resolution), had densities equivalent to bulk Si and Ge, and were free of incorporated impurities.

The semiconductor industry has a critical need for techniques that can deposit films and grow epitaxial layers at relatively low temperatures. This need arises from the fabrication requirements of future integrated circuits where device features and deposition thicknesses will have submicron dimensions. These technologies demand many sequential processing steps where insulating oxides, implanted buried layers, and metal conducting lines must be integrated onto a single semiconductor chip, and temperatures as high as those currently used (700° to 1200°C) can destroy circuit functions by causing unacceptable interactions among these disparate materials separated by such small dimensions. IBD offers great promise in this area because the energy of the ions can be accurately controlled from 0 to 1000 ev by simply adjusting the energy of the deceleration lens system. Normal evaporation, sputter deposition, and MBE and CVD techniques deposit atoms whose energies are a small fraction or a few electron volts. The kinetic energy associated with the IBD process and the fact that ions, not atoms, are being deposited should enhance surface-atom mobilities, alter the kinetics of nucleation (crystal birth) and growth, and encourage low-temperature epitaxial growth processes. We tested this concept by investigating the deposition characteristics of Si and Ge on single-crystal substrates. Thin, epitaxial, single crystalline Ge films were obtained by depositing ^{74}Ge ions at 40 eV onto Ge (100) at only 400°C. Although Si was more difficult, we obtained very high-quality epitaxy for deposition of 20-eV ^{30}Si on Si (100) at 600°C and good epitaxy even at 400°C (see Fig. 5). Silicon epitaxy is much more sensitive to interfacial impurities than Ge, so initial cleaning procedures and high vacuums during deposition were much more important. Even this problem was solved by using IBD; "cleaning" the surface was accomplished by an initial in situ bombardment with 40-eV chlorine (Cl) ions, which formed volatile Si and carbon chlorides that "etched" the surface without damage. This application of IBD in itself is a promising field of study because most surface cleaning in present-day semiconductor processing is done using reactive ions created in a plasma discharge; unfortunately, in reactive-ion processing, no

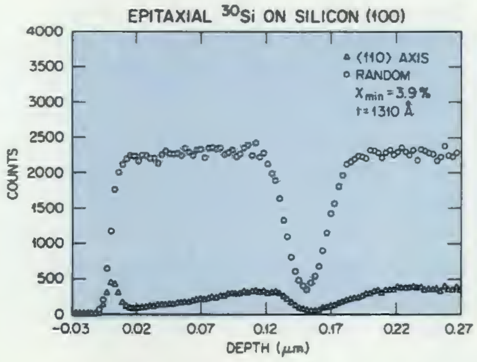


Fig. 5. This ion-scattering analysis shows the epitaxial growth of a ^{30}Si film on a Si(100) single crystalline substrate. One of the most exciting accomplishments of ion-beam deposition is the epitaxial growth of such films at low temperatures (400–600°C). This analysis shows that the sensitivity of the ion-scattering effect to the mass of the scattering atoms makes it possible to separate kinematically the ^{30}Si deposit from the underlying Si crystal. This also makes it possible to study surface reordering, interface interactions, and diffusion phenomena of Si on Si. The ion channeling effect (triangles), which is sensitive to crystal perfection, shows that the ^{30}Si deposit is a highly ordered single crystal—an indication of good epitaxy.

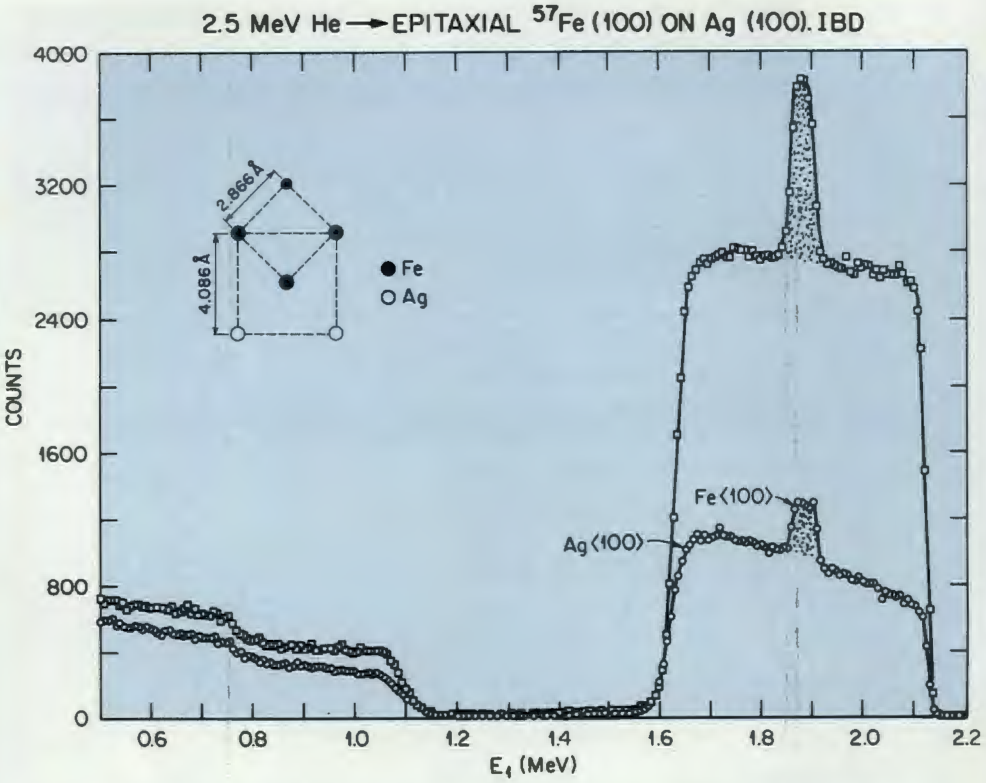


Fig. 6. The successful growth of isotopic iron (^{57}Fe) films on silver (Ag) is not only interesting for epitaxial growth studies but also provides unique samples for future Mossbauer and magnetic analysis investigations. This ion-scattering–channeling analysis was taken from an ^{57}Fe crystal grown on Ag, which had been grown on a sodium chloride substrate. This and other ion-channeling analyses show that the Fe crystal lattice grows rotated 45° relative to that of Ag, as indicated in the figure. The shaded peaks correspond to ion scattering from the Fe film, which happens to fall on top of that from the Ag film because of the ion-scattering conditions. The upper curve (open squares) was taken with the ion beam incident in a random direction of the sample. The lower curve (open circles), which was obtained for incidence along the <100> crystal direction, shows reduced scattering as a result of the ion-channeling effect.

controllable way exists to parameterize the importance of ion energy, flux, and other variables in the etching process. IBD provides the necessary link.

IBD may also offer the solution to yet another nagging problem in Si device processing, that of producing a thin, highly insulating oxide at low temperatures. Currently, such oxides are produced by thermally oxidizing Si at temperatures of 1000°C. We have produced near-stoichiometric silicon dioxide (SiO_2) films 7 nm thick by IBD of oxygen ions at only 400°C. We are still studying this energy-saving oxidation process and, so far, are encouraged by our findings.

The promise of IBD extends well beyond these applications in semiconductor processing, however. We recently conducted an experiment that shows that isotopic deposition is applicable to metal epitaxy as well—for example, the epitaxial growth of iron-57 (^{57}Fe) single-crystal films on single crystals of silver (Ag), as shown in Fig. 6. Because the ^{57}Fe isotope is uniquely sensitive for making Mossbauer measurements, such films provide a new method to tag and probe interface reactions, diffusion, mixing, and numerous other induced materials interactions. An interesting aspect of the epitaxial deposition is that the body-centered cubic ^{57}Fe film was forced to grow epitaxially onto the face-centered cubic Ag single crystal with their <100> axes parallel but with the Fe crystal rotated 45° with respect to the underlying Ag lattice. This direction of growth was necessary to achieve the best lattice match.

The features that make ion implantation doping and ion-beam mixing nonequilibrium processing techniques also offer the promise that IBD will be a method capable of creating new materials properties. Increasing ion energies during IBD, for example, can form defects at the surface that alter nucleation phenomena, change the probabilities of impurity incorporation, or cause ion mixing of a film at the same time it is deposited. Because any species can be produced in an ion-implantation accelerator, any combination of thin-film composites can be produced. Thus, IBD opens the way for whole new combinations of materials that are not readily

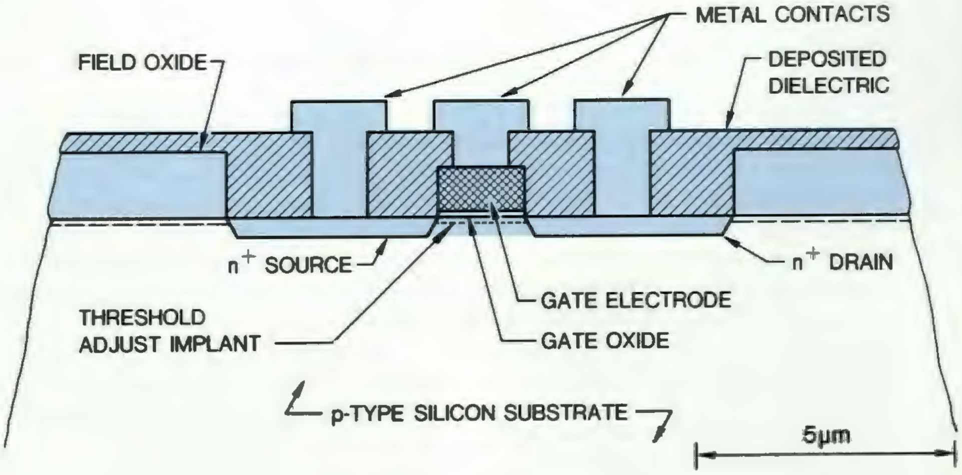


Fig. 7. This schematic illustrates some of the complex deposition, epitaxial growth, and etching steps that must be accomplished to fabricate a simple, present-day semiconductor device. Future integrated circuits will demand fabricating many such structures onto a single wafer, and the dimensions of each device will be one-tenth of the one shown here. Thus, it is essential to understand the characteristics of surface modification techniques capable of atomic alterations such as the ion-beam and laser techniques discussed here.

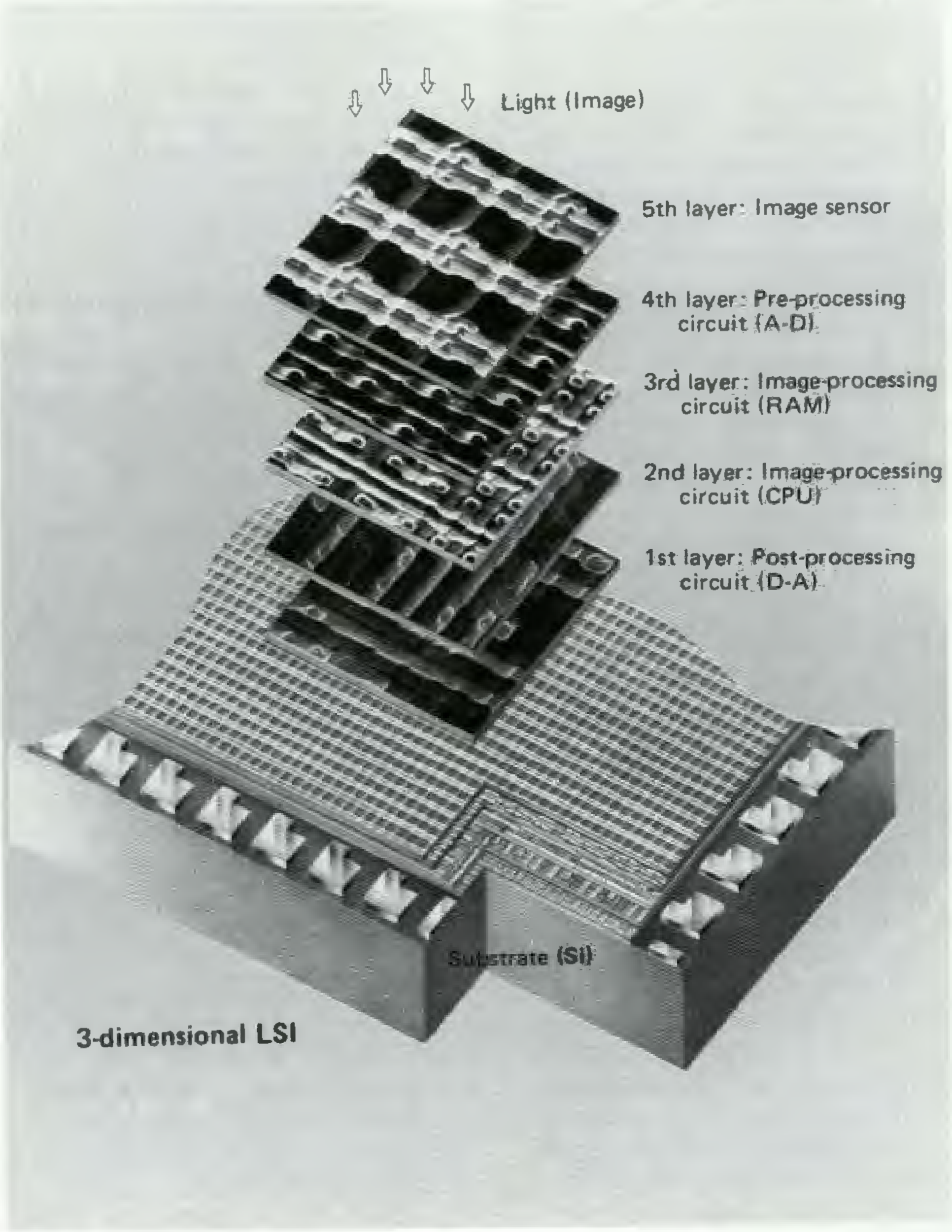


Fig. 8. The reasons why surface processing techniques that will be used to fabricate future device structures must be capable of low-temperature processing and extreme precision and control can be seen from this conceptual, three-dimensional, integrated circuit proposed by Mitsubishi Electric of Japan. In this device each layer would contain thousands of individual, submicron devices integrated into circuits and five layers of such functional circuits would be fabricated one on top of the other. High temperatures associated with any of the various processing steps could destroy underlying or adjacent circuits, and any slight misalignment of one circuit relative to another would make the total device inoperable. It is generally accepted that the processes used to make such future structures will be heavily dependent on ion-beam, laser, electron-beam, and plasma-processing techniques.

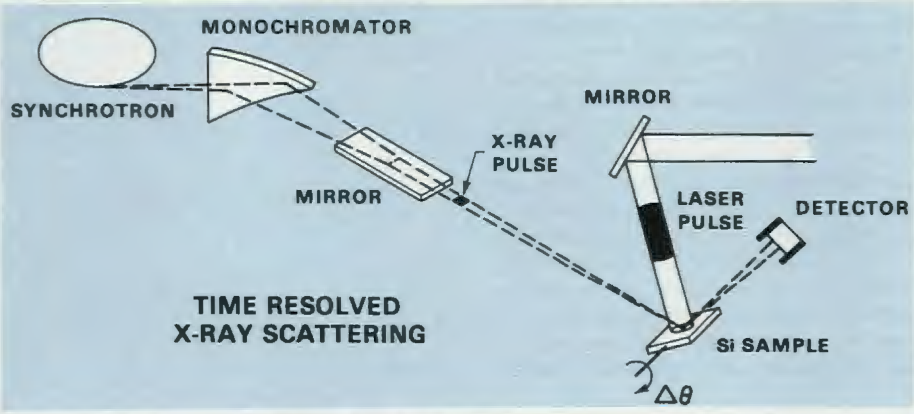
Overheating and Undercooling in Silicon during Pulsed-Laser Irradiation

Many of the fundamental aspects associated with nonequilibrium thermodynamic and kinetic effects in materials can be investigated only through measurements performed during transient processes. The establishment of thermal melting as the mechanism of pulsed-laser annealing in silicon was, for instance, possible only after the development of techniques for nanosecond-resolution, time-resolved, X-ray measurements by Ben Larson, Woody White, and Tom Noggle of the Solid State Division, and Denny Mills of Cornell University. The time-resolved X-ray measurements showed directly that the lattice temperature in silicon reached the melting point during the laser pulses. Extending this work in silicon, Larson, Tischler, and Mills have made nanosecond-resolution X-ray measurements of the overheating and undercooling at the liquid-solid interface required to sustain the rapid laser-induced melting and regrowth rates.

The pulsed time–structure of the Cornell High Energy Synchrotron Source has been used to make these nanosecond-resolution measurements of the temperature of the liquid-solid interface in silicon by monitoring the thermal-expansion-induced strain in the crystal lattice at the interface. As illustrated schematically in the drawing, nanosecond-resolution X-ray diffraction was obtained by synchronizing the firing of the 25-ns laser pulses such that the 0.15-ns probing X-ray pulses reached the sample at the desired measuring time relative to the laser pulses. The crystalline silicon below the liquid-solid interface then acted as a self-thermometer as the lattice temperature distribution was determined from Bragg reflection profile measurements of the thermal strain.

Measurements on <111> oriented silicon during and immediately following 25-ns ultraviolet (249- nm) laser pulses have shown that the interface temperature during regrowth was 110 K lower than that measured during the melting phase. This temperature difference represents the sum of the overheating to obtain 11 m/s melting and the undercooling necessary to achieve 6 m/s regrowth. Surprisingly, interface temperature measurements made at zero velocity as the melt penetration stopped and crystal regrowth began showed that nearly all of the temperature difference was associated with regrowth, even though the melting velocity was nearly twice as large as the regrowth velocity. The underlying reason for this asymmetry in the driving forces is not currently known; the result, however, does indicate that crystal growth is significantly more difficult than melting under these laser conditions. Measurements made on <100> silicon have yielded an interface temperature difference of only 50 K, suggesting that the growth kinetics are easier for the <100> interface geometry.

Detailed measurements of thermodynamic and kinetic parameters such as these are needed in formulating a fundamental understanding of pulsed-laser-induced materials phenomena. Effects in silicon that are important from a materials-processing point of view are the dependence of segregation coefficients on crystallographic orientation and interface-velocity, the amorphization of silicon at growth rates exceeding ∼12 m/s, and the orientation dependence of the onset of amorphization of silicon during rapid regrowth.—*B. C. Larson*



accessible with MBE and CVD. We believe that the versatility of this technique will eventually lead to a host of new materials properties.

Ion-beam and laser techniques offer many opportunities in materials research. In this discussion the emphasis has been on the nonequilibrium aspects of materials processing with these techniques and on their usefulness in fundamental materials studies. Ion and laser beams are also sensitive and versatile analysis probes of the state of matter that can offer unique insights into materials interactions. Although not emphasized here, it should be recognized that beam processing has many practical applications as a surface modification tool. These techniques hold a special place in surface modification because they alter surfaces on the atomic scale. The brief allusion to the use of ion beam and laser processing in the semiconductor industry is really a prophecy of their importance in the future. As electronic device structures become smaller and smaller, deposition, etching, epitaxy, and all other processing steps will require the kind of resolution and control that only techniques such as these can provide (see Figs. 7 and 8). Of course, this control can be useful only if we understand the materials interactions in sufficient detail, thus bringing us full circle to the importance of fundamental research.

BOOKS

The Joy of Science: Excellence and Its Rewards, *Carl J. Sindermann, Plenum Press, New York, 1985, 256 pages. Reviewed by Carolyn Krause, ORNL* Review *editor.*

What does it take to be a successful scientist? What are the job satisfactions of doing good science? What are the career options for scientists? Can women make it in science these days? These are some of the questions addressed in depth by *The Joy of Science.*

The author of *Winning the Games Scientists Play* (reviewed in the No. 3, 1984 issue of the *Review*), Carl J. Sindermann is director of the Sandy Hook Marine Laboratory in New Jersey and adjunct professor of oceanography at the University of Rhode Island. He writes clearly, concisely, and humorously about a variety of subjects that may be of interest to all scientists and many nonscientists as well.

The title of this upbeat book is a little misleading because it is not 100% concerned with the joy of science. In fact, sometimes the book discusses science's negative aspects (e.g., fraud) and even its sorrows (e.g., regrets about not devoting enough time to spouse and children because of the need to work long hours in the laboratory). The author recognizes this problem and tries frequently to relate the subject matter at hand to the joy of science, which he defines as "a sense of internal well-being and satisfaction."

The book relates many case histories (the names used are usually fictitious) about male and female scientists who make it and how they did it. It also contains many useful lists (e.g., ways to successfully communicate research results).

What is the recipe for success in science? According to Sindermann, if you practice excellence in science—choose research problems correctly, design experiments logically, derive significant insights from interpreting research results, keep up with the literature in your field, communicate your research results effectively, maintain a high level of productivity, and consistently enjoy your work, you are a successful scientist.

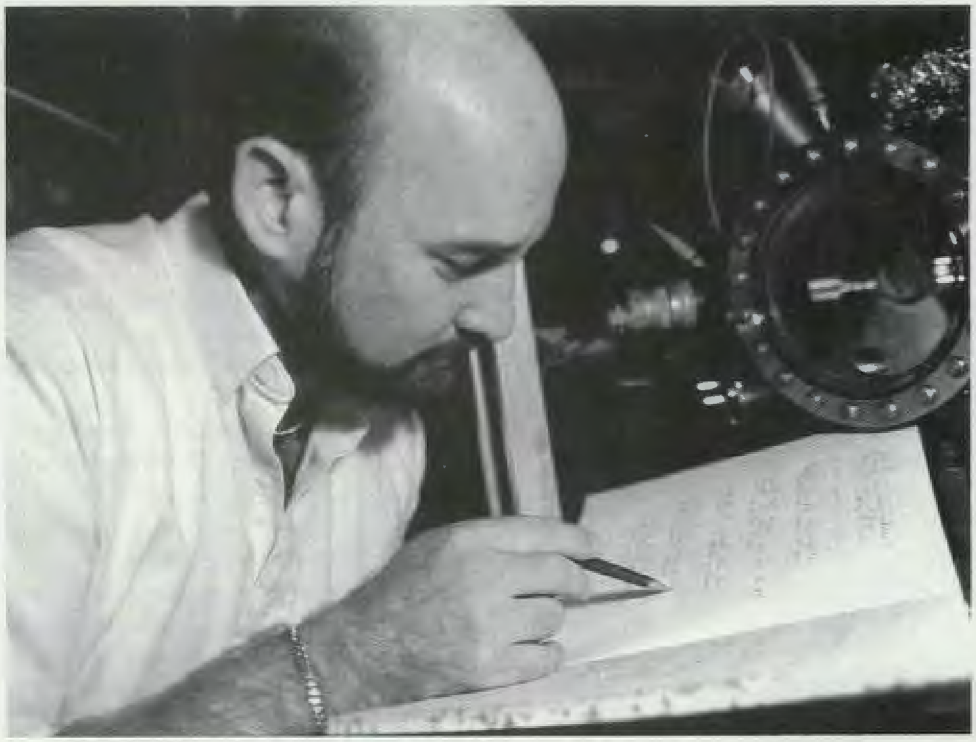
However, to the outside world, the author argues, the most successful scientists appear to combine technical achievement with skills in interpersonal relations. The "scientific elite" are highly productive professionals endowed with charisma who usually surround themselves with people ("loyal support infrastructure"). They maintain close professional relationships with colleagues, participate in activities of professional societies, serve as reviewers or editors for journals, organize or chair workshops, and win prestigious awards.

Various chapters in Sindermann's book may appeal to some groups of scientists more strongly than others. Older scientists should be interested in the chapter on "Managing Career Transitions," which states that the four principal motivations for career changes are a financial crisis, midlife crisis, divorce, or death of someone close. The chapter on "Career Destinations," which describes the various types of jobs open to scientists (e.g., researchers, educators, administrators, bureaucrats, entrepreneurs, consultants, and international scientists), may be of particular interest to graduate students and scientists who have just started their careers. A similar chapter, "Scientists Outside the Laboratory," describes other roles for scientists: advocate, expert witness, political liaison, and public scientist (e.g., Carl Sagan).

Women scientists may be particularly drawn to the chapter on "The Ascendant Female Scientist." Sindermann, who is careful to write in nonsexist language, states that the most successful female scientists work in the upper echelons of science-based federal regulatory agencies, the middle bureaucracy of government granting agencies, government research laboratories, and scientific communications in all media. "Good female scientists," he adds, "are finally making it into senior positions—as measured by salary and support staff—in federal research laboratories."

All in all, I basically agree with the review excerpt quoted on the book's jacket by W. S. (Bill) Lyon, consultant to ORNL's Analytical Chemistry Division: "Sindermann has the rare ability to combine clear entertaining prose with unique observational and synthesizing talents. . .[He] has captured the joy, the special emotion that goes with scientific achievement, and has expanded upon it. But he has done more than merely describe the successful scientist; he shows us a number of options that the scientist has open to him at various stages of his career. . .But just as important the book can provide the nonscientist with a rare view of what the scientific life is like. Its deceptively simple style conveys a world of truth."

David Zehner is head of the Surface Physics Group in ORNL's Solid State Division. He joined the division in 1971 after earning his Ph.D. degree in physics from Brown University. His thesis work for Harrison Farnsworth, a pioneer in surface physics, focused on using low-energy electron diffraction to characterize the surface properties of clean rhenium surfaces and to examine the interaction of small molecules with them. At ORNL he has used a wide variety of spectroscopic techniques to examine the surface properties of both metals and semiconductors and the interactions of small molecules on them. He is also involved in carrying out experiments at the National Synchrotron Light Source at Brookhaven National Laboratory using a beam line recently constructed in conjunction with the University of Pennsylvania.



A View of the Surface on the Atomic Scale

By DAVID M. ZEHNER

When was the last time you thought about a surface? From day to day most of us pay little attention to the role of surfaces in our interaction with the environment. Although they are all we ever see, they usually are taken for granted. Each day we use the surfaces of kitchen counters, smoothly paved roads, and desks, but few of us ever think much about them.

Beneath these surfaces, with which we interact everyday, structural supporting material provides strength and rigidity. The surface scientist, however, focuses on the surface and examines how atoms on this "platform" interact with each other. For that scientist, the bulk of a solid simply holds the surface in place so that it may be carefully studied. In fact, the outermost atomic layers of solids (the "surface" layers), constituting perhaps only one-millionth of the mass of a macroscopic sample, play a disproportionate role in how the whole solid sample interacts with its environment. Thus, surface science has applications in the electronics and computer industries, the world of chemistry and especially catalysis, and a host of other energy-related technologies.

The most detailed microscopic description of a surface possible is the ultimate goal of a surface scientist. What does a surface look like, what foreign atoms or molecules are on it, and where do they sit? Answers to these questions are needed to gain the level of understanding required for efficient use of materials for technology. Fortunately, advances in surface science during the last two decades have put this objective within our reach. Advances in two other areas have contributed to this success. It is now routine to achieve an ultrahigh vacuum (UHV) environment to slow the rate at which gas molecules are adsorbed on a solid to the point that it takes days for a single layer of molecules, or a monolayer, to cover the surface; this type of environment is needed to perform detailed experiments. In addition, the development of spectroscopies that are both sensitive to only the surface region and provide for rapid data acquisition with extremely good resolution has permitted us to answer more and more difficult questions.

The extent of activity in the area of surface science at Oak Ridge National Laboratory has increased markedly during the last decade. Physicists, chemists, and

Surface science has increased markedly at ORNL in the last decade. Studies have shown that metal surface layers have different structures than do bulk layers, that the spacings between layers near the surface differ from spacings between bulk layers, that copper cooled to the right temperature can serve as a catalyst to produce a desired reaction product, and that different types of atoms bond similarly to a molybdenum surface.

material scientists in many divisions at ORNL now routinely perform detailed investigations of surface properties (see the sidebar by Steve Overbury on page 40 for a review of the many surface spectroscopies and approaches employed in a number of divisions at the Laboratory).

The Look of a Surface

What does a surface look like? The truncation of a solid creates a surface. If the solid is a crystal, the geometric positions of the atoms within the solid, or the "lattice structure," can be determined. Can we assume that this structure continues outward to the surface in a so-called bulk truncation? Bulk-to-surface continuity may exist in some special cases; however, the evidence acquired during the last decade indicates that it is not typical. Instead, it has been determined that the atoms within the surface region respond to the changes in the electrostatic environment induced by the creation of a surface and are displaced from their bulk positions. In an extreme case, changes result in a surface being reconstructed, a situation in which either massive displacements of, or the actual removal of, atoms from a given plane occur.

Scientists have developed a wide variety of techniques to determine the structure within the outermost layers of a crystal. Low-energy electron diffraction (LEED) is probably the most durable of the surface-sensitive techniques for determining surface crystallography. It was first used as a probe of the surface region in 1927 when C. J. Davisson and Lester Germer from Bell Telephone Laboratories serendipitously discovered electron diffraction from a nickel oxide (NiO) surface. Today, it is still one of the more precise modern techniques and has been employed extensively in ORNL's Solid State Division. In a LEED analysis the surface geometry is determined by examining the elastically scattered electrons. Fortunately, electrons interact very strongly with the solid, and elastic scattering occurs only in the top few layers, just the region we are interested in investigating. Also, electrons behave like waves. Because the wavelengths for electrons having energies between 20 and 500 eV are 2.7–0.5 Å, it is possible to use the information obtained by observing the wave diffraction of these particles from a surface (in which the atoms are separated by distances of 1–4 Å) to determine interatomic spacings within the outermost layers. By examining the angular positions of the reflected beams, called spot patterns, we can determine the symmetry and size of the surface unit cell. Any differences in these spot patterns from those expected for a bulk truncation reflect changes in the geometric arrangement of atoms within the surface region. Reconstruction within the outermost layers is usually observed in this way. To obtain detailed information about the positions of atoms within the unit cell, as well as interlayer spacings, we must measure the changes in the diffracted intensity as a function of the changes in the incident energy (I vs V profiles) for a number of different reflected beams. These profiles are then compared with results of model calculations, and by means of a trial-and-error procedure, a model for the geometric structure is obtained.

The combined efforts of two Solid State Division scientists—the experiments of John Noonan in the laboratory and the persistence of theorist Harold Davis at the computer terminal—have significantly improved both the experimental and the theoretical aspects of LEED analysis during the last decade. These improvements have allowed a much more reliable determination of surface structures than thought possible a decade ago. Although the improvements are noteworthy, the real significance of the increased reliability is that it has contributed to our understanding of surfaces. Recent LEED analyses have shown that the structure of all metal surfaces is fundamentally different from that of the bulk, even in solids whose atoms have the same periodicity parallel to the surface as they have within the bulk.

Surface Relaxation

What changes can occur within the surface region? One change is surface relaxation, which was first discovered in aluminum in 1972. In the analysis of the Al(110) surface, the relaxation was identified as an "inward contraction" of the top layer of the crystal with respect to the second layer; in other words, the spacing between the top two layers is smaller than the spacing between similar layers, or planes, in the bulk. However, the size of the contraction was not precisely determined; values ranged from −5 to −15% of the bulk interlayer spacing, depending on which group performed the study.

In an extensive study of the Al(110) surface in 1982, Noonan and Davis compared the measured intensity of nine diffraction beams with the results of a large number of model calculations. In these calculations it is important to account for nonstructural parameters such as the scattering potential, the electron attenuation, and thermal vibrations, as well as structural parameters (i.e., the geometric positions of the atoms). After an exhaustive search, it was determined that the best agreement achieved was for the following set of interlayer displacements, Δd_{ij}:

$\Delta d_{12} = -8.5 \pm 1\%$,
$\Delta d_{23} = 5.5 \pm 1.1\%$,
$\Delta d_{34} = 2.2 \pm 1.3\%$,
$\Delta d_{45} = 1.6 \pm 1.6\%$,

where the Δd_{ij} are changes in the spacing between layers i and j with respect to the bulk spacing. These results, shown in Fig. 1, indicate that displacements of several layers can be determined from a LEED analysis and that, in many cases, an oscillatory change occurs in the sign of the displacements (e.g., the spacing between the first two layers is smaller than the bulk-layer spacing, and the spacing between the second and third layer is larger).

The Al(110) surface was selected to illustrate how LEED analysis can be employed to identify the displacements between the outermost layers of metal surfaces. It has recently been determined that some surfaces exhibit not only displacements perpendicular to the surface but also uniform displacements parallel to the surface. For example, the stacking sequence of the W(211) surface is such that in the bulk-truncation structure the atoms within the second layer are not positioned at the center of the rectangular unit cell of the first layer. However, in a LEED analysis performed by Gwo-Ching Wang and Harold Davis, it was determined that atoms within the top layer shift laterally as well as inwardly in order to center the surface unit cell around atoms within the second layer. Therefore, even though the spot pattern is the same as that expected for bulk truncation, the surface is significantly distorted from the ideal truncated bulk lattice.

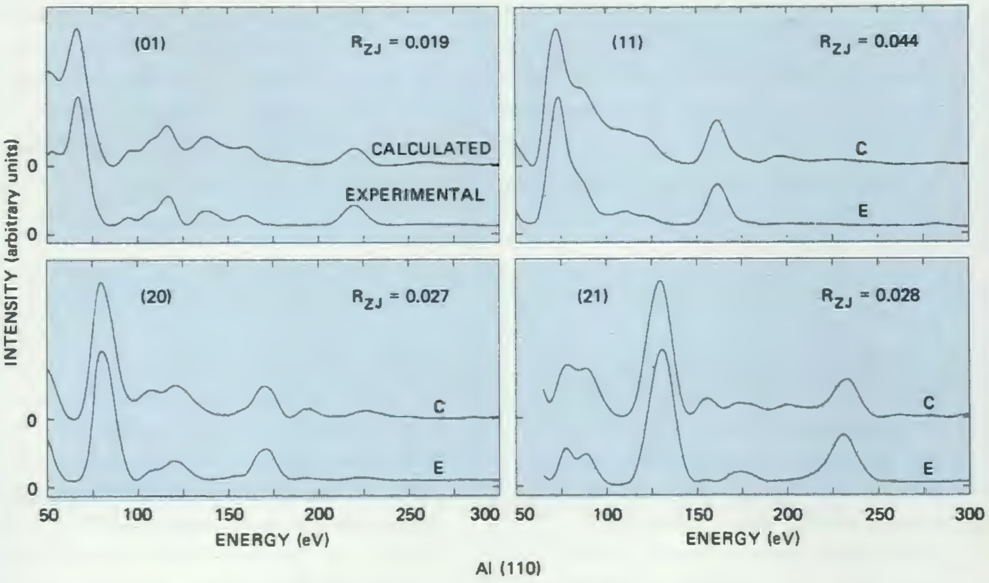


Fig. 1a. This comparison of calculated and experimental I-V profiles for Al (110) illustrates the current level of accuracy of LEED analysis. The numbers R_{ZJ} are numerical measures of the quality of agreement; values less than 0.1 are normally considered quite good.

Rippled Surfaces

Not surprisingly, the complexity of surface structure increases in a multicomponent alloy crystal such as nickel aluminum. The structure of the NiAl(110) surface shows how surface-induced forces affect a binary system. NiAl is an intermetallic compound that orders in the CsCl structure (i.e., two interpenetrating simple cubic sublattices of Ni and Al forming a body-centered-cubic lattice). An examination of the (110) surface shows that it consists of alternating chains of Ni and Al atoms. Fortunately, such a surface having the bulk composition can be prepared for experiments.

This surface recently has been examined by Noonan and Davis using LEED. By comparing the measured and calculated I-V profiles, they identified a novel feature of the NiAl(110) surface—a reconstruction in which chains of Ni atoms are contracted toward the bulk and chains of Al atoms are expanded away from the bulk. This reconstruction, shown in Fig. 2, can be viewed as a "rippled surface" that has an amplitude of separation of 0.2 Å. Such a ripple was also observed in the second layer, although the amplitude of separation was reduced to 0.02 Å. This example shows how different kinds of atoms within the outermost layers respond to the change in environment caused by the truncation of the bulk.

The information obtained from these analyses is useful because, in the real world, surfaces are continually being modified by interaction with the environment (e.g., oxidation and corrosion). To understand these changes, we must know where the atoms at the

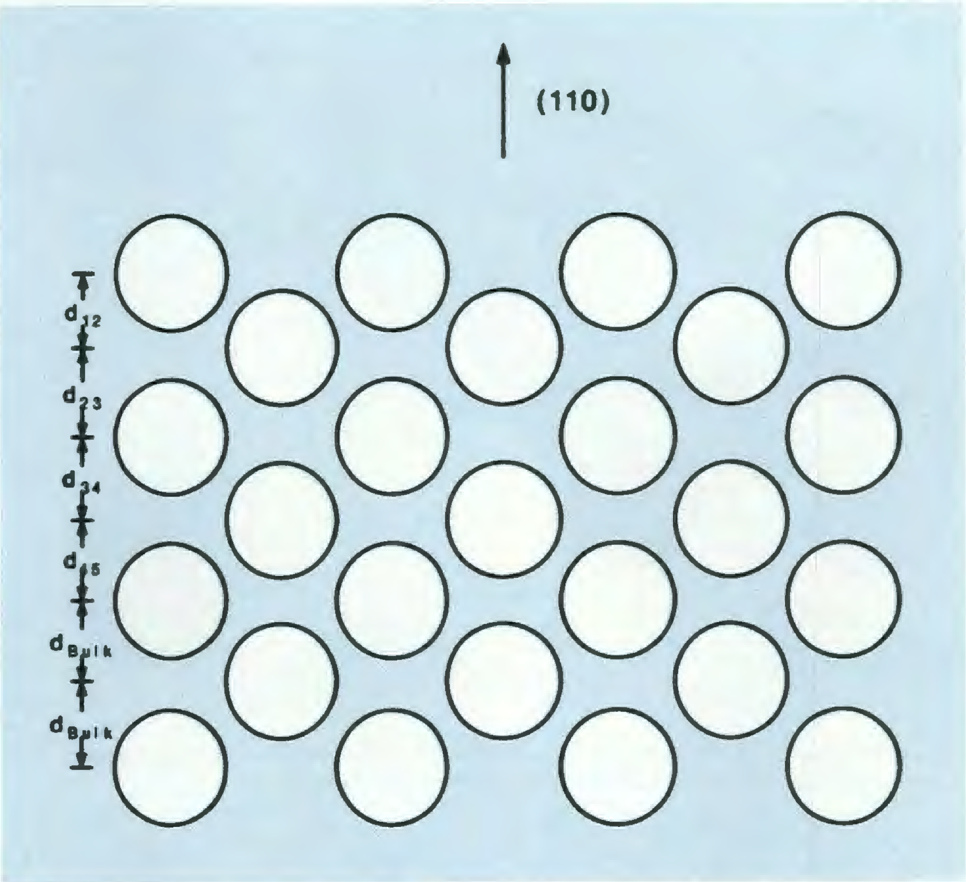


Fig. 1b. Interlayer spacings that are determined in this analysis are identified in the illustration of the ball model.

surface are positioned. Investigations such as those described above have the potential for advancing the understanding of more complex problems in solid-state physics. For example, as our knowledge of pair interactions at surfaces becomes more quantitative, it can be used to understand internal interfaces, such as grain boundaries and transitions between epitaxial layers.

What's on the Surface?

Now that we know what a surface looks like, the next question to address is, What's on the surface? In the examples discussed previously, I focused on surfaces containing only those types of atoms that make up the particular solid being investigated. However, in their usual environment, surfaces are covered with a variety of impurities such as oxygen, carbon deposits, organic molecules, and metal particles. Also, in many situations various chemical species are intentionally deposited or adsorbed onto a surface that was previously cleaned in the hope of understanding interactions at the surface. To determine which molecules are present on the surface, we need some method of identifying elements. Two very popular surface-sensitive techniques, photoemission spectroscopy and Auger electron spectroscopy (AES), can identify specific types of atoms by exploiting one property of elements—they each contain electrons bound with unique well-defined energies. These techniques are popular because of their ease of implementation and interpretation as well as their relative simplicity and low cost. Both start by removing an electron from a deeply bound energy level, leaving a core hole.

In photoemission (see Fig. 3), an incident photon ejects an electron from a core level of an element, and the kinetic energy of the emitted electron is measured. If we know the energy of the incident photon, we can determine the binding energy of the emitted electron and therefore identify the element from which it was emitted. AES also depends on the emission of an electron. In the so-called Auger process, the hole, usually created by either an incident photon or electron, is filled by an electron from a higher-energy level accompanied by the simultaneous ejection of an additional electron. Each element has its own characteristic "Auger emission" spectrum. In both processes, the core level can be viewed as a window for identifying types of atoms present.

Why are these techniques used to determine what's on the surface? As mentioned previously, surface scientists often desire an atomically clean surface to perform an investigation. However, in almost all cases, the surface is covered with contaminants when it is inserted in the UHV chamber. To guide the preparation of a clean surface, identifying the foreign species is essential. The most commonly used approaches to surface cleaning are to (1) heat the sample to a relatively high temperature, sometimes in the presence of a gas or (2) sputter the sample with ions to remove the unwanted contaminants and then heat it to anneal out the damage. A new and rather novel approach was discovered in 1980 when Gary Ownby, Woody White, and I were involved in trying to determine whether intense laser beams could be used to alter or modify the outermost layers of a surface. We discovered that atomically clean surfaces could be produced by laser annealing in very short times.

These observations were made when we examined the effects of irradiating single crystals of silicon (Si) in UHV with laser light. As shown in Fig. 4, an Auger spectrum obtained from the air-exposed Si sample after insertion into the UHV system showed that oxygen (O) and carbon (C) were present on the surface and that much of the Si present was in the form of SiO_2. From these and additional measurements we determined that an overlayer, 20 Å thick, covered the surface. We also discovered that irradiating this surface with an intense laser pulse (~2.0 J/cm^2) substantially reduced the levels of O and C present in the surface region. After exposing the same spot to five laser pulses, we obtained an Auger spectrum showing that, for the same detection conditions, the O and C signals were within the noise level and corresponded to O and C surface concentrations of 0.1% of a monolayer. In addition, the Si Auger lineshape was found to be that expected for a clean Si surface. Consequently, we found that irradiating the crystal with about five laser pulses reduced the O and C contaminant levels by factors of at least 500 and 50, respectively. These reduced contaminant levels, which can be obtained in a processing time of 30 ns, are comparable to those obtained by repeated sputtering and conventional thermal annealing over several days. In the electronics world, which is dominated by Si technology, these results may eventually prove useful.

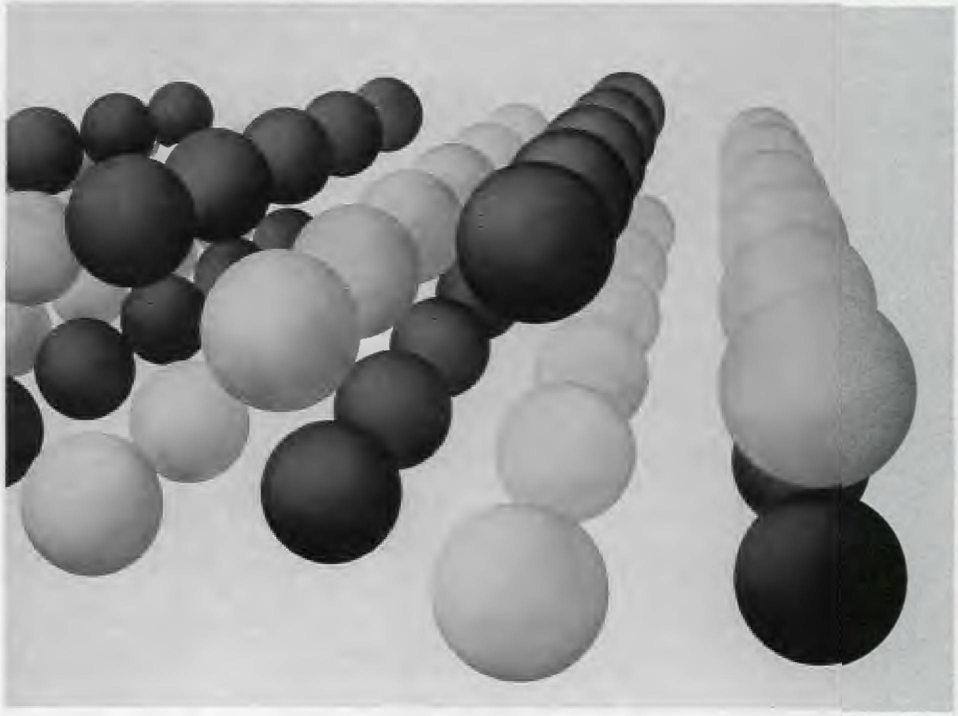


Fig. 2. Rippling in the outermost layers of the NiAl (110) surface viewed as chains of Al atoms expanded outward and chains of Ni atoms contracted inward.

Surface Modification

Once a clean surface is prepared and characterized, it is ready to be modified in some way if it is desired to do so. The adsorption of a gas atom or molecule is a simple surface-modification technique. Characterizing the steps leading to the formation of an oxide on the surface illustrates this modification. Thermodynamically, metal oxides are normally more stable than pure metals. However, because they are easier to form and are tougher than their more stable oxides, unstable metals are used to build cars, bridges, etc. Their use is possible because a thin oxide film forms at low temperatures and slows or stops the subsequent conversion of the metal to an oxide. Thus, the subject of room temperature oxidation is important. Many techniques have been used to study the phenomena occurring during the transition from an atomically clean metal surface to a metal covered with an oxide. An extremely useful probe is X-ray photoemission spectroscopy (XPS) because it reveals how atoms are chemically attached to the surface and how many atoms are present.

During the last several years, Greg Gruzalski, John Wendelken, and I have been using this technique to examine the interaction of oxygen with single-crystal surfaces of several materials. We wanted to determine the probability of oxygen adsorption (sticking coefficient), the amount adsorbed, and if the adsorbed atoms formed ordered overlayers. We examined oxygen adsorption on the (110) surfaces of nickel, copper, and nickel aluminum. To make these measurements, we examined the samples using XPS following the adsorption of oxygen. Our measurement of the binding energy of the (1s) level of oxygen shows that for room-temperature adsorption on all three surfaces, the molecule dissociates in the presence of the surface and that only atomic oxygen is present. However, the similarity ends here. In the case of Ni, the initial rate of uptake of oxygen (i.e., the sticking coefficient) is very rapid (see Fig. 5). It begins with dissociative chemisorption, a stage that is completed by an exposure of 20 L (where 1 Langmuir = 1×10^{-6} Torr · s). This stage is followed by a reduced adsorption rate, the nucleation of NiO, and its lateral growth to coalescence over the nickel surface. Eventually a film thickness equivalent to about

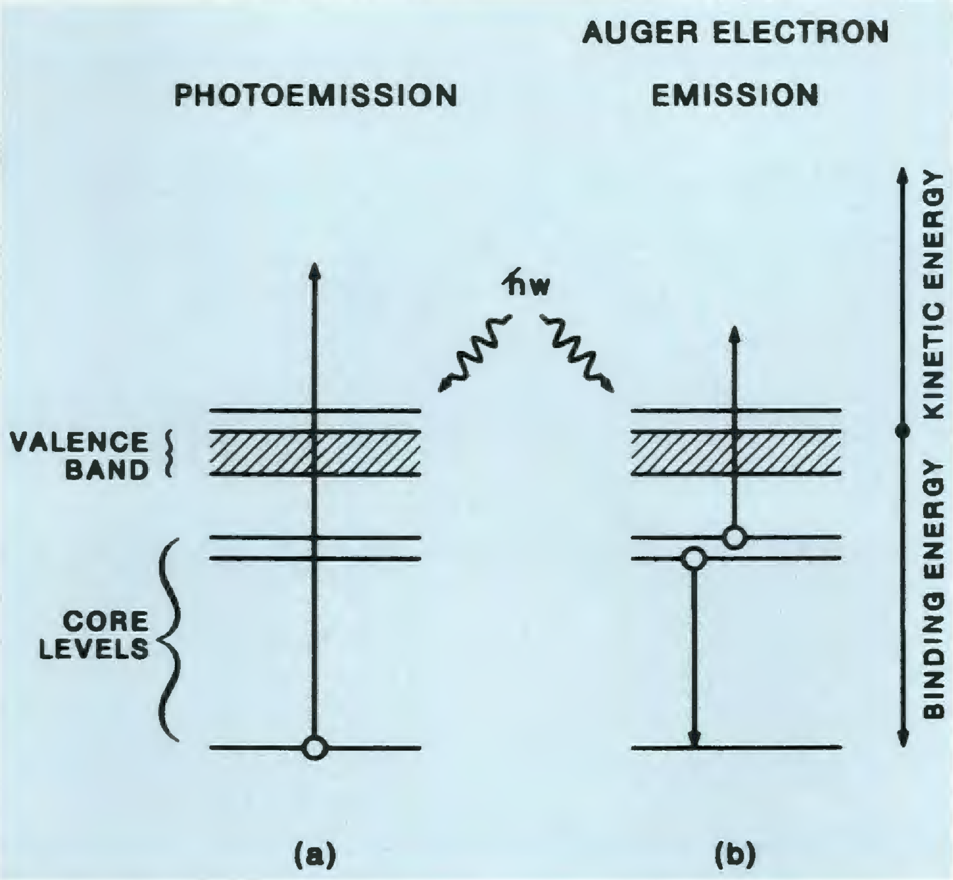


Fig. 3. Incident photons interact with the solid, resulting in the emission of electrons (commonly known as photoemission spectroscopy). Auger electrons are emitted when the core-hole is filled by an electron accompanied by the simultaneous ejection of an additional electron. By measuring the intensity and energy of the emitted electrons, scientists obtain information about the physical and chemical properties of the surface region.

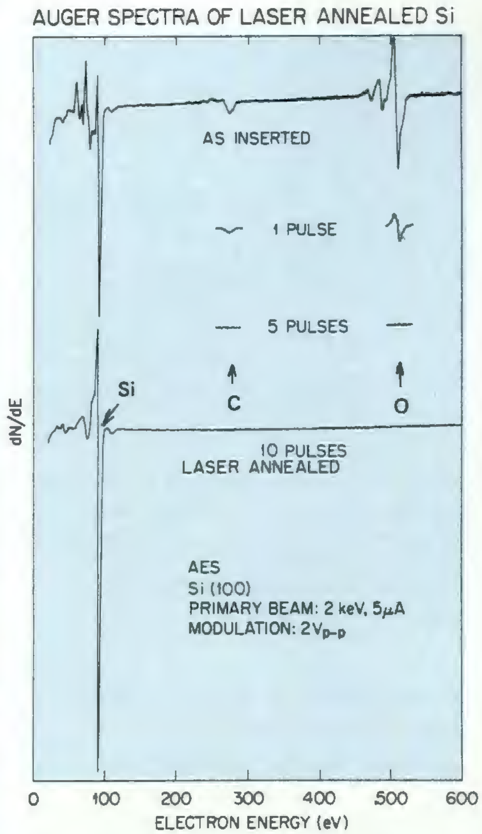


Fig. 4. Auger spectra obtained from a silicon surface. The spectrum from the as-inserted surface shows it to be covered with large quantities of carbon and oxygen. By irradiating the surface with the output of a ruby laser, the impurities are desorbed from the surface and thus are not detectable in the Auger spectrum.

3 monolayers of NiO is formed following an exposure of 150 L. The behavior on copper (Cu) is quite different. Initially it also rapidly adsorbs oxygen, but after a half monolayer is adsorbed, the surface resists further uptake (i.e., the sticking coefficient becomes quite small). In fact, oxygen exposures of 10^5 L or greater are required for copper to adsorb appreciably more oxygen on the surface, resulting eventually in the formation of an oxide film. During oxygen adsorption on both Ni and Cu, oxygen atoms order in regular periodic arrays that produce new spots in the LEED patterns. In fact, these spot patterns are used to determine the surface coverage and thus permit calibration of the X-ray photoemission intensity plots. The behavior of the NiAl surface is remarkably different. The initial sticking coefficient is quite small, so oxygen exposures of 10^2 L or greater are required to induce NiAl to adsorb even a small amount of oxygen. Eventually, after an exposure of 2×10^3 L or greater, an oxide layer is formed. However, the oxygen is not ordered on this surface, and thus the calibration is made by comparing these data with those obtained from the Ni surface. In the case of NiAl, it is also possible to use X-ray photoemission to determine that the oxygen is preferably bound to the Al atoms by observing the chemically shifted Al core levels. These results indicate that the behavior of an alloy surface can be quite different from that for the surface of either of the constituent elements.

Another challenge for surface scientists is the chemical identity of foreign species. Is it possible to determine the chemical state of an atom in contact with the surface? If it is present as part of a molecule, can we identify the molecular species? Consider adsorption of molecules from the gas phase on the Cu (110) surface. While investigating the oxidation of this surface, Gruzalski, Wendelken, and I also examined the reaction of nitric oxide (NO) with the copper surface as a function of both exposure and substrate temperature. Because of the unique energy level structure of each element, XPS is an ideal probe for identifying atoms at the surface.

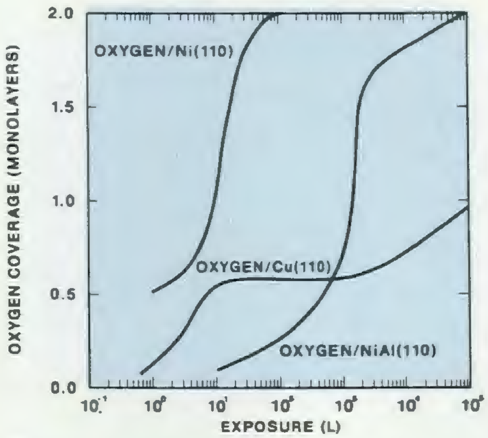


Fig. 5. Oxygen coverage as a function of exposure for the (110) surfaces of Ni, Cu, and NiAl. The differences in the shapes of these "uptake" curves result from different sticking probabilities for oxygen on each surface.

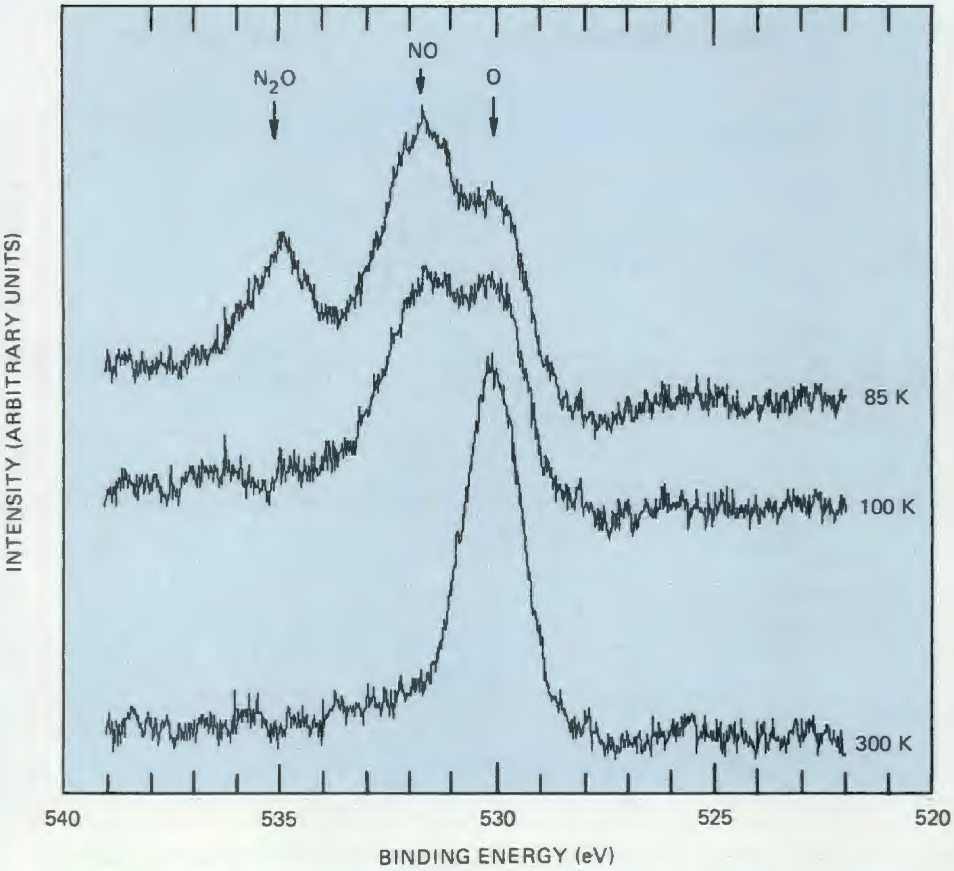


Fig. 6. X-ray photoemission spectra from the Cu (110) surface following the adsorption of oxygen and nitric oxide at different crystal temperatures. Each peak in the spectra reflects oxygen in a different chemical environment. The formation of nitrous oxide is catalyzed on the surface only when the crystal temperature is below 85 K.

Furthermore, in many cases the binding energy of a core-level electron is very dependent on the chemical state of the species. In particular, the binding energy of the (1s) electron of O, the most deeply bound core electron, is very sensitive to its chemical environment. As previously mentioned, molecular oxygen dissociates when interacting with the Cu surface at room temperature, resulting in the adsorption of atomic oxygen. This result is also observed when the crystal is cooled to near liquid nitrogen temperature, 85 K.

But, what happens when the clean Cu surface is exposed to NO at this same temperature? When we examine XPS spectra for the O (1s) core-level region, we find three peaks (see Fig. 6). One peak occurs at the same energy as that observed during the oxidation studies, thus indicating that atomic oxygen is present. Obviously, some of the NO dissociated into nitrogen and oxygen when it contacted the Cu surface. To identify the other two peaks, we raised the substrate temperature to 100 K and performed the same experiment. We observed only two peaks in the spectra. In the course of comparing these and other spectra, we determined that at a substrate temperature of 85 K, in addition to dissociating and also adsorbing as a molecule, the NO reacted with O to form N_2O. Clearly, the three peaks we observed reflected three different chemical environments of oxygen. At a substrate temperature of 100 K, however, we found that the formation of N_2O was inhibited and only NO and O were present. Thus, by controlling the surface temperature we can selectively use it as a catalyst for the formation of N_2O.

Where Does an Atom Sit on the Surface?

Where does a foreign atom or molecule reside when it sits on a surface? By answering this question we can determine both its position and whether its presence causes the atoms in the outermost surface layers to reorganize themselves into different arrangements from those observed for the clean surface. To show how these questions can be answered, I will discuss two examples at ORNL employing two additional spectroscopic techniques.

Low-energy ion scattering can be used to provide information about surface structure and the location of adsorbed atoms. Steve Overbury in the Chemistry Division has been a pioneer in the development of this technique for studying chemical interactions at a surface. An ion-scattering experiment can be viewed as billiards on an atomic scale. Imagine a billiard table with balls arranged in a cluster but somehow obscured from the player's view. The player's goal is to determine the arrangement of the balls by shooting a cue ball at them and observing the final direction and velocity of the cue ball after it bounces off the cluster. In the ion-scattering experiment the incident ions are like cue balls and the surface is the cluster of unknown geometry. The final velocity, or energy, of the ions and their final directions are determined by an electrostatic analyzer and detector. This analogy is quite accurate because, at the ion energies used, the motion of the ions is governed by the laws of classical mechanics.

Overbury has applied this technique to study the adsorption of small molecules such as oxygen, ethylene, sulfur, and carbon monoxide on single-crystal surfaces of molybdenum (Mo). At or above room temperature, the molecules spontaneously decompose on a clean (100) Mo surface, as has been determined by other techniques. This decomposition occurs because the bonding of the individual atoms to Mo is stronger than the bonds between the atoms in the molecules. But, do the resulting "ad-atoms" bond to one, two, or more Mo atoms and where do these ad-atoms stick? To put it another way, do they go to an atop site, bridged site, or fourfold hollow site?

To answer these questions, Overbury oriented a Mo crystal with respect to the incident ion beam in a preferred geometry for scattering (see Fig. 7). A detector was positioned so that it could detect only ions scattered in a particular direction. Under these circumstances the observed scattered ions are predominantly of two energies—that is, they have lost either about 65% or about 75% of their initial energy. From analysis of the energetics, Overbury found that the two energies correspond to trajectories in which the particle scatters from only one atom ("single scattering") or in which it scatters sequentially from two atoms ("double scattering"). If oxygen is adsorbed on the surface, the scattering spectrum changes. Double scattering is no longer observed, as would be expected if the oxygen atoms blocked the path of the double scattering ions, causing them to lose a much larger fraction of their energy. This observation and those at other angles support the conclusion that oxygen is bonded at the fourfold hollow site. Overbury found that carbon, sulfur, and nitrogen atoms also tend to adsorb at this site.

Below sufficiently grazing incident angles, even the single-scattering type of trajectory is blocked by oxygen atoms bonded above the surface. Measurement of this angle and comparison with results of computer simulations of the ion trajectories has permitted the determination that oxygen atoms are located about 0.3 Å above the plane of the first layer of Mo atoms.

As the amount of material adsorbed on a surface increases, it is reasonable to expect that more than one type of adsorption site would become populated. This phenonemon might result as a consequence of the complete filling of one kind of site or might simply be a competition between two or more kinds of sites, each having a different sticking probability. To illustrate that this adsorption by sites of more than one type indeed occurs and that it is possible not only to distinguish between two types of sites but also to determine how they are populated, consider the adsorption of oxygen on a clean tungsten [W (112)] surface. At room temperature oxygen adsorbs dissociatively on this surface and forms a variety of ordered overlayer structures that have been characterized by their LEED patterns. One type of LEED pattern is observed at a coverage of 0.5 monolayers, and then a second pattern develops as the monolayer is completed with additional exposure. Further oxygen may then be adsorbed in a second layer, leading to a total coverage of 1.5 monolayers, and a third LEED pattern is observed. It has been postulated that two different sites are populated in this adsorption sequence. Initially oxygen atoms are thought to bond in bridge sites in the troughs, which are present because of the open nature of this surface. This is thought to be followed by adsorption into bridge sites in the top layer. These ideas about bonding result from an examination of the surface structure (see Fig. 8a).

The electron energy loss spectroscopy (EELS) technique can be used to provide concrete evidence in support of these ideas. In the EELS technique, electrons having relatively low energy, usually between 1 and 10 eV, are directed at the surface, and the energies and intensities of the scattered electrons are measured using a very high-resolution detector. When the electrons interact with the surface, some of them will lose energy as a result of exciting a vibration between two atoms. By measuring the vibrational energy losses in the back-scattered spectra and comparing them with either other types of data or the results of calculations, it is possible to obtain information about the positions as well as the identity of adsorbed atoms.

Vibrational electron-energy-loss spectra were obtained by John Wendelken for each of the three coverages mentioned following oxygen exposures at room temperature. As shown in Fig. 8b, after a low exposure, a loss peak at 82 meV dominates the spectrum, which includes a much weaker peak at 52 meV. However, after a higher exposure, the lower peak becomes dominant. These two loss peaks, which behave independently, may be associated with two distinct

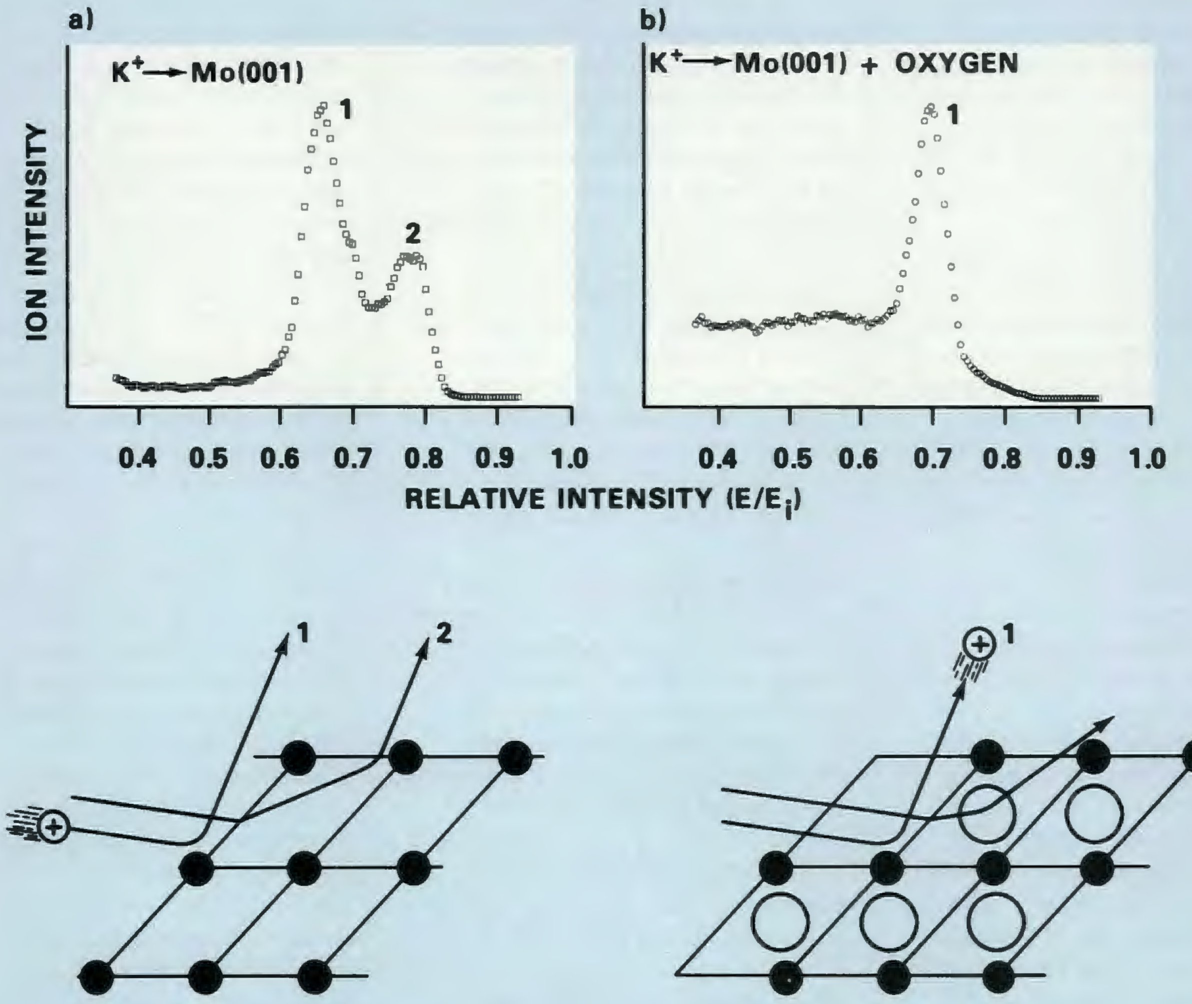


Fig. 7. Scattered K^+ ion energy distributions are shown for a clean (a) and oxygen-covered (b) Mo(001) surface. The trajectories responsible for the peaks in the energy distributions are shown schematically. On a clean surface, single and double collision-type events occur. When oxygen is present, only ions that scatter from a single Mo atom are observed. Those which would have been double-scattered are blocked by oxygen atoms, which either deflect them or cause significant energy loss.

adsorption sites, in which the first is more tightly bound to the surface than the second. Both loss peaks shift up in energy when the coverage increases above 0.5 monolayers, but the behavior of the 82-meV peak is particularly interesting in that its intensity decreases after reaching a maximum peak intensity at 0.5 monolayer coverage. The most probable cause is surface reconstruction.

As mentioned previously, it had been determined in a LEED analysis of the clean surface that the top layer was uniformly shifted parallel to the surface. It is believed that the adsorption of oxygen causes the atoms to shift back to their bulk-truncated positions. Thus, if the oxygen atoms in the first monolayer are adsorbed in bridge sites in the trough as suggested, the bonding site should be strongly affected by this changing substrate geometry, leading to a shift in vibrational energy as well as in intensity. Although the oxygen adsorption is generally discussed as the formation of one layer followed by a second layer, the vibrational data indicate that some oxygen atoms occupy the second layer before the first layer is complete. It has been shown by Gwo-Ching Wang that the growth of the first layer up to 0.5 monolayers occurs through an island mechanism. These data suggest that higher-density islands may develop concurrently with the adsorption of some oxygen in the second-layer sites.

The examples of surface research presented herein were

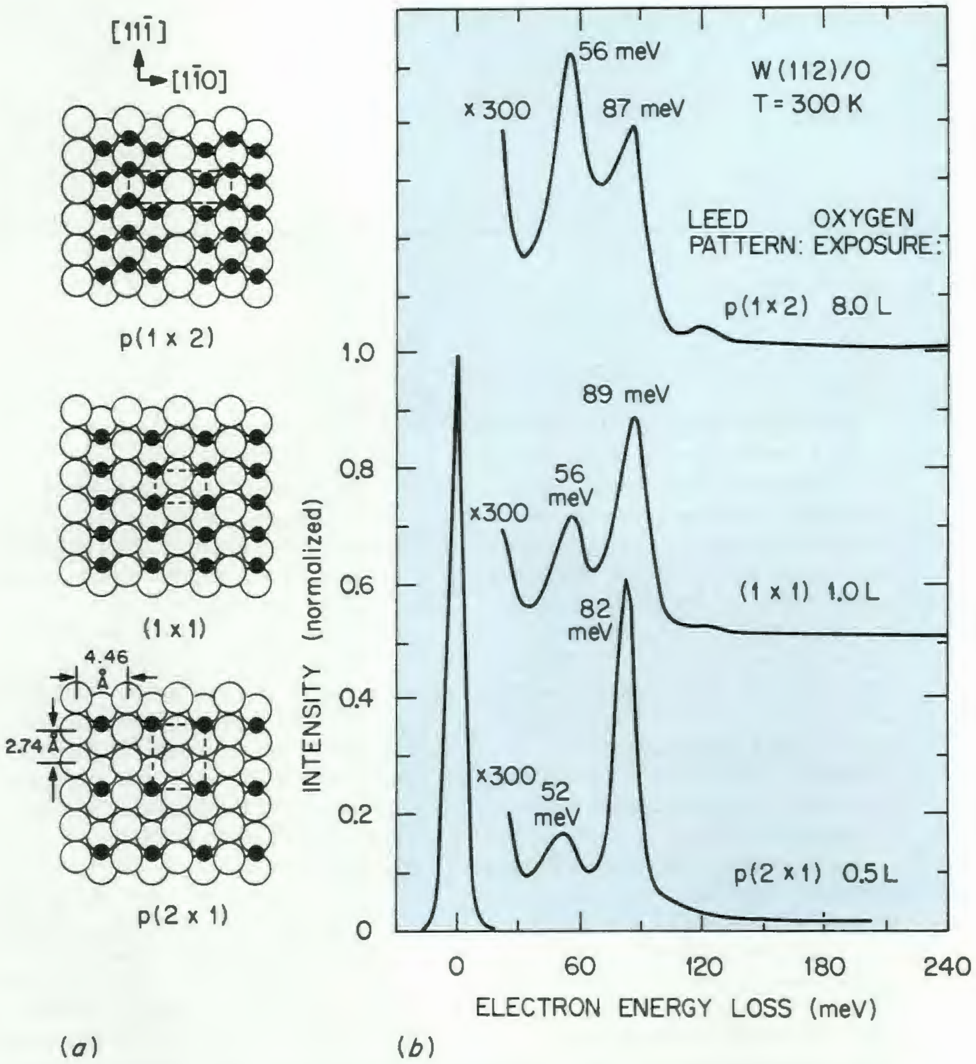


Fig. 8. (a) Ball models illustrating possible placements of oxygen on the W(112) surface for coverages of 0.5, 1.0, and 1.5 monolayers. (b) Electron-energy-loss spectra obtained for each oxygen coverage. The two peaks observed are the result of excitations of the oxygen-metal stretch in two different bonding configurations.

intended to illustrate not only the types of problems that can be attacked but also the level of detailed information that can be obtained. These examples only touch on the vast amount of information that is available to the surface scientist. They show that each of the questions raised can be answered in great detail. The underlying theme of the answers is the energetics of the interaction. Ideally, it would be nice to understand the energetics sufficiently well to predict what will happen. This ability would then allow surface scientists to examine more complex systems and add to their contributions of improving the quality of life for most people, including those who take surfaces for granted.

Scratching the Surface: Tools of the Trade

Our understanding of the surface of materials and of the chemical reactions that occur there has advanced considerably in the last decade with the help of many new kinds of surface analytical techniques. ORNL has been at the forefront of development of several of these techniques and their application to many problems related to DOE's mission. The work has been carried out under a variety of projects in several different divisions, reflecting the cross-disciplinary nature of surface research.

What are these techniques and how do they work? Most involve analyzing either the scattering of primary particles from a surface or the production of secondary particles stimulated by the passage of the primary particles. The particles may be electrons, photons, ions, atoms, or positrons. In some cases the techniques include analyzing atoms, molecules, or ions after they desorb from a surface as a result of heating or application of a high electric field. A common feature of the techniques is surface sensitivity—that is, the information obtained derives from only the top few atomic layers of the surface rather than from the whole of the material. This surface sensitivity comes about by the use of particles that interact strongly with the material and therefore do not penetrate deeply. For example, a low-energy electron can travel only a few Angstroms in a solid before it undergoes some scattering process that results either in a measurable change in energy or direction of travel or in the excitation of a secondary electron that can be detected.

Electrons. Various schemes based on the possible physical interactions in the scattering process can be used. Low-energy electrons, for example, may scatter from a surface in several ways. Some electrons will scatter elastically and be diffracted by the lattice of a crystalline solid. The characteristic angular dependence of the diffraction (the diffraction pattern) and its evolution with electron energy is the basis of the technique of low-energy electron diffraction (LEED). The diffraction yields information about the crystal structure of the solid surface.

Besides being diffracted, the primary electrons excite vibrations within molecules adsorbed at a surface, resulting in measurable losses in the primary electron energy. The energy losses are characteristic of the type of molecule present at the surface. Measuring these losses is the basis of electron energy loss spectroscopy (EELS).

Higher-energy electrons having energies of 0.1 to 10 keV may ionize atoms, resulting in the creation of secondary electrons called Auger electrons. These electrons have energies characteristic of the type of atoms from which they originate. Analysis of these electrons provides information about the types and quantities of atoms at the surface and is the basis of Auger electron spectroscopy (AES). Because these higher-energy primary electrons can be focused to spot sizes of less than 5000 Å and rastered across a surface, it is possible to do spatially resolved AES, giving rise to scanning Auger microscopy (SAM).

Photons. Variations in these techniques can be introduced by changing the nature of the excitation. For example, photons can be used as primary "particles" to excite photoelectrons. Although the photons penetrate deeply, only electrons generated near the surface give rise to measurable signals, so the surface sensitivity is preserved. Photons are the source of excitation in the techniques of ultraviolet photoemission (UPS) and X-ray photoemission (XPS) spectroscopies.

Ions. Many important techniques are based on the use of ions. Primary ions are not diffracted under usual conditions, but they scatter elastically and lose energy to various inelastic processes by exciting secondary ions and electrons. This opens up several possibilities for analysis schemes that yield new information about surface structure and composition.

Many of these techniques are being applied at ORNL to problems in materials science, for example, in metallurgy, catalysis, and corrosion, and to studies intended to increase our fundamental understanding of surfaces and interfaces. Cal White, Bob Clausing, and co-workers of the Metals and Ceramics Division have been using SAM to characterize microalloying and the segregation of impurities at grain boundaries and at the surface of metals.

Properties of materials such as strength, ductility, or corrosion resistance can be either enhanced or degraded by the concentration of trace materials at grain boundaries. These studies generally involve in situ fracture or heating followed by SAM analysis of selected microstructural features. In collaboration with the Fusion Energy Division, they also study the interactions between high-temperature plasmas and the surface of materials used inside tokamaks.

In the Chemistry Division, Deborah Huntley and I are applying surface techniques to investigate problems related to reactions catalyzed at metal and metal-sulfide surfaces. We are building a system that will allow model catalysts to be brought directly from a reaction chamber into vacuum for analysis by AES and EELS. Our goal is to understand a certain class of reactions by characterizing the surface species present before and after exposure to realistic reaction conditions. We also use low-energy ion scattering as a probe of surface structure because low-energy ions scatter from the top few layers. We have a system equipped with AES, LEED, and ion-scattering capabilities for this purpose. We have shown that the technique provides information about the locations and ordering of surface adsorbate atoms and about reconstruction and relaxation on clean metal surfaces.

In a group in the Solid State Division, Steve Withrow and Bob Culbertson perform surface crystallography on clean surfaces by high-energy ion scattering. They are using an ion accelerator that is also employed for ion beam processing of materials (see article by B. R. Appleton on page 18). The more deeply penetrating high-energy ions allow them not only to determine surface-atom locations but also to obtain information about bulk composition and structure.

In the Analytical Chemistry Division, Warner Christie and co-workers have applied the technique of secondary ion mass spectroscopy (SIMS) to numerous analysis problems. This technique is based on analysis of ions removed from a sample surface by ion impact. They use a focused ion beam giving them microprobe capabilities. They have analyzed dopant redistribution in photovoltaics, oxide growth in heat-exchanger tubes, and mechanisms of thermocouple failure. They have also developed microanalysis techniques for nuclear materials (see Christie's article in the ORNL *Review*, Vol. 18, No. 1, 1985).

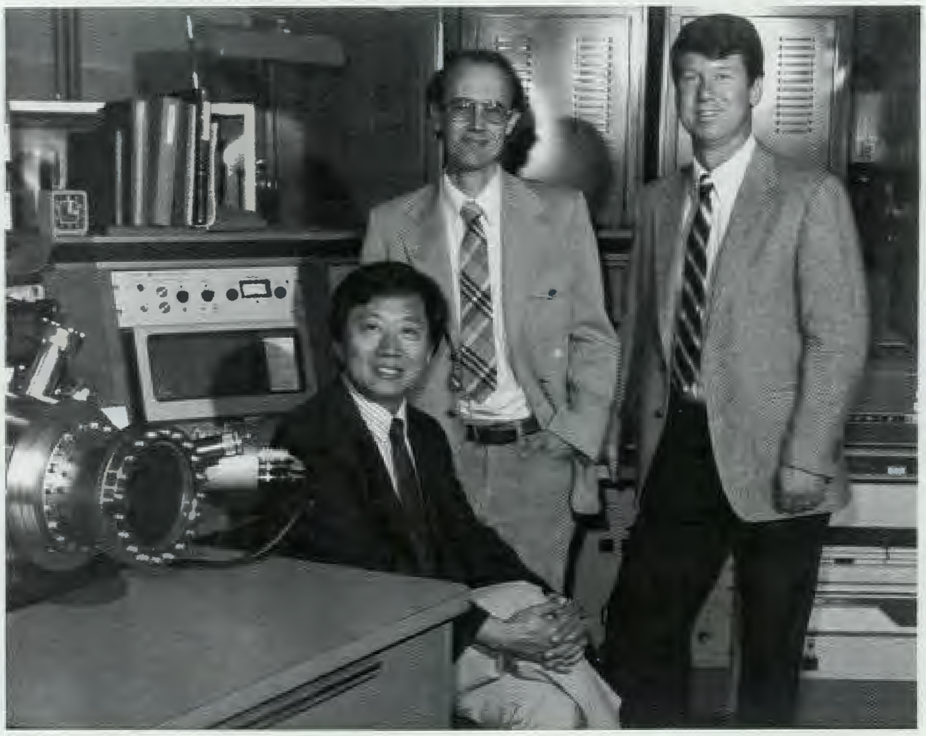
Perhaps the largest group at ORNL devoted to studies of fundamental properties of solid surfaces is that of Dave Zehner and co-workers in the Solid State Division. They use at least five separate vacuum systems equipped with some combination of EELS, AES, LEED, and XPS, and have applied these techniques to a variety of fundamental studies of metal and semiconductor surfaces (see main article).

A technological improvement in the ability to produce and control particles or photons usually benefits surface analysis techniques. A good example is the recent development and use of synchrotrons as high-intensity sources of X-ray and vacuum ultraviolet (VUV) photons. Zehner and collaborators at the University of Pennsylvania have been active in setting up an experimental station at the VUV ring at Brookhaven National Synchrotron Light Source. They will make use of the large photon energy range and the high intensity to perform XPS/UPS studies.

The work of John Dale and Les Hulett of the Analytical Chemistry Division is another example of technological developments leading to new surface analytical techniques. They are developing surface spectroscopies based on the use of positrons and are collaborating with Bob Peelle and T. A. Lewis of the Engineering Physics and Mathematics Division to build a high-intensity monoenergetic positron beam line at the Oak Ridge Electron Linear Accelerator.

Recognizing the depth and variety of surface research at ORNL and the accumulation of surface-science equipment and resources, a group of scientists at ORNL has recently created the Center for Thin Films and Interfaces. The center held an information meeting for interested researchers in October 1985. It is hoped that increased awareness of these resources may stimulate greater internal collaboration and create new research possibilities, allowing materials scientists to continue to scratch the surface.—*Steve Overbury, Chemistry Division.*

Three years ago ORNL began conducting basic research on the physical metallurgy and mechanical behavior of ordered intermetallics. The studies have focused on mechanisms governing brittle fracture, deformation behavior of intermetallics at both low and elevated temperatures, and the influence of alloy variables on defect structures, microstructural features, and phase stability. The ultimate goal of this research is the development of a scientific basis for design of intermetallic alloys for high-temperature structural uses.



Design of High-Temperature, Ordered Intermetallic Alloys

By C. T. LIU

The thermal efficiency of heat engines and energy conversion systems can be improved by operating them at the highest possible temperatures. However, because of the temperature limitations of available structural materials, many advanced energy conversion systems must operate at reduced temperatures and thermal efficiencies. To solve the problem, the materials community has made substantial efforts to develop high-temperature structural materials during the last 50 years. The most successful example of this effort is the design of nickel-base superalloys for gas turbines being developed for jet-engine applications.

We now understand that further development of nickel-base superalloys is limited by certain technical factors. First, all superalloys melt around 1300°C, and the strength drops to zero near the melting point (T_m). All efforts to control processing variables, microstructure, and alloy composition have failed to make these alloys useful in the vicinity of T_m. Second, most superalloys contain substantial amounts of critical strategic elements, such as cobalt and chromium, the supply of which could become insecure in an international emergency. Third, superalloys have been intensively developed for the past 40 years, leaving little room for further improvement. Thus, in the past few years, metallurgists started to search for new high-temperature structural materials.

Ordered intermetallic alloys constitute a unique class of metallic materials that form long-range ordered crystal structures below a critical temperature in the solid state. The various atomic species in ordered alloys tend to occupy specific sublattice sites and form superlattice structures (Fig. 1). During the 1950s and 1960s, many ordered intermetallics were evaluated extensively; their structures were determined and many attractive properties were revealed.

One outstanding characteristic of intermetallics is that their

Chain T. Liu, who is well known locally for his work in designing new alloys, is leader of the Alloying Behavior and Design Group in ORNL's Metals and Ceramics Division. He received his bachelor's degree in mechanical engineering from National Taiwan University and his master's and Ph.D. degrees in materials science from Brown University. Since coming to ORNL in 1967, he has won numerous awards. In 1985 Martin Marietta Energy Systems, Inc., designated him as a Corporate Fellow and named him "Scientist of the Year," and Martin Marietta Corporation awarded him a Jefferson Cup. Brown University recently honored him as a Distinguished Alumnus for his scientific and technological achievements. A Fellow of the American Society for Metals, Liu has won two I-R 100 awards from *Research & Development* magazine. He was granted an Honorary Platinum Membership in the International Precious Metals Institute (IPMI) and, in 1980, became the first recipient of IPMI's Henry J. Albert Award. He has received awards from the National Aeronautic and Space Administration and the U.S. Department of Energy for his contributions to the development of special structural alloys for space application. His research interests center on alloy development and design, high-temperature deformation and fracture, precious metal alloys, refractory alloys, and ordered intermetallic alloys. Here, from left, Liu, Joe Horton, and Cal White enjoy the recognition they received from DOE, which in 1984 gave them a Materials Science Research Competition Award in the category of "significant implication for energy technology" for their work on the design of ductile nickel aluminides for high-temperature structural use.

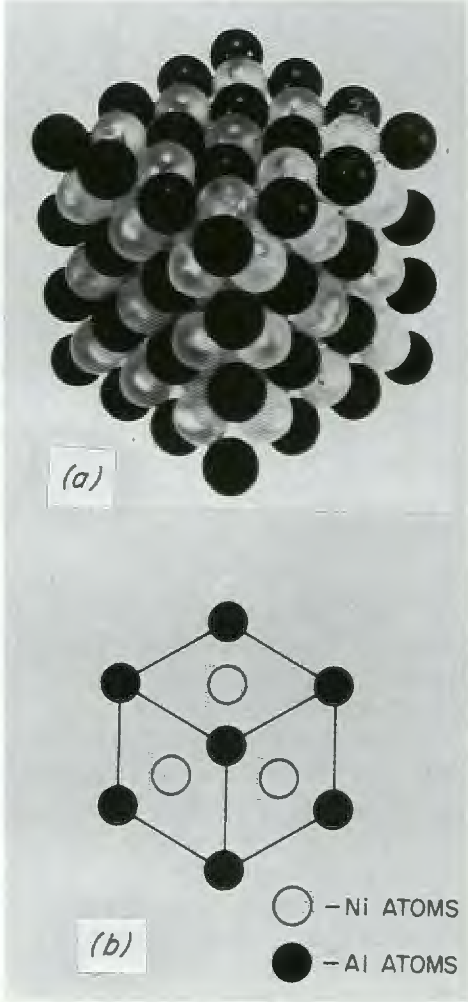


Fig. 1. L1$_2$-type ordered crystal structure formed in Ni$_3$Al: (a) atomic model showing cubic planes and (b) unit cell having an ordered face-centered cubic structure.

strength does not decline rapidly with increasing temperature. In many cases, the yield stress of these alloys increases rather than decreases with test temperature, in contrast to conventional alloys such as austenitic stainless steels. This behavior makes intermetallic alloys particularly suitable for use at elevated temperatures.

Interest in ordered intermetallics subsided in the latter part of the 1960s because of severe embrittlement problems. The brittleness of these alloys can usually be attributed to either of two major causes: an insufficient number of slip systems (bulk brittleness) or grain-boundary weakness. Many intermetallics are so brittle that they simply cannot be fabricated into useful structural components. Even when fabricated, their low fracture toughness severely limits their use for structural applications. Recent research at Oak Ridge National Laboratory and other laboratories has demonstrated that the ductility and fabricability of a few intermetallic systems can be significantly improved through control of metallurgical variables (e.g., by deliberately adding precise amounts of certain impurities). The success of these efforts has stimulated a great interest in ordered intermetallic alloys.

Three years ago the physical research program at ORNL initiated an effort on high-temperature alloy design. The objective of this task is to conduct systematic, basic research on the physical metallurgy and mechanical behavior of ordered intermetallics. These studies have focused on three critical areas: (1) mechanisms governing brittle fracture, (2) deformation behavior of intermetallics at both low and elevated temperatures, and (3) the influence of alloy variables on defect structures, microstructural features, and phase stability. The ultimate goal of this research is the development of a scientific basis for design of intermetallic alloys for high-temperature structural uses. This article summarizes our past, current, and future research efforts under a program sponsored by the Department of Energy's Office of Basic Energy Science (BES).

It should be noted that separate efforts on alloy development of nickel and nickel-iron aluminides as

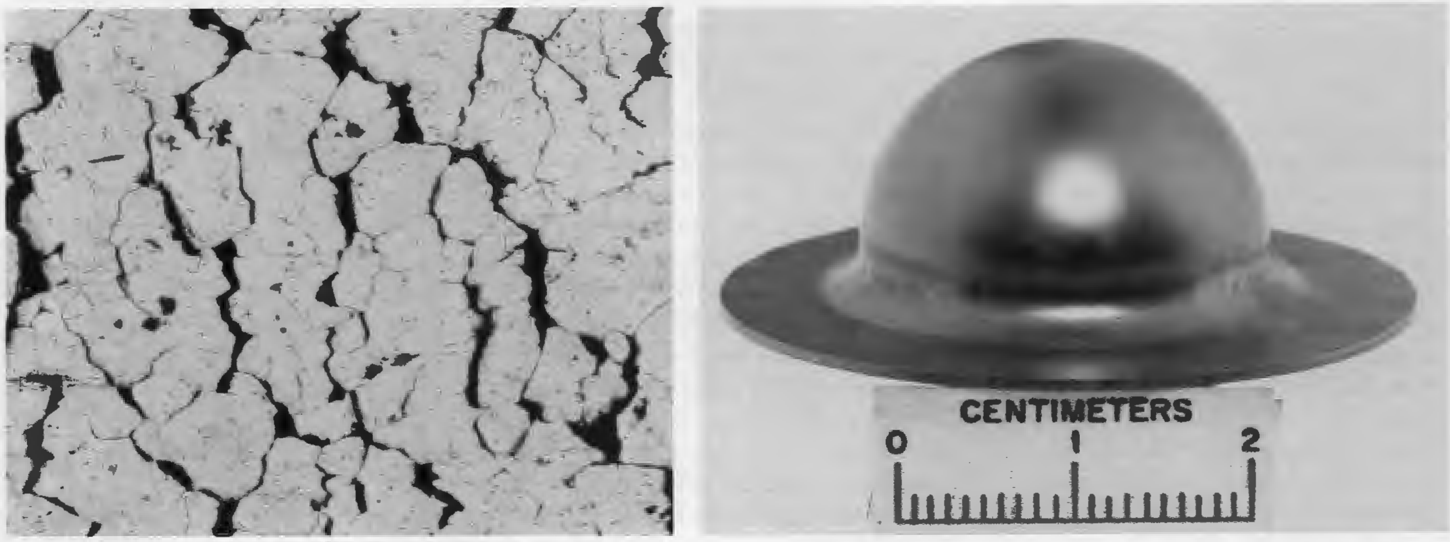


Fig. 2. Comparison of fabricability of Ni_3Al without and with boron doping: (a) undoped Ni_3Al cold-rolled at room temperature shows grain-boundary cracking and (b) a cup of boron-doped Ni_3Al (24% Al, 0.1% B) can be fabricated by deep drawing at room temperature.

new structural materials for use in advanced heat engines (Stirling engines, adiabatic diesel engines, gas turbines) and advanced coal conversion systems (coal gasifiers, fluidized-bed combustors, fuel cells) have been jointly supported by DOE's Energy Conversion and Utilization Technologies (ECUT)/Energy Conservation Program and Fossil Energy Materials Program. The technological development of aluminides sponsored by those programs will not be discussed here in detail because it is outside the scope of this article. (For information on technological development and commercialization of ORNL's modified aluminides, see the article on page 19 of the ORNL *Review*, No. 4, 1985.)

Nickel Aluminides Based on Ni_3Al

We chose nickel aluminides having the base composition of Ni_3Al as a model material for study of ordered intermetallics. This nickel aluminide forms an $L1_2$-type ordered crystal structure, as illustrated in Fig. 1. The unit cell of Ni_3Al has a face-centered cubic (fcc) lattice in which nickel atoms occupy face-centered positions (Ni-sublattice sites) and aluminum atoms occupy corner positions (Al-sublattice sites).

Alloys based on Ni_3Al are of interest because of their attractive properties at elevated temperatures. Unlike most conventional alloys, the yield stress in Ni_3Al increases substantially with increasing temperature. This alloy is the most important strengthening constituent (γ' phase) of commercial nickel-base superalloys and is responsible for their high-temperature strength and creep resistance. The Ni_3Al alloys are resistant to air oxidation because of their ability to form adherent oxide surface films that protect the base metal from excessive attack.

In spite of these attractive properties, the development of nickel aluminides for structural use had been hampered by their propensity for low ductility and brittle intergranular fracture in polycrystalline forms. The Ni_3Al materials produced by casting exhibit almost no ductility at ambient temperatures and fail by brittle intergranular fracture [Fig. 2(a)] without appreciable plastic deformation within the grains. Although considerable effort has been devoted to improving the ductility of the aluminides, significant progress has been achieved only recently through careful control of alloy stoichiometry and through microalloying—the addition of minor concentrations, usually in the part per million (ppm) range, of alloying elements to control grain-boundary composition and structure.

Grain-Boundary Fracture and Microalloying with Boron

Many intermetallics exhibit severe brittleness that originates at grain boundaries. A classic example is Ni_3Al, which has an $L1_2$-ordered crystal structure. Single crystals of Ni_3Al are highly ductile, whereas polycrystals are extremely brittle at ambient temperatures. The grain-boundary brittleness in Ni_3Al arises from both extrinsic and intrinsic factors. The extrinsic

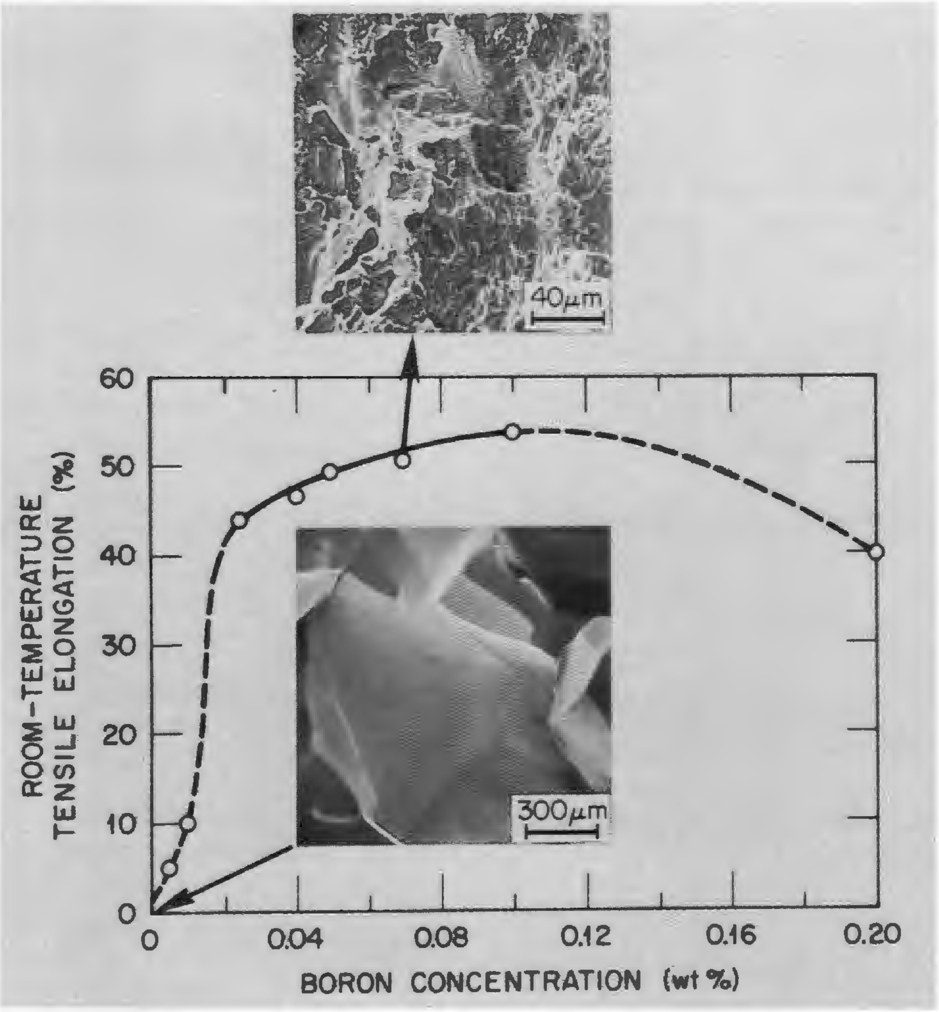


Fig. 3. Microalloying Ni_3Al (24 at. % Al) with boron dramatically improves the alloy's tensile ductility and suppresses brittle grain-boundary fracture.

brittleness results from segregation of certain impurities that embrittle grain boundaries (areas where two grains having different orientations impinge). Sulfur has been identified as a trace element that strongly segregates to, or concentrates in, grain boundaries in impure Ni_3Al, causing embrittlement. Studies at ORNL of fracture in high-purity polycrystalline Ni_3Al, however, have revealed intergranular fracture without appreciable concentration of impurities in grain boundaries. The grain boundary is, therefore, intrinsically weak relative to the grain interior because of poor grain-boundary cohesion.

To overcome the grain-boundary brittleness in Ni_3Al, microalloying has been used. Alloy design research at ORNL and in Japan has indicated that minute additions of boron (B) are very effective in improving the ductility and fabricability of Ni_3Al. Further research at ORNL has shown that the beneficial effect of boron is very sensitive to deviations from alloy stoichiometry (i.e., deviations of the aluminum concentration from the exact stoichiometric composition of 25 at. %). By careful control of aluminum concentration, boron content, and thermomechanical treatment, tensile elongations greater than 50%, and virtually 100% transgranular failure, were achieved in Ni_3Al (24% Al) containing 0.02 to 0.10 wt % B (Fig. 3). With further increase in boron concentration, the ductility gradually decreases, and the yield stress increases sharply. This striking effect of boron on the ductility of Ni_3Al occurs over a wide range of boron concentrations where boron is in solid solution. Boron-doped Ni_3Al alloys exhibit an excellent cold formability, as demonstrated in Fig. 2(b) for a full cup deep-drawn at room temperature.

Basic research at ORNL has focused on understanding the beneficial effect of boron. The solubility limit for boron in Ni_3Al is approximately 1.5 at. % (or 3000 wt ppm), and the boron in solution occupies both kinds of interstitial sites in the bulk and in grain boundaries. An ion-beam channeling study (by Jim Williams of ORNL's Solid State Division and Hans Bohn of the Metals and Ceramics Division) of single-crystal, boron-doped Ni_3Al indicates that boron atoms in the bulk lattice tend to occupy the octahedral interstitial sites rather than the tetrahedral sites. This behavior of boron can be explained by the size of the octahedral sites, which are considerably larger than the latter sites in an fcc lattice. Using Auger electron spectroscopy, a powerful technique for determining the chemistry of top atomic layers on surfaces, Cal White of ORNL's Metals and Ceramics Division discovered an unusual segregation behavior exhibited by boron in Ni_3Al. He found that boron tends to segregate strongly to the grain boundaries in Ni_3Al but not to free surfaces (Fig. 4). This relationship between grain-boundary and free-surface segregations contrasts with the well known behavior of sulfur and other embrittling elements, which tend to segregate more strongly to free surfaces than to grain boundaries.

Our observations are in agreement with the prediction from a classical thermodynamic theory developed by Jim Rice of Harvard University. According to this segregation theory, solutes which tend to segregate more strongly to grain boundaries should increase the grain boundary cohesive energy (and thus increase ductility), whereas solutes segregating more strongly to free surfaces should lower grain-boundary cohesion (and ultimately cause embrittlement). Our research appears to provide the first direct confirmation of Rice's prediction of the behavior of beneficial solutes in an alloy. If the relationship between segregation behavior and its effect on grain-boundary cohesion proves to be general, it could provide a basis for selection of beneficial dopants for other alloy systems.

Our work on microalloying of Ni_3Al with boron additions received a "Significant Implication for Energy Technology" award in DOE's 1984 Materials Sciences Research Competition in the Metallurgy and Ceramics Category (see photograph on page 42).

Stoichiometric Effects

At ORNL alloy stoichiometry was found to have a strong effect on the ductility and fracture behavior of boron-doped Ni_3Al. The boron dopant is most effective in improving the ductility and suppressing intergranular fracture in Ni_3Al containing 24% Al. At higher aluminum concentrations, the ductility drops sharply (Fig. 5) and the failure mode changes from transgranular to mixed mode and then to completely intergranular. Our Auger electron spectroscopy studies of freshly fractured surfaces of boron-doped samples indicate that the aluminum content has no observable effects on carbon, oxygen, and sulfur segregation. Instead, the intensity of boron segregation decreases significantly, and the grain-boundary aluminum concentration increases slightly with increasing bulk aluminum concentration. These results simply suggest that a deviation from alloy stoichiometry strongly influences grain-boundary chemistry, which, in turn, affects the grain-boundary cohesion and overall ductility of nickel aluminides.

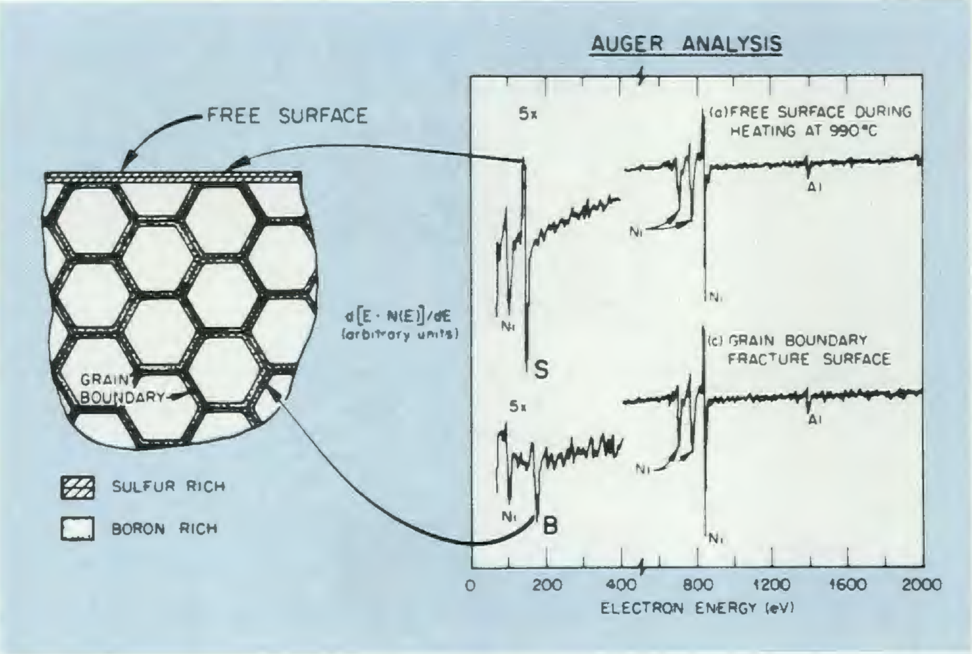


Fig. 4. Auger electron spectroscopy study showing the striking differences in interfacial segregation behavior of boron and sulfur in Ni_3Al *(24% Al); whereas boron segregates strongly to grain boundaries and not at all to free surfaces, the reverse is true of sulfur.*

To further understand how alloy stoichiometry affects the boron segregation in Ni_3Al, researchers at ORNL (Amit DasGupta) and Argonne National Laboratory (L. C. Smedskjaer, D. G. Legnini, and R. W. Siegel) jointly studied the defect structure in the alloys containing 24 to 26% Al and 0 to 500 wt ppm B (0 to 0.2 at. %) using positron-lifetime and Doppler-broadening measurements. Positron annihilation studies are among the most sensitive of ways to detect defects with low electron density, such as vacancies or vacancy clusters. The measurement of the trapped-state intensity showed that Ni_3Al with 24% Al trapped no positrons, whereas alloys having 25% Al and 26% Al trapped about 10% of the positrons bombarding the material (i.e., about 10% of the positrons destroyed themselves by colliding with electrons). With the addition of boron to these alloys, the degree of positron trapping increased strongly to about 30% in the 25% Al alloy. An estimate based on the positron trapping gives a constitutional vacancy concentration of 10^{-6} to 10^{-5} in the 25%- and 26%-Al alloys.

The positron annihilation study provides a clue to explain the effect of alloy stoichiometry on boron segregation and ductilization of Ni_3Al. The inability of boron to increase the ductility of polycrystalline Ni_3Al having stoichiometric (25% Al) or hyperstoichiometric (>25% Al) compositions may be related to the fact that boron clustering at both

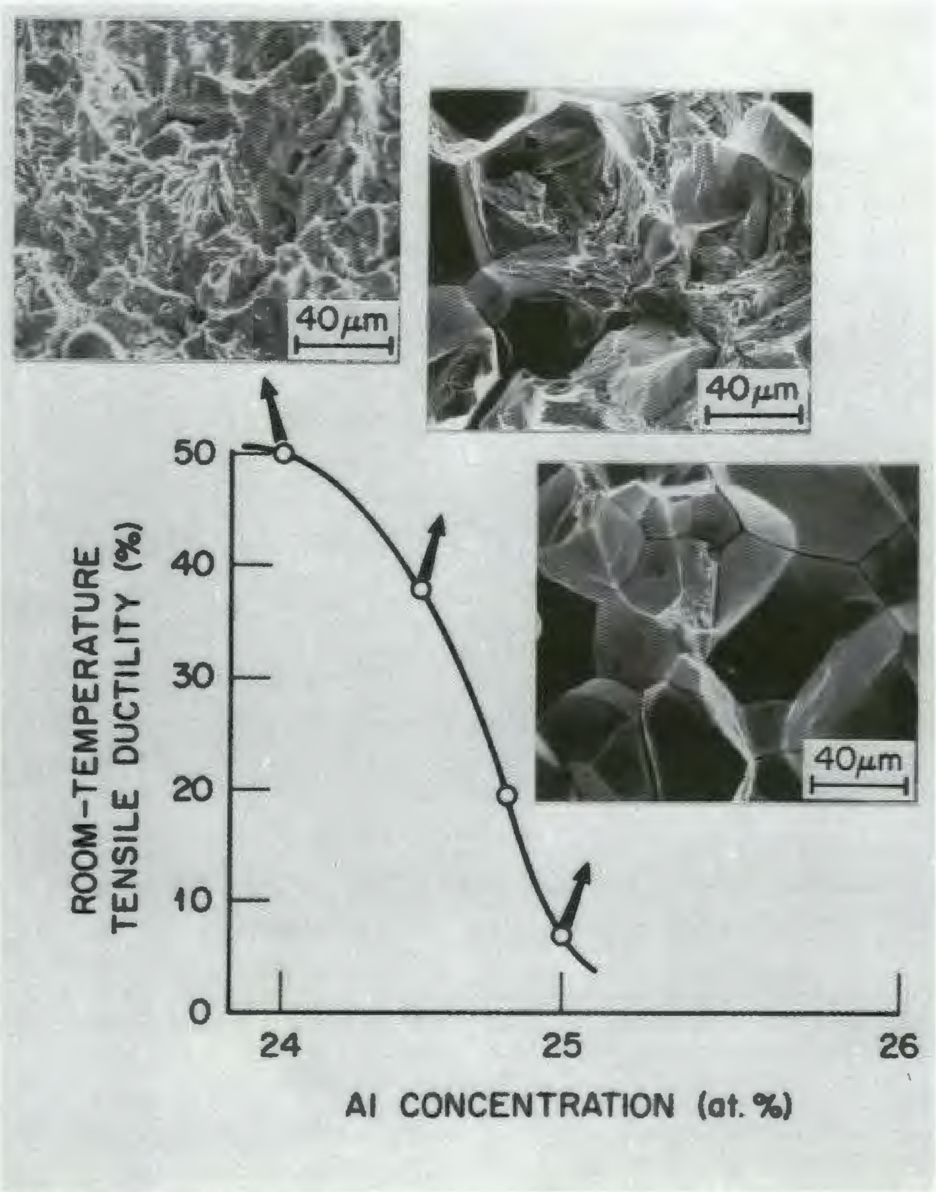


Fig. 5. Increasing aluminum content from 24% to 25% sharply decreases tensile ductility and promotes grain-boundary fracture in Ni_3Al alloys doped with 0.2% boron.

constitutional vacancies and vacancies associated with boron-doping limits the long-range transport of boron to grain boundaries. Boundaries remain brittle when the amount of boron segregated to them is insufficient. Recent studies by transmission electron microscopy at ORNL and small-angle neutron scattering at Argonne appear to provide additional evidence for constitutional vacancies and boron clustering in the 25%-Al alloy doped with boron.

Environmental Effects and Ductility At Elevated Temperatures

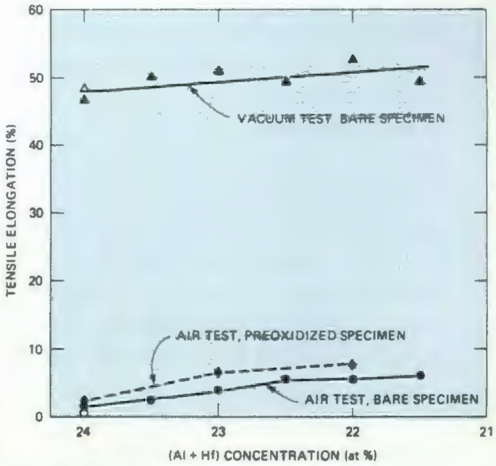


Fig. 6. Effect of test environment (vacuum vs. air) on tensile ductility of Ni_3Al alloys containing 21.5 to 24.0% (Al + Hf). Closed symbols are for alloys with 0.5% Hf; open symbols, alloys without hafnium.

Nickel aluminides are very resistant to oxidation in air at temperatures up to at least 1100°C. Mechanical testing of alloy specimens in controlled environments, however, indicates that the test atmosphere strongly influences the ductility and fracture behavior of boron-doped Ni_3Al at elevated temperatures (500° to 900°C). Figure 6 compares the tensile elongation of Ni_3Al alloys as a function of aluminum and hafnium (Hf) concentration in air and in a vacuum at 600°C. (Hafnium is deliberately added along with the boron.) All the alloys show excellent ductility (45 to 53%) when tested in a vacuum, and the ductility appears to increase somewhat with decreasing Al and Hf concentration. In contrast, the ductility of the alloys is dramatically lower when tested in air. The loss in ductility is accompanied by a change in fracture mode from transgranular to intergranular. (The Ni_3Al alloys show a small but steady increase in ductility with decreasing aluminum concentration.) Similar embrittlement was observed in pure oxygen.

Although the results indicate that the embrittlement at 600°C is caused by oxygen, it is apparently not associated with oxidation per se (e.g., formation of oxide scales, grain-boundary oxidation) because preoxidation does not significantly affect the ductility and fracture mode. In fact, preoxidation causes a slight increase rather than a decrease in ductility in air (Fig. 6). Furthermore, the gage section of specimens air-tested at 600°C remained ductile and showed ductile transgranular fracture, indicating that the embrittlement is not caused by penetration of oxygen into the grain boundaries by a purely diffusional process. All these observations lead to the conclusion that the air-tested aluminide is embrittled by an effect simultaneously involving high localized stresses, elevated temperature, and gaseous oxygen. Such a dynamic effect might involve weakening of atomic bonds, particularly Ni-Al bonds, across grain boundaries, as a result of oxygen adsorption at crack tips opened up to oxidizing atmospheres (Fig. 7).

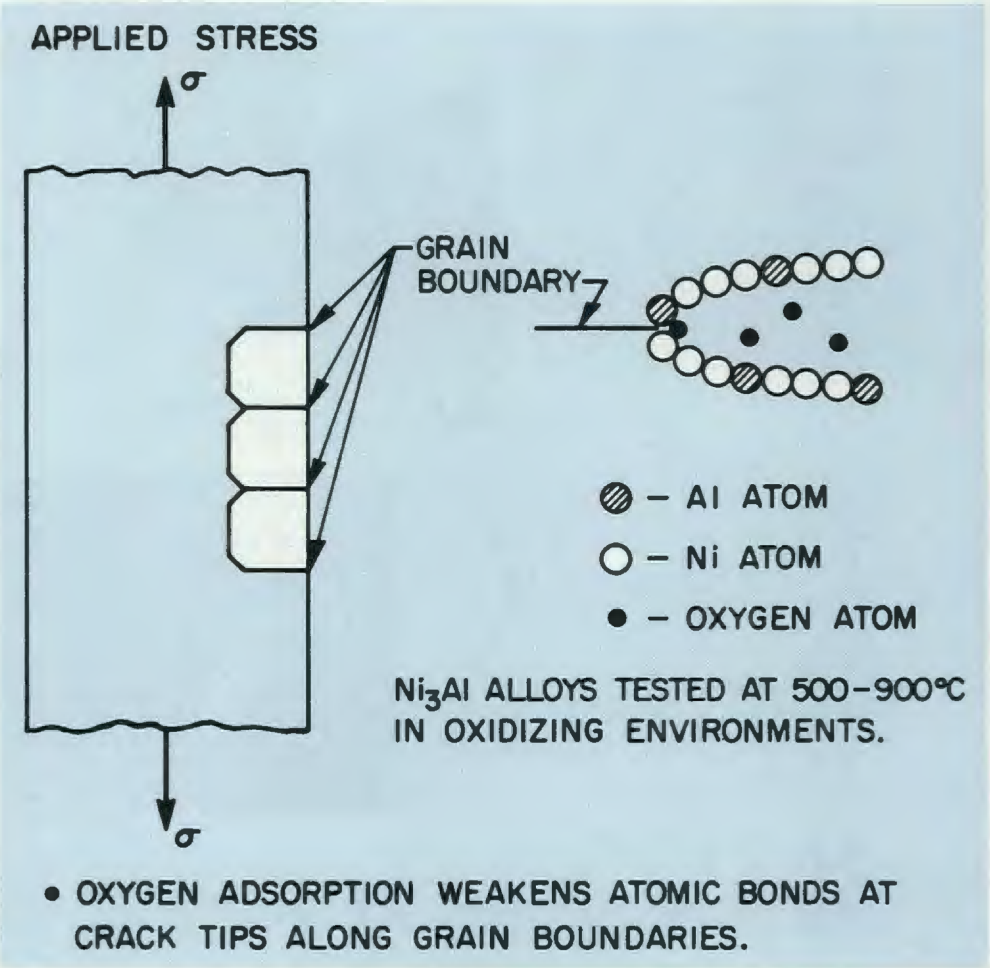


Fig. 7. A sketch to show tensile test and adsorption of oxygen atom at a crack tip formed along grain boundaries exposed to oxidizing environments at elevated temperatures. The oxygen adsorption results in weakening Ni-Al bonds.

Identification of the mechanism responsible for the dynamic embrittlement suggests metallurgical solutions to the problem. The possible ways to alleviate the problem include (1) lowering aluminum content, (2) preoxidizing alloy specimens (Fig. 6), (3) preparing directionally solidified materials with columnar grain structures, and (4) making macroalloying additions. The embrittlement appears to result mainly from sluggish kinetics of formation of protective Al_2O_3 surface films; the best solution to this sluggish response is to enhance the kinetics of oxidation through alloying additions. An alloy development effort sponsored by other DOE programs has demonstrated that dynamic embrittlement can be effectively reduced by increasing the oxidation rate.

Many nickel-base superalloys exhibit some degree of embrittlement in air at intermediate temperatures. It has been thought that the loss of ductility results from either an intrinsic factor (e.g., inherent grain-boundary weakness) or an extrinsic factor related to segregation of harmful impurities. Our study has suggested a third possibility: the dynamic embrittlement results from an environmental effect. Clearly, further work is needed to verify the embrittling mechanism we have suggested.

Hardening Mechanism and Mechanical Behavior

Boron-doped Ni_3Al exhibits unusual mechanical behavior (Fig. 8). The yield stress of this alloy increases rather than decreases with test temperature. Because of this increase, the aluminide becomes stronger than such commercial solid-solution alloys as Hastelloy X and type 316 stainless steel at elevated temperatures. The yield strength of Ni_3Al begins to decrease above 600°C because of a gradual change in slip systems from $\{111\}$ to $\{100\}$ crystallographic planes.

A similar increase in yield stress with temperature has been observed in other $L1_2$-type ordered intermetallic alloys. Of the various models suggested to explain such behavior, the cross-slip model

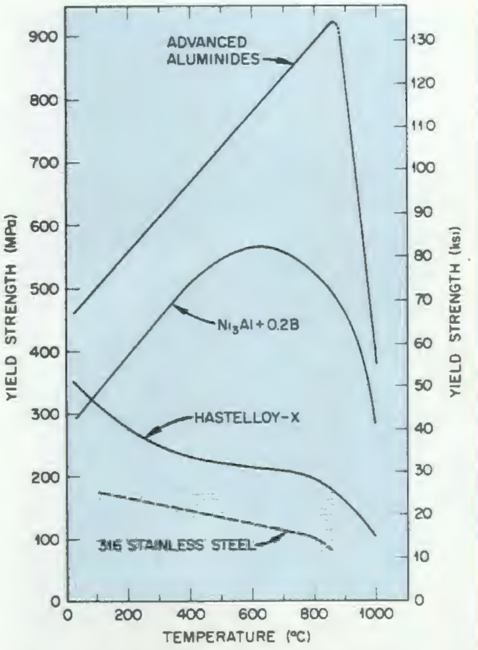


Fig. 8. Yield stress as a function of test temperature for Ni_3Al alloys and commercial alloys Hastelloy X and type 316 stainless steel. Advanced aluminides are alloyed with 1.5% hafnium.

proposed by Barnard Kear and H. G. W. Wilsdorf of Pratt and Whitney and S. Takeuchi and E. Kuramoto of the University of Tokyo is the most successful one for describing the yield stress behavior of Ni_3Al. Basically, the model assumes a lower energy for antiphase boundaries (APB, an interfacial defect where two ordered domains impinge on each other) on {100} planes than on {111} planes. A TEM study (by Joe Horton) of the APB morphology of as-quenched (a nonequilibrium case) and annealed (an equilibrium case) Ni_3Al foils produced by rapid solidification shows alignment of the APBs along {100} planes in the annealed foil (Fig. 9), indicating the lowest energy of APB along {100} planes. We regard these results as experimental evidence for the cross-slip model.

Ni_3Al can be hardened by solid-solution effects because it can dissolve substantial amounts of alloying additions without losing its long-range order. As shown in Fig. 8, alloying with 1.5% hafnium substantially increases the strength of Ni_3Al. Interestingly, hafnium is more effective in hardening Ni_3Al at elevated temperatures (e.g., 850°C) than at room temperature. This phenomenon cannot be simply explained by classic solid-solution hardening theories developed mainly for disordered lattices.

Studies of phase stability in ordered Ni_3Al indicate that the solute elements having significant solute solubility in Ni_3Al can be divided into three groups. Elements such as hafnium and zirconium substitute almost exclusively for aluminum atoms at sublattice sites; on the other hand, cobalt and copper atoms occupy nickel lattice sites. Elements in the third group, such as iron and chromium, substitute for both aluminum and nickel atoms at sublattice sites. It is currently believed that only those solutes that substitute for aluminum atoms produce significant hardening in Ni_3Al.

Recent studies, however, show some contradictory results regarding the sublattice occupation of hafnium atoms in Ni_3Al. Ion-beam channeling studies conducted by Williams and Bohn suggest that Hf atoms in a single crystal containing 1% Hf preferentially occupy the nickel sublattice sites rather than the aluminum sublattice sites. On the other hand, studies by Michael Miller and Horton (using an atomic probe field ion microscope) and by Jim Bentley (using electron channeling) indicate that Hf atoms in polycrystalline Ni_3Al alloys preferentially occupy the aluminum sublattice sites. Obviously, additional studies are needed to reconcile these opposing findings. Such studies of sublattice occupation are essential for understanding the solid-solution hardening behavior in ordered lattices.

The constant-load deformation (creep) behavior of Ni_3Al alloys has been studied at ORNL as functions of applied stress, test temperature, and grain size. Joachim Schneibel and I (both of the M&C Division) have found that diffusional creep based on the Nabarro-Herring model is the mechanism controlling creep deformation at stresses less than 10 MPa at 760°C and that the dislocation creep based on a viscous-glide model appears to be the mechanism at higher stresses. Grain-boundary sliding apparently plays an important role in both creep deformation and rupture processes. The creep rupture in Ni_3Al is linked to nucleation, growth, and coalescence of grain-boundary cavities (Fig. 10). The kinetic factors governing these processes are sensitive to minor impurities that tend to segregate strongly to grain boundaries and cavity surfaces. Man Yoo of the M&C Division is currently working on modeling of creep deformation in bulk material and also of localized microplastic deformation in grain-boundary regions.

Summary and Remarks

Significant progress has been made in understanding physical metallurgy and mechanical behavior of ordered intermetallic alloys based on nickel aluminides. Polycrystalline Ni_3Al alloys are inherently brittle because of poor grain-boundary cohesion. Ductility and cold fabricability of Ni_3Al containing less than 25% Al (hypostoichiometric compositions) can be dramatically improved by microalloying with a small quantity of boron. The improvement results from the unusual segregation behavior of boron in Ni_3Al, first revealed at ORNL using Auger electron spectroscopy.

Boron has a strong tendency to segregate to grain boundaries but

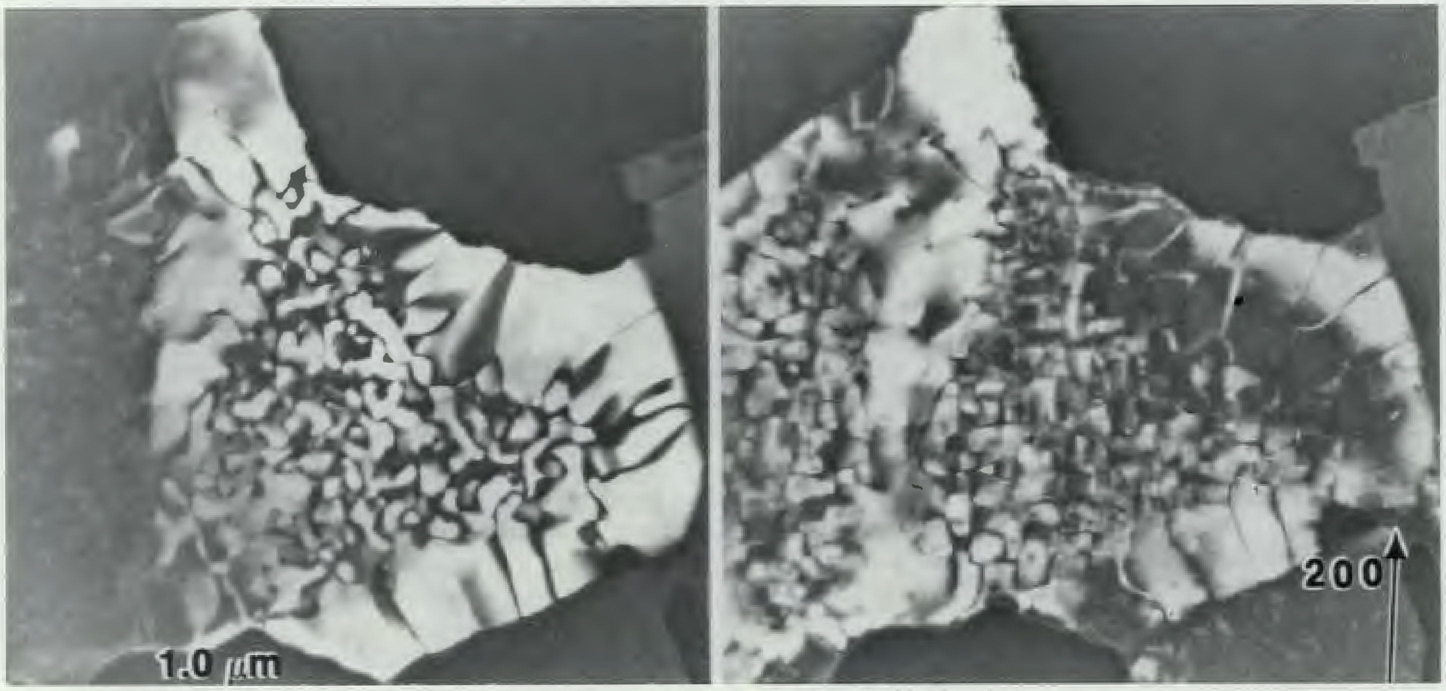


Fig. 9. Annealing of rapidly solidified Ni_3Al foil having 1000 ppm boron resulted in anisotropic antiphase boundaries along {100} planes. The electron micrograph made at 25°C (with a beam direction within 5° of {001} pole) shows (a) before the annealing and (b) after the annealing for 25 min at 750°.

not at all to free surfaces. This segregation behavior leads to a decrease in grain-boundary energy and an increase in free-surface energy, resulting in a substantial increase in grain-boundary cohesive energy in Ni_3Al. Our observation of boron segregation is the first direct confirmation of Rice's theory for the case of beneficial grain-boundary segregants. Positron annihilation studies reveal the formation of constitutional vacancies in Ni_3Al with >25% Al, and the clustering of boron around these vacancies is proposed to be the controlling factor that limits the long-range transport of boron to grain boundaries in stoichiometric and hyperstoichiometric alloys.

The test environment does not affect the yield stress but does strongly influence ductility and fracture behavior of boron-doped Ni_3Al tested at elevated temperatures, particularly in the range from 500 to 900°C. Our study reveals that the embrittlement is caused by a dynamic effect, simultaneously involving high localized stresses, elevated temperature, and gaseous oxygen. Identification of the mechanism responsible for the dynamic embrittlement leads to metallurgical solutions to the problem.

Microstructural features and sublattice occupation of solute atoms have been examined using TEM and ion-beam channeling techniques. The APB energy in Ni_3Al is anisotropic, with its lowest energy on {100} planes. This observation provides the first experimental support to the cross-slip model proposed to explain the increase in yield stress with temperature in Ni_3Al and other ordered intermetallic alloys. Ni_3Al alloys can be most effectively hardened by alloying with hafnium and zirconium, which are in solid solution. Contrary to the previous studies on solutes that exhibit significant solid-solution hardening, we have found that hafnium atoms preferentially occupy the nickel sublattice sites rather than the aluminum sublattice sites. This study provides critical information needed for modeling of solid-solution hardening in ordered lattices.

Clearly, further studies are needed to understand some important basic phenomena observed in nickel aluminides. For example, why is the grain boundary in Ni_3Al intrinsically brittle? What are the basic factors controlling segregation of boron (a beneficial element) and sulfur (an embrittling element) to grain boundaries and free surfaces in Ni_3Al? Answers to these questions require detailed study of electronic structure, atomic arrangement, and defect structure at grain boundaries and free surfaces. Recently, DOE's Division of Materials Sciences, at the initiative of Frank Nolfi, organized a series of inter-laboratory workshops that

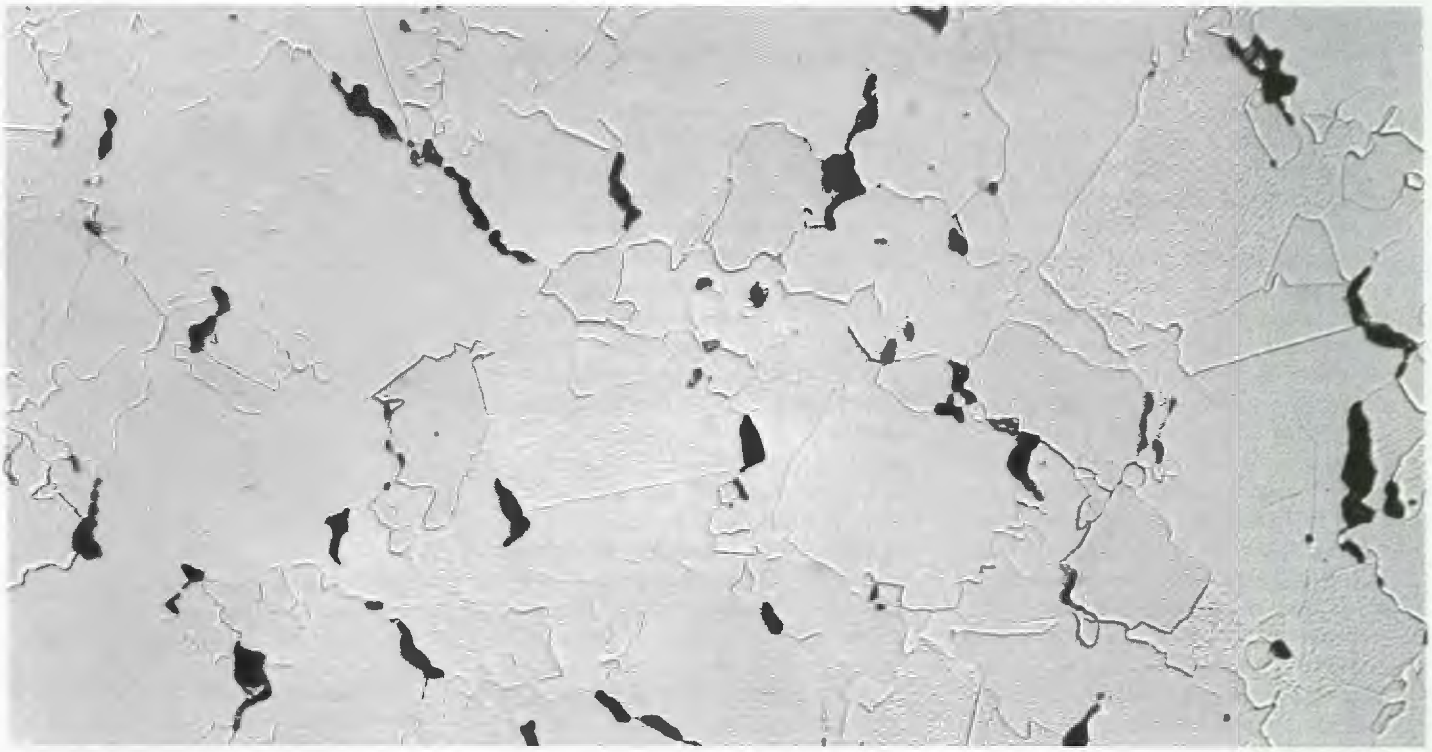


Fig. 10. Optical micrograph showing the formation of cavities along grain boundaries in boron-doped Ni_3Al creep tested at 138 MPa (20 psi) and 760°.

emphasize understanding the grain-boundary structure and interfacial segregation in boron-doped Ni_3Al with on- and off-stoichiometric compositions. The participants include S. Sass from Cornell University, K. G. Lynn from Brookhaven National Laboratory, H. K. Birnbaum from the University of Illinois, N. L. Peterson from Argonne National Laboratory, M. S. Daw from Los Alamos National Laboratory, S. S. Brenner from the University of Pittsburgh, and several scientists from ORNL. This workshop series assembles an excellent team, in terms of expertise and facilities, to attack basic questions associated with intergranular fracture and boron segregation in Ni_3Al. The first meeting, coordinated by Don Kroeger, was held at ORNL on September 19, 1985; it was very informative and productive. We have just initiated a new effort on modeling of dislocation mobility and microplasticity in Ni_3Al at ambient and elevated temperatures at ORNL.

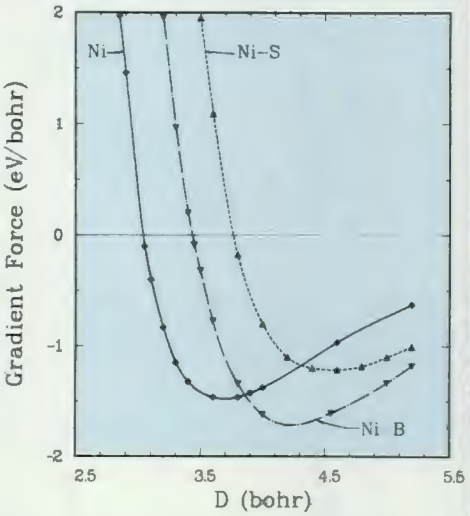
A unique feature of this BES program is our close interaction with other DOE programs, as well as U.S. industry. The information generated from this basic study has been transferred immediately to applied programs such as the Energy Conservation Program and Fossil Materials Program. For example, the recent identification of the mechanism responsible for the embrittlement in oxidizing environments at elevated temperatures has led to the development of advanced nickel aluminides that are modified by adding chromium. The chromium addition is beneficial because it increases the oxidation rate and the rate of formation of protective oxide films.

Industrial interest in ductile aluminides is high. Several companies are currently involved in different stages of the development process aimed at alloy scale-up and commercialization. Vinod Sikka, Jim Weir, Tony Schaffhauser, and Jim Stiegler of the M&C Division are currently coordinating all efforts on technology transfer to U.S. industry. Martin Marietta Energy Systems, Inc., has been negotiating with several companies to obtain license agreements for the use of nickel aluminides as heat-resistant and corrosion-resistant components in advanced heat engine systems. In December 1985, Energy Systems and Cummins Engine Company signed an exclusive license agreement for development of nickel aluminides developed at ORNL for commercial use in high-temperature diesel engines manufactured by Cummins. The agreement is the first licensing by Energy Systems (rather than DOE) of a patented ORNL-developed technology.

Understanding Grain-Boundary Microchemical Interactions

Understanding the effects of segregation of impurities to grain boundaries in alloys is immensely important to the development of advanced materials to meet the increased demands of new technological applications. Most often behavior at the macroscopic level is determined not by the intrinsic properties of the ideal alloy but rather by the characteristics imparted by defects, particularly those associated with interfaces. Very recently, we have achieved an exciting breakthrough at ORNL in our theoretical effort to understand the differences in segregant effects at grain boundaries. The way in which impurities strongly affect alloy mechanical properties begins with the polycrystalline structure, which is characterized microscopically as an interlocking of many individually crystalline regions (grains). In the interfacial, or grain-boundary, volume (2 to 4 atom diameter wide), misorientation of the grains causes a mismatch between lattice planes. In this region, atoms show displacements from regular lattice sites leading to the presence of open "hole" sites. These grain-boundary hole sites are often favored bonding sites for impurities present in the alloy.

Most impurities (e.g., sulfur) usually present in parts-per-million amounts even in the purest material concentrate at the grain boundaries and cause a decrease in cohesion between adjacent grains. Such interfaces often fracture between the grains in a brittle mode (grain-boundary embrittlement). A relationship between grain-boundary segregation and intergranular cohesion is well documented by Auger electron spectroscopic (AES) studies. Some elements, however, produce the opposite effect of reducing brittle behavior, usually by scavenging other harmful impurities or, in a very few cases, directly enhancing the cohesive strength of the grain boundary itself (carbon in iron alloys is an ancient example). Boron displays remarkable beneficial effects in the nickel aluminide Ni_3Al by inducing significant increases in the grain-boundary cohesion (see C. T. Liu's article in this issue on page 42). The AES work of Calvin White of ORNL's Metals and Ceramics (M&C) Division in collaboration with Charlie Brooks and a graduate student, Ashok Choudhury (both from the University of Tennessee), has recently been complemented by new atom probe field ion microscopy studies by Mike Miller and Joe Horton of the M&C Division.



The gradient (quantum mechanical) force plotted vs grain boundary hole size (D = distance from impurity site at origin to one of nickel atoms of the host octahedral cluster) for pure nickel and clusters containing boron and sulfur. Attractive forces on a reference nickel site are negative; repulsive forces are positive. Boron increases the value of the maximum sustainable force; sulfur decreases this value

These experimental studies have established a strong correlation between the presence of boron at grain boundaries and enhanced intergranular cohesion. This finding has motivated a

ORNL's Atom Probe: An Exciting New Instrument for Materials Research

An impressive addition to ORNL's surface and materials characterization research capabilities is a newly acquired atom-probe, field-ion microscope. The ORNL atom probe, which was delivered in late 1985, is a microanalytical tool for studies in materials science.

The ORNL atom probe actually combines four instruments into one—namely, a field-ion microscope, a time-of-flight energy-compensated mass spectrometer, an imaging atom probe, and a pulsed laser atom probe. The field-ion microscope provides atomic-resolution micrographs of a specially prepared specimen. The atom probe can determine the identity of individual atoms and the elemental composition of small regions of the specimen. The distribution of a selected element with atomic resolution can be made in the imaging atom probe. The pulsed laser allows examination of semiconducting materials as well as metallic specimens. The atom probe will be used to complement high-resolution analytical electron microscopy.

Scientists in ORNL's Metals and Ceramics Division are using the atom probe to study a wide range of materials. One application of the new instrument has been to investigate why a small addition of boron to a nickel aluminide alloy makes the material ductile. Because boron has such a low atomic weight, other techniques cannot directly observe its location. The atom probe detected the segregation of boron to the alloy's grain boundaries, where the boron prevented the material from becoming brittle and possibly cracking.

The atom probe is a valuable new tool that will help ORNL scientists characterize the microstructure of materials at a new level, thus providing a better understanding of the factors influencing the properties of materials.—*M. K. Miller, Metals and Ceramics Division.*

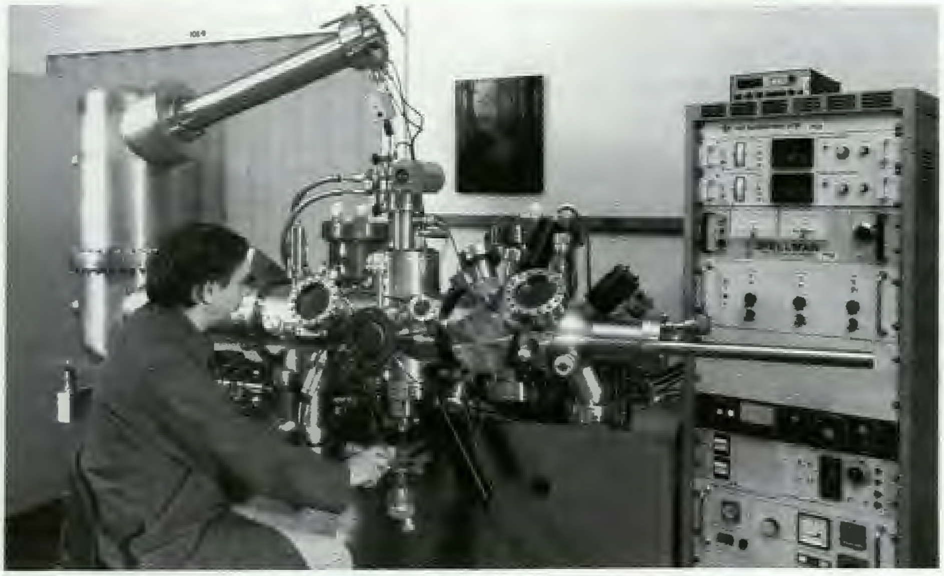
number of theoretical efforts to understand *why* boron produces such strong and unusual effects.

In spite of the great practical importance and inherent scientific value of achieving this understanding, little progress had been made before our recent study. These systems are very difficult to treat in first-principles theory. The lattice distortions present in grain-boundary systems places them outside the scope of current alloy theories. Furthermore, to properly address the most important questions requires evaluation of energetics (the total energy as a function of atomic spacing) at a higher level of completeness than normally feasible in simpler alloy methodologies.

The approach Frank Averill (Judson College, Illinois) and I devised goes beyond the limitations of these methods by focusing on a *cluster* of atoms, treating them explicitly within the local spin density formalism (the quantum theory basis of first-principles calculations), and coupling this cluster to the rest of the system through an "embedding" approximation. The new approach Averill and I developed is particularly well-suited for the type study required for this problem because it is capable of evaluating total energies with unprecedented precision for transition-metal clusters in arbitrary geometries. The only input data required are the atomic numbers.

Using this technique and choosing sulfur and boron as impurity atoms, we calculated the binding-energy curves vs atomic spacing curves for nickel clusters chosen to represent octahedral grain-boundary hole sites of various sizes (total energy minus the sum of all atom energies). The energetics strongly supported the experimental observations that boron segregates more strongly to grain boundaries than to free surfaces, whereas sulfur shows the opposite behavior in the same alloy. Next, introducing a major innovation in technique, we calculated the vector force field in the cluster (describing the quantum mechanical force on each atom) as a function of displacement of host nickel atoms. By comparing results for the pure nickel cluster and clusters containing boron and sulfur, we directly determined the effect of the impurity bonding on the maximum restoring force the cluster could provide. For the first time, the weakening influence of sulfur and the strengthening effect of boron in nickel were quantified. We found that the nickel-nickel bonds could sustain 16% more elongation before reaching the point of instability and 11% more stress in the presence of cohesion-enhancing boron than could pure nickel, whereas sulfur (an embrittling element) reduced the maximum attainable stress in nickel by 17%.

Our calculations identify a number of microchemical factors fundamental to understanding the effects of segregants at grain boundaries. The basis of the boron effect is ultimately a consequence of the absence of a large ion core in boron and the compact nature of its valence orbitals compared with those of sulfur. These characteristics permit boron to form strong direct bonds in nickel (and its alloys) at grain boundary sites where lattice distortions are not too large and available hole sites are small. The unusual strengthening effect of boron segregation has emerged as the most important research topic in this field. If properly characterized and theoretically understood, this "boron effect" could demonstrate convincingly that the field of alloy design has changed from an art to a science. The agreement obtained between the first-principles calculations and experimental observations of mechanical properties offers the exciting prospect of using such fundamental microscopic knowledge to optimize interfacial properties of new materials.—*Gayle S. Painter, Metals and Ceramics Division.*



Mike Miller works at ORNL's newly acquired atom-probe, field-ion microscope, a microanalytical tool for studies in materials science.

With the help of supercomputers, theorists at ORNL and elsewhere are breaking new ground in accurately calculating—from first principles—properties of materials (e.g., lattice constants, ordering tendencies, heat of mixing, electrical resistivity, and other electrical and magnetic properties). As their techniques and theories improve, theorists can help designers of materials predict which materials "on the drawing board" are most likely to have the properties desired.

William H. Butler is a member of the Theory Group in ORNL's Metals and Ceramics Division. In 1984–1985 he was manager of computer planning at ORNL. Before coming to ORNL in 1972, he was assistant professor of physics at Auburn University. Butler has a Ph.D. degree in solid-state physics from the University of California at San Diego. His research interests include theory of alloys, theory of transport, and theory of superconductivity.

Materials Science Theory at ORNL

By WILLIAM H. BUTLER

The discovery and development of new materials is an experimental and largely empirical process in which theory has played only a minor supporting role. The role of theory has been limited to providing a qualitative understanding of the basic properties of simple materials. The reason for this limitation is the extreme complexity of materials, especially those that are important to modern technology. Because of this complexity, theorists have been forced to work on overly simplified models that bear only a qualitative resemblance to the real physical systems that the materials scientists would like to understand.

Recent developments may, however, allow theory to play a more central role in the discovery and development of new materials. These developments consist of (1) refinements of theoretical techniques so that they can handle more realistic models of materials and (2) improvements in electronics that have increased the speed and reduced the cost of computation.

At Oak Ridge National Laboratory the Theory Group in the Metals and Ceramics (M&C) Division is attempting to calculate the fundamental properties of materials from first principles. In a "calculation from first principles," a theorist begins with only the basic laws of physics and the atomic numbers and concentrations of the atoms that make up the system under investigation, and from these attempts to calculate the property of interest.

Only a few years ago this goal would have been dismissed by most experts as utterly impossible because of the complexity of the forces that bind atoms together. These forces act between the positively charged nuclei and the negatively charged electrons that are constantly moving around and between the nuclei. These forces are complex largely because the electrons, of which there can be more than 10^{24} per cm^3 (a bouillon cube has a volume of approximately 1 cm^3), interact with each other as well as with the positively charged nuclei. To calculate the properties of a material from first principles, theorists must first solve the problem of how all of these electrons move. These calculations are difficult, however, because the electrons do not follow the familiar (classical) laws of physics; instead, they obey the complex laws of quantum mechanics.

Density Functional Theory

Surprisingly, first-principles calculations are proving to be not

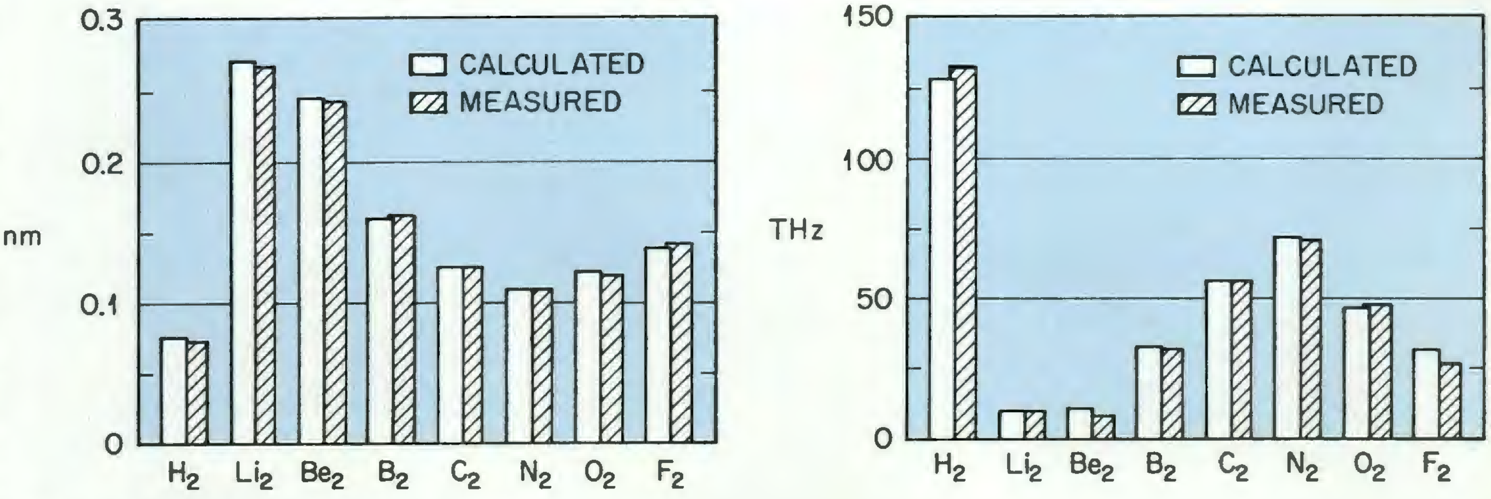


Fig. 1. Calculated and experimental values for the interatomic spacings and the vibrational frequencies of pairs of atoms, from hydrogen through fluorine. One nanometer (nm) is a billionth of a meter, and one terraherz (Thz) is 1,000 billion cycles per second.

only feasible but also highly useful and informative. They are feasible mainly because of the development of "density functional theory." This approach to treating the problem of many interacting electrons originated in work done by Walter Kohn, Lou Sham, and Pierre Hohenberg during the mid to late 1960s. Although density functional theory is now nearly 20 years old, only in recent years have the detailed calculations and careful comparisons with experiments been done to demonstrate its capability of predicting properties of materials based only on information about the types and arrangements of atoms.

Density functional theory starts from the concept that the energy of a system of interacting electrons depends only on the electron density (i.e., on the number of electrons per unit volume). From this starting point it is possible to deal with the "many-electron" problem by treating only one electron at a time because each electron moves in a self-consistent field determined by the positively charged nuclei and by the other electrons. This treatment simplifies the problem immensely. Interestingly, the equations describing the motion of a single electron that result from density functional theory are very similar to those that had been used previously to calculate the spectrum of electronic energy levels. Density functional theory showed that these equations *cannot* rigorously be used to calculate the energy spectrum, but they *can* be used to obtain the total energy and charge density of the system.

Some of the important calculations that established the accuracy and feasibility of calculations based on density functional theory were performed at ORNL during the past five years by Gayle Painter and Frank Averill. They have developed computer codes that can accurately solve the equations that describe the density functional approach for an arbitrary arrangement of atoms and for arbitrary types of atoms. For example, they have done calculations for the test case of pairs of atoms (see Fig. 1). Density functional theory reproduces very well the equilibrium distances between the atoms and also the frequencies at which the atoms vibrate. Painter and Averill are now using their codes to gain a better understanding of how impurity atoms affect the bonding of the constituent atoms in a material (see sidebar on page 52).

According to the laws of quantum mechanics, electrons act as if they were waves rather than ball-like particles. To a good approximation, the electrons in a metal may be divided into two groups. Some are so strongly attracted to the positively charged nucleus that they will remain tightly bound to it. The other electrons may be thought of as waves that propagate among "spherical scatterers," which are composed of the positively charged nuclei and the tightly bound electrons.

One important technique used by the Theory Group to understand how electrons propagate through a metal divides the problem into two separate parts. ORNL theorists first calculate how an electron wave will be scattered by a single atomic scatterer. Second, they calculate how an outgoing wave coming from one scatterer appears as an incoming wave to another scatterer. The first part of the calculation

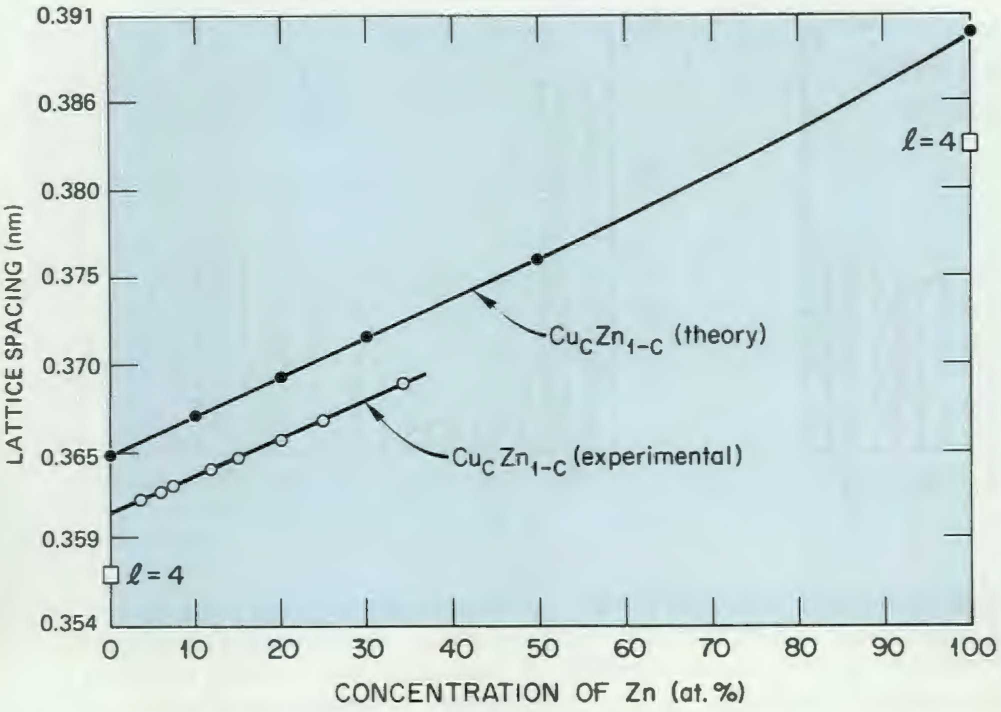


Fig. 2. Calculated and experimental lattice constants for copper-zinc (Cu-Zn) alloys.

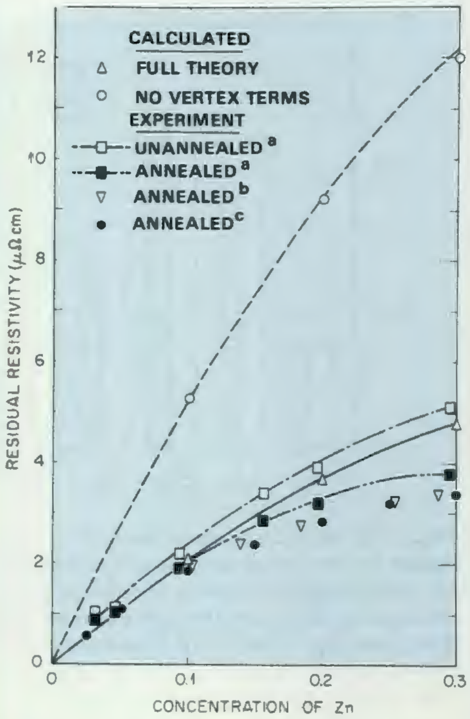


Fig. 3. Calculated and experimental electrical resistivity of Cu-Zn alloys. Vertex terms that take account of the fact that scattering events which only scatter the electron through a small angle do not contribute as much to the resistivity as those in which the electron scatters through a large angle are very important for this system. The experiment values for unannealed wires include resistivity from scattering by dislocations and should be slightly greater than the calculated values. The experimental values for annealed wires are reduced slightly by the effects of short-range order, an effect that is not included in the calculations.

contains all the information about the interactions of the scatterer with an electron. The second part contains all the information about the location of the scatterers. The solution is completed by requiring that the results of the two parts be consistent. The incoming waves on one atom must equal the sum of all of the outgoing waves from all of the other atoms. This consistency requirement leads to a set of equations that must be solved to determine the metal's electronic structure—the relative location and movement of its electrons.

In practice, these equations can be solved using a computer if the number of scatterers is not too large. They can also be solved for an infinite number of scatterers if these scatterers are all exactly alike and are arranged in perfect order on a lattice. When this technique is applied to such a periodic system, it is known as the KKR method, after its originators Jan Korringa, Walter Kohn, and Norman Rostoker. Work on the scattering approach was pioneered at ORNL by Sam Faulkner of the M&C Division and Harold Davis of the Solid State Division.

In a disordered metallic alloy, the atoms are usually arranged periodically on a lattice, but they are not all alike; thus, for these alloys, the ordinary KKR method does not apply. Unfortunately, it is extremely difficult, if not impossible, to calculate the electronic structure of an infinite number of atoms except in the special case of a periodic system. So, over the years, many attempts have been made to find a way to replace a disordered system by an effective periodic one that has the same electronic structure. Replacing the differing atomic scatterers on each site in the alloy by a simple "average" scatterer does not work very well.

Best Averaging Technique

An averaging technique that does seem to work well was discovered in 1967 by Paul Soven and David Taylor at AT&T Bell Laboratories. The technique, called the coherent-potential approximation, is based on the following idea. Suppose that you wish to calculate how electrons propagate in a disordered alloy that consists of a fraction *f* of type A atoms and a fraction *(1-f)* of type B atoms. Imagine that you have an infinite periodic lattice consisting of identical "scatterers." The identity of these scatterers is not specified in advance, but you wish the electronic structure of this periodic system to approximate that of the disordered one. Imagine that one of these scatterers is replaced by an atom of type A. Using an extension of KKR techniques, it is possible to calculate the "additional" scattering of electron waves as a result of this "impurity" atom. Now imagine taking out the A atom and replacing it with a B atom. You can also calculate the additional scattering caused by a B atom in an otherwise perfect lattice. The coherent-potential approximation consists of choosing the scatterer that makes up the infinite periodic system such that the average additional scattering caused by the A and B atom impurities is zero.

Marriage of Theories

The KKR method is an extremely powerful but rather complicated technique for calculating the movement of electrons in a periodic lattice of metal atoms. The coherent-potential approximation step used to include the effects of disorder in an alloy introduces significant additional complications. A final step is necessary, however, to accurately calculate the properties of an alloy. To apply the principles of density functional theory, the calculation must be made self-consistent.

The atomic scatterers are modified by their presence in the alloy. The densities and shapes of the electron clouds surrounding the positively charged nuclei of the scattering atoms will change when the atoms are made part of a solid such as an alloy. These changes can be calculated from the solution to the KKR-CPA equation. However, because the new scatterers are not the same as the ones used in the calculation, theorists must iterate (using the new scatterers as input to the KKR-CPA equations, which are solved and used to calculate a new set of scatterers). This process must be repeated until a set of consistent scatterers results.

The successful marriage of the KKR-CPA theory and local density theory was achieved recently by Malcolm Stocks and Don Nicholson of the M&C Division Theory Group and Frank Pinski and Duane Johnson of the University of Cincinnati. It promises to open up a new era in alloy calculations.

Calculated Properties

ORNL theorists have begun to calculate several properties of alloys. Results of these calculations have agreed well with experimental measurements.

Calculations of this type are difficult and use a lot of computer time, but the results seem to be worth the effort. For example, the lattice constants that ORNL theorists calculated for copper-zinc (Cu-Zn) alloys, or brass, are in good agreement with experiment (see Fig. 2). It appears that we can calculate the lattice constants of alloys and obtain results within about 1% of experimental measurements. This level of accuracy is about the same as that obtained in calculating the lattice constant of a pure system using current versions of density functional theory, so it seems that the CPA works very well.

Most alloys develop short-range order. If an alloy consists of A and B atoms, only in idealized cases do they occupy lattice sites in a perfectly random fashion. Generally, an A atom will have a preference for the type of atom it wants to sit next to. It may prefer to sit next to another A atom, in which case we say the alloy tends to cluster, or it may prefer to sit next to a B atom. In this case we say there is a tendency for short-range order. It is possible to calculate these ordering tendencies using KKR-CPA theory and to calculate how they will dictate the pattern that is observed when X rays scatter from an alloy. Recent calculations of these "X-ray diffuse scattering maps" agree very well with experimental observations.

It is very important to know how much energy is gained or lost when the atoms of two different metals are mixed to form an alloy. This "heat of mixing" determines, for example, whether the atoms tend to separate into a mixture of two separate phases or to form a homogeneous "solid-solution" alloy. Preliminary calculations of the heat of mixing look very promising.

It is also possible to calculate the electrical resistivity of alloys from first principles. For example, the resistivity of Cu-Zn alloys were calculated recently at ORNL by Jim Swihart of Indiana University, Stocks, and me (see Fig. 3). The only experimental quantities needed for this calculation are the atomic numbers of copper and zinc. Good results have also been obtained for the electrical resistivities of other alloys and for other electrical and magnetic properties such as the Hall coefficient and the thermopower.

In summary, with the help of supercomputers, theorists at ORNL and elsewhere are breaking new ground in accurately calculating properties of materials, such as lattice constants, ordering tendencies, heat of mixing, electrical resistivity, and other electrical and magnetic properties. As their techniques and theories improve, theorists can help designers of materials predict which materials "on the drawing board" are most likely to have the properties desired.

From left are Alan Bleier, Sunggi Baik, John Bates, and Paul Becher.

Recent Advances in the Science of Ceramics

By PAUL BECHER, SUNGGI BAIK, JOHN BATES, and ALAN BLEIER

Ceramics comprise a wide variety of materials, some of which have been used since ancient times. Clays were formed into useful cooking and storage vessels, then dried in the sun; later, they were "fired" to make them last longer and resist weakening by water. Sun-baked clay blocks were used for construction; later blocks, reinforced with straw, were found to be stronger than the original clay bricks and became the first known composites for structural or load-bearing use. Natural glasses were highly prized for jewelry and decorative pieces but were also used to make tools.

Later, people learned to use colorants (such as reddish iron oxide), sand, and fluxing agents (such as soda ash) that melted at low temperatures and fused the sand grains. Melting of the fluxes between the sand grains and the outer layer of the grains resulted in a solid object—the first product of what is known as liquid-phase sintering of ceramics. This general process is an extremely important technology in preparing very hard, very high-temperature materials such as tungsten carbide and titanium diboride. The optical qualities of glasses also provided the means to develop lenses and mirrors, which allowed important discoveries in inner space—the structure of living and inanimate objects which are not discernible by the human eye—as well as outer space.

Recent Advances

More recently, we have begun to use and consider ceramics in more complex and sophisticated applications. For example, the leapfrogging advances in electronics technology have relied heavily on the use and development of ceramics. The ceramics in this case are quite advanced materials, far removed from the materials made by mixing clays or sands lying about in nature's stockpile. Rather, high-purity compounds (such as alumina) that could meet quite demanding performance criteria had to be developed. In other cases, magnetic ceramics and ceramics which produced an electrical signal when subjected to a force/pressure (piezoelectric ceramics) were

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Sunggi Baik has been a senior staff member of the Structural Ceramics Group since 1983. He was a postdoctoral research associate at Cornell University for two years after receiving his Ph.D. degree there in materials science. His research interests include ceramic processing sciences and related surface and intersurface behavior. He is a member of the American Ceramic Society and the American Society for Metals.

John Bates is leader of the Solid Electrolytes Group in ORNL's Solid State Division. Before coming to ORNL in 1969, he was a research associate at the University of Maryland. He received his Ph.D. degree in physical chemistry from the University of Kentucky in 1968. His research interests focus on the properties of solid interfaces, fast ionic transport, and transport in oxides. He was co-chairman of the 1986 Gordon Conference on Solid State Ionics and now serves as associate editor of *Solid Ionics*. He has served on various international committees. Bates is a Fellow of the American Physical Society.

Alan Bleier joined the Structural Ceramics Group in 1983 as a senior staff member. Earlier, he was a faculty member in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology and a research chemist at Union Carbide Corporation's Research Center at Tarrytown, New York. He earned a Ph.D. degree in physical chemistry from Clarkson University in 1976. His research has focused on colloid and surface science. He has served as program chairman of the American Chemical Society's Division of Colloid and Surface Science and is currently the chairman-elect of the division's Fellowship Committee. He also serves as an abstractor and editor for the American Ceramic Society.

discovered, as were the processes to synthesize them. As a result, we have developed an understanding of what controls ceramic properties and how properties relate to the crystal and atomic/electronic structure of materials. This understanding allows us to describe their behavior quantitatively. We are now expanding this basic knowledge and developing other insights into the processes and mechanisms that control many properties of these materials. Through advances in a multitude of disciplines, scientific understanding in this field has been expanding rapidly for the past 15 years.

The following are only a few examples of the research at ORNL contributing to this understanding and the resulting development of new ceramic materials and new ideas.

Structural Ceramics

Structural ceramics are materials which must sustain a load or force without breaking. They are used in a wide variety of chemical environments (e.g., air, water, and corrosive chemicals) and over a range of temperatures. Structural ceramics must be strong enough to tolerate the stresses (force/unit area) encountered in service. Ceramics exhibit an elastic response up to the stress at which they fail instead of deforming at a yield stress as metals do. As a result, ceramics have very high strengths when loaded in compression. This same feature, however, limits their strength when they are pulled or loaded in tension.

Only a small tensile stress is required to advance a pre-existing crack in a ceramic and cause failure. This is because the applied stress is magnified many-fold at the crack tip and reaches the levels required to break the chemical bonds in the ceramic (see Fig. 1).

In metals, by contrast, the material near the crack tip usually

Advances in the science of ceramics allow today's ceramists to control the microstructure and thus tailor the properties of these ancient and important materials. Toughened, high-strength ceramics and ceramics having desirable electrical or optical properties can result from ceramic processing techniques refined by ORNL. These improved ceramics are sparking the interest of a variety of industries ranging from cutting-tool companies to automotive industries.

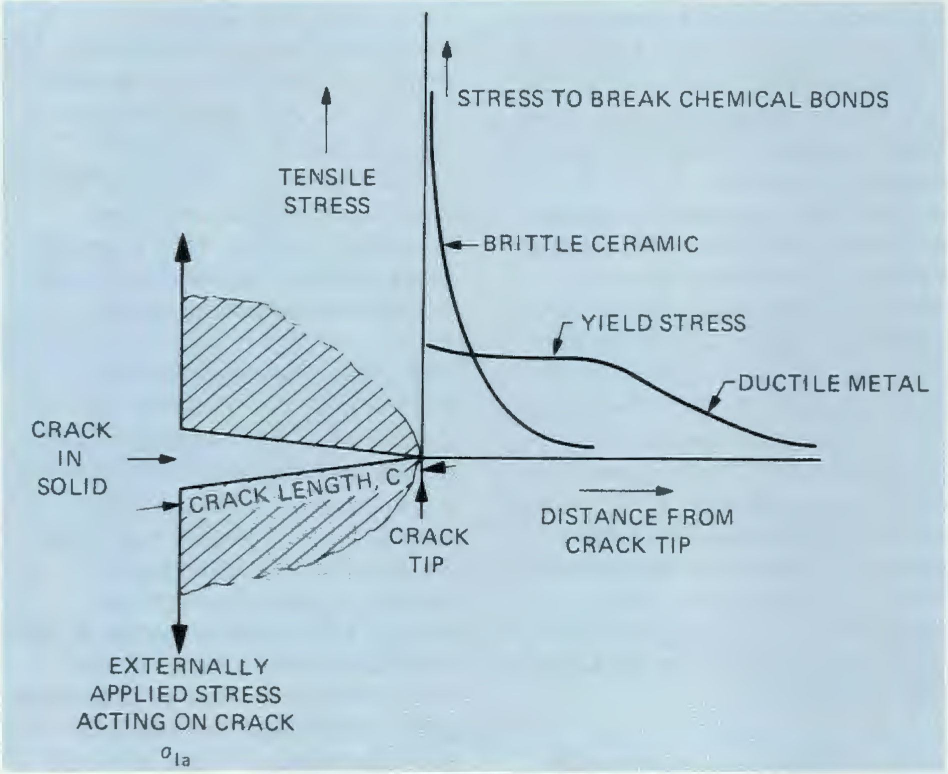


Fig. 1. The tensile stress acting on a crack is substantially amplified at the crack tip. In metallic materials, this is limited by plastic deformation in the region around the crack, which toughens the metal. However, in ceramics this does not occur and the crack-tip stresses readily reach levels that rupture the chemical bonds, resulting in low fracture toughness.

deforms plastically by the motion of dislocations before the crack-tip tensile stress reaches levels that break the metallic bonds (see Fig. 1). The crack-tip stresses in metals are spread out around the crack by this plastic deformation, and the applied stress must be increased to raise the crack-tip stress sufficiently to advance the crack. This is why metal bends instead of fracturing as ceramics do.

Because the crack-tip behavior in ceramics is considerably less forgiving than that in metals, ceramists are eager to learn what processes control this behavior and what can be done to improve the fracture resistance of ceramics.

Some terms are important in any discussion of fracture in materials. The stress concentration at an atomically sharp crack tip in the ceramic when a tensile stress is applied (see Fig. 1) is defined as the stress intensity K_{IA} such that

$$K_{IA} = Y\sigma_{IA}C^{1/2} \qquad (1)$$

where c is the crack length/size, σ_{IA} is the externally applied tensile stress, and Y is a factor which accounts for the crack geometry. Thus, the stress intensity at the crack tip increases as either the stress or the crack size increases. This relation explains why, when we want to break a piece of glass, we scratch it with a hard scribe: this introduces a large crack, allowing us to break the glass with less force or pressure. Otherwise, in nearly perfect, nearly flaw-free glasses (e.g., glass optical fibers) a stress of a few gigapascals (several hundred thousand pounds per square inch) is required to fracture the glass.

The property of materials that determines this resistance to rapid crack growth is known as the critical fracture toughness K_{IC}, which is

$$K_{IC} = (2E \cdot \gamma_{IC})^{1/2} \qquad (2)$$

where E is the Young's modulus and γ_{IC} is the external energy that must be supplied to advance the crack to form a unit area of new crack surface. Note that K_{IA} and K_{IC} are related: K_{IA} acts on the crack to advance it, and K_{IC} is the response of the ceramic in resisting the crack motion.

Mechanisms for Toughening Ceramics

Because they generally have much lower fracture toughness than metals, ceramics in tension are much more sensitive to the size of the cracks present in them. Cracks and flaws are invariably present in ceramics, and even cracks which are only 50 μm (~0.002 in.) or less can significantly reduce the strength of most ceramics. Clearly, we need to explore processes which increase the toughness of ceramics to minimize their sensitivity to the size of flaws that are always present. Studies in the Metals and Ceramics Division by Paul Becher, Terry Tiegs, and George Wei (now at GTE Sylvania Laboratories) illustrate two approaches for increasing the fracture toughness of monolithic ceramics: transformation toughening and whisker reinforcement.

Transformation Toughening

Transformation toughening involves a phase/crystal structure change triggered by the stress at the crack tip, which, in turn, alters the crack-tip stress. In many ways this is similar to the plastic deformation in metals in the vicinity of crack tips, which we discussed earlier. In fact, the crack-tip stress field will be similar to that of the metal shown in Fig. 1. However, it is the phase transformation, rather than dislocation motion and plastic deformation, which alters the crack-tip stress and increases the toughness. When subjected to a tensile stress, for example, the tetragonal crystal structure of both ZrO_2 and HfO_2 can be transformed to the monoclinic structure, which involves an expansion in volume e^T. When this occurs, as in ZrO_2 particles dispersed in a matrix near a crack tip, the volume expansion of the ZrO_2 introduces local compressive stresses and reduces the tensile stress acting on the crack tip.

As in the case of metals in which plastic deformation is initiated at a well-defined stress level (the yield stress), the phase transformation is triggered at a stress level known as the critical transformation stress σ_c^T. The lower the value of σ_c^T, the easier it is to transform the ZrO_2; the size r_T of the region around the crack tip where the transformation occurs increases as follows:

$$r_T \propto (K_{IC}^M / \sigma_c^T) \quad , \qquad (3)$$

where K_{IC}^M is the fracture toughness of the matrix in which the ZrO_2 is dispersed.

When we lower σ_c^T, the transformation zone size increases, which leads to an increase in the contribution from transformation toughening ΔK_{IC}^T increases:

$$\delta K_{IC}^T \propto V_f r_T^{1/2} \ . \qquad (4)$$

The transformation toughening contribution also increases as the volume fraction V_f of tetragonal ZrO_2 that transforms increases. Because these are composite systems, the total fracture toughness is the sum of the toughness of the matrix and the contribution from transformation,

$$K_{IC}^C = K_{IC}^M + \Delta K_{IC}^T \ , \qquad (5)$$

and the fracture toughness is increased.

Studies by George Begun of the Chemistry Division that use laser Raman spectroscopy techniques showed that the size of the transformation zone around the cracks in partially stabilized zirconia (PSZ) ceramics, which contain tetragonal ZrO_2 precipitates in a cubic ZrO_2, does indeed increase as the toughness increases in the manner predicted by Eqs. 4 and 5 (Fig. 2).

Additional studies showed that r_T increases as the value of σ_c^T decreases as predicted by Eq. 3. The question that remained was how could we further define σ_c^T in terms of the stability of the tetragonal ZrO_2. We know that such tetragonal particles in a matrix can be transformed by lowering the sample temperature T to a temperature $<M_s$, which is the temperature at which the tetragonal phase begins to spontaneously transform to the monoclinic phase. In studies by Paul Becher, Matt Ferber (now at the University of Illinois), and Mike Swain (with the Materials Science Division, CSIRO, Melbourne, Australia), analytical descriptions were derived by considering the thermodynamics of the tetragonal-to-monoclinic transformation of particles in a matrix. Briefly, the strain energy required for the stress-induced transformation of such a tetragonal particle in a matrix ΔU_{SE} is a function of the product of σ_c^T and the transformation strain. This, in turn, is determined by the sum of the chemical free energy, surface energy, and internal strain energy changes:

$$\Delta U_{SE} = \sigma_c^T e^T = (T - M_s) dS. \quad (6)$$

where dS is the entropy change associated with the transformation.

From Eq. 6 we see that σ_c^T will decrease as $(T - M_s)$, e^T, or dS decreases. By substituting Eq. 6 into Eqs. 3 and 4, one obtains

$$\Delta K_{IC}^T \propto V_f K_{IC}^M / (T - M_s) \ dS, \quad (7)$$

which predicts that the fracture toughness increases as M_s approaches T (or vice versa), as long as $T > M_s$. The value of the term $(T - M_s)$ tells us how easy it is to transform the tetragonal ZrO_2; the smaller the value of $(T - M_s)$, the lower the value of σ_c^T needed to start the transformation and the greater the toughness. This is consistent with the behavior of PSZ ceramics at room temperature (Fig. 3) and the toughness at various temperatures. This description of the transformation is also consistent with the toughening behavior of ZrO_2-toughened aluminas.

One can introduce other chemical compounds into the tetragonal ZrO_2 to make it more or less stable (i.e., lower or raise its M_s temperature). Increasing amounts of compounds like Y_2O_3 and CeO_2 lower M_s, while HfO_2 raises M_s. Studies by Paul Becher with Walt Bond of the Chemical Technology Division, Eric Funkenbusch of 3M Corporation, and George Begun show that modification of solute content has a profound effect on M_s, σ_c^T and fracture toughness obtained by transformation toughening. These effects are evident in both zirconia ceramics containing the tetragonal phase and in other ceramics, such as alumina, which contain dispersed tetragonal ZrO_2 particles. Studies are now addressing the mechanisms whereby these alloying compounds alter the tetragonal-to-monoclinic phase transformation.

Whisker Reinforcement

Another way to toughen ceramics is to introduce very small, but very strong, whiskers into the ceramic. An example involves the

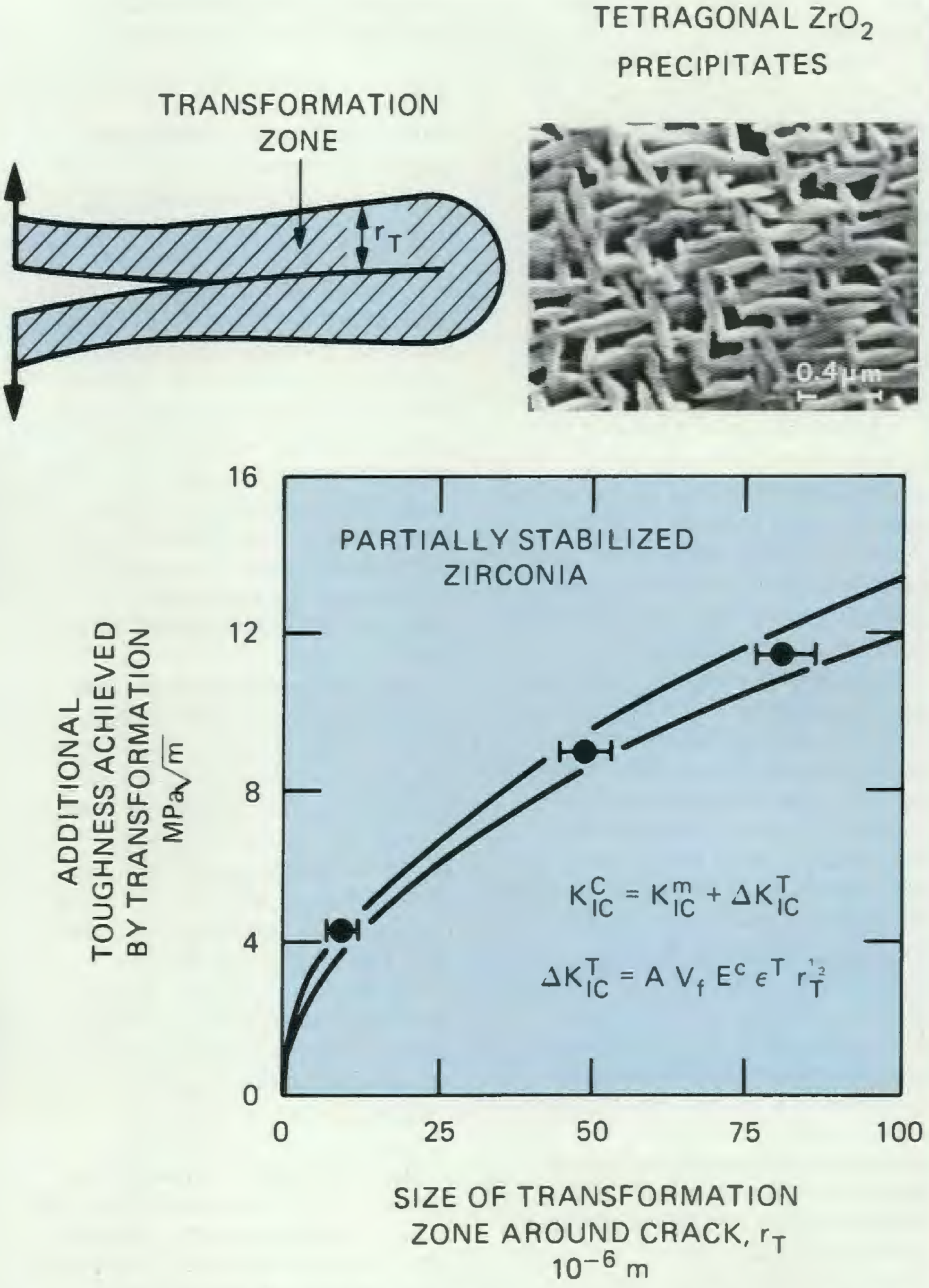
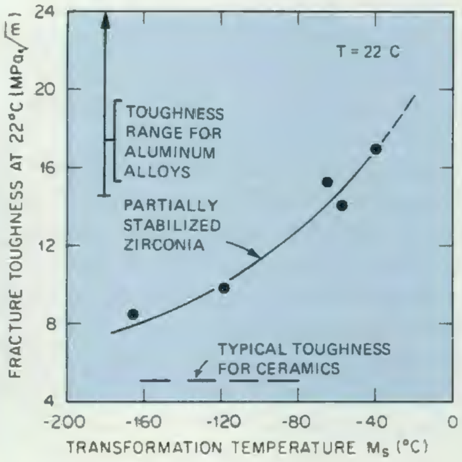


Fig. 2. Transformation toughening in ZrO_2-bearing ceramics involves a stress-induced tetragonal-to-monoclinic phase change in the region surrounding a crack. The amount of toughening achieved increases as the size of this transformation zone (r_T) increases.



TETRAGONAL TO MONOCLINIC ZrO_2 TRANSFORMATION

Fig. 3. The stress-activated phase transformation in ceramics containing tetragonal ZrO_2 particles imparts greater toughness when the phase transformation temperature is only slightly lower than the temperature of interest.

use of microscopic SiC whiskers (0.6 μm diameter by 30 μm long), which can be grown at elevated temperatures using rice hulls as the source of silicon and carbon. This process produces single-crystal whiskers of SiC, which can have very high tensile strengths—in excess of 7 GPa (1,000,000 psi), or at least ten times the strength of most polycrystalline ceramics.

When these SiC whiskers are incorporated into a ceramic, the combined strength of the whiskers and the properties of the interface between the whiskers and the matrix force a crack to advance through the ceramic matrix but the whiskers remain intact, so that they bridge the crack in the region behind the crack tip (Fig. 4). Thus, the strongest whiskers effectively hold the ceramic together and resist crack advancement. Only if the external stress is increased will the whiskers fracture, allowing the crack to move ahead. This process results in toughening the material.

This technique is not unlike nailing two boards together. To pull or wedge the boards apart, we must either pull out the nails or break them. The more nails we use, the more energy is required to separate the boards. SiC whisker–reinforced ceramics are at least two to three times tougher than the ceramic alone, and their toughness increases as we increase the whisker content (see Fig. 4).

The force required to pull the whisker out will depend on how tightly it is bonded to the material around it. In the ceramic composite, this is determined both by how well

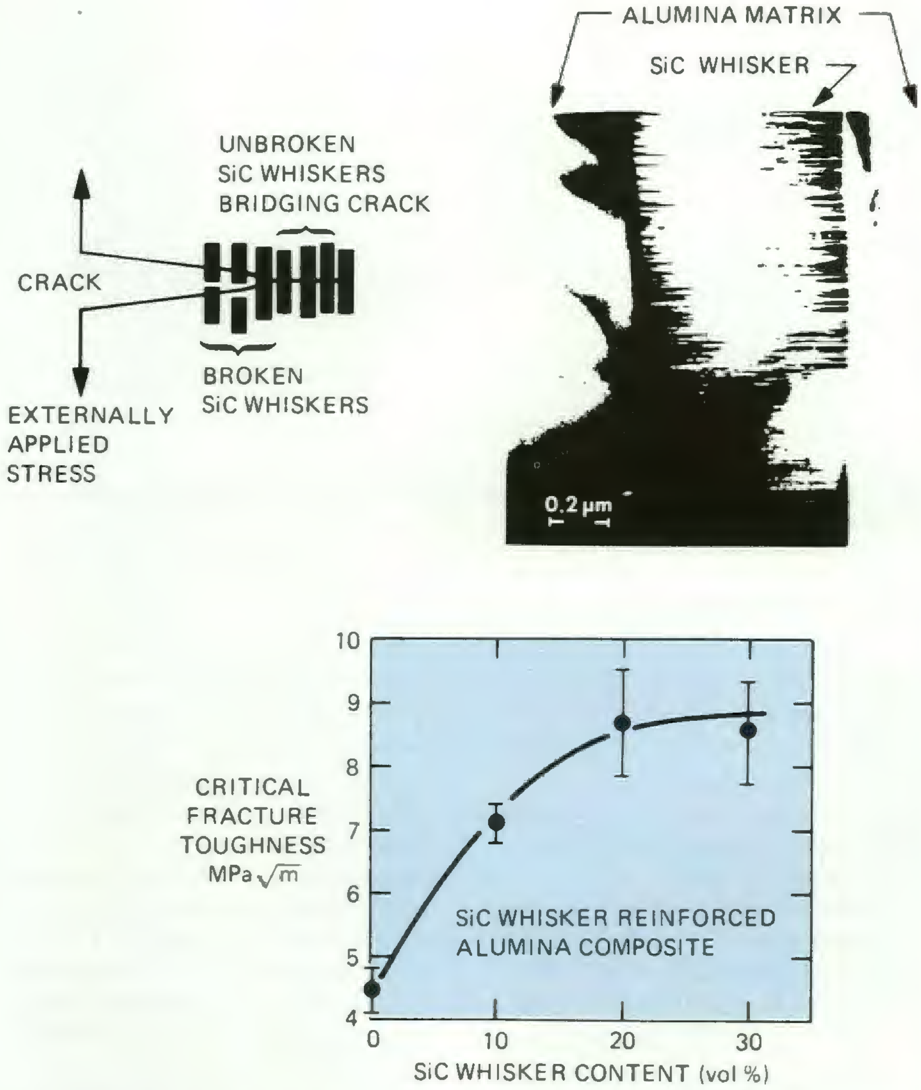


Fig. 4. SiC whisker-reinforced ceramics are made tougher by incorporating very strong microscopic whiskers that effectively hold the ceramic together during fracture.

the whisker is bonded to the ceramic and by how much force is exerted on the whisker by the matrix ceramic when it cools and shrinks around the whisker after fabrication of the composite. This shrinkage force is determined by how much more the matrix ceramic contracts than does the whisker; thus, it depends on the difference in thermal expansion coefficients. The greater the contraction of the matrix or the stronger the chemical bonding between the whisker and matrix, the more difficult it is to pull the whisker out. The whisker must be very strong, or it will break before it imparts toughness to the composite. Thus, it is important to examine the behavior and character of the interface between the whisker and the matrix.

Studies are now under way to examine these factors. Pete Angelini of the Structural Ceramics Group is conducting transmission electron microscopy studies at the Max Planck Institute in Stuttgart, Federal Republic of Germany, on the behavior of whiskers during crack growth and the nature of the whisker-matrix interface. Initial electron microscopy studies by Larry Harris of the Ceramics Technology Group indicate that SiC whiskers in alumina matrix composites are acted on by considerable compressive force, which will influence the whisker pullout processes.

The effectiveness of these toughening mechanisms is shown by the two-fold to five-fold increases in toughness in these composites compared with conventional ceramics. Fracture toughness values of 12 to 18 MPa√m are observed in PSZ and ZrO_2-toughened aluminas and of >10 MPa√m in the SiC-whisker-reinforced aluminas. These increases in toughness lessen the flaw-size sensitivity of fracture strength by factors of 4 to 25. As a result, high fracture strengths can be obtained in such materials even when cracks are 200 to nearly 1000 µm. (Remember, we noted earlier that in conventional ceramics, even cracks below 50 µm substantially decreased the fracture strength.)

These increases in toughness also reduce the ceramics' vulnerability to rapid heating or cooling—thermal shock. In addition, the toughened materials are more resistant to time-dependent failure resulting from sustained stresses less than those required to cause rapid fracture. This improvement will have important benefits in a wide variety of ceramic applications. We are developing basic knowledge of toughening mechanisms that allows us to explore and test entirely new concepts.

Ceramic Electrolytes and Metal-Ceramic Interfaces

Some types of ceramics known as solid electrolytes have exceptionally high ionic conductivities even at room temperature. These materials have important applications as the separators in high-energy-density batteries and fuel cells and as the active elements of chemical sensors.

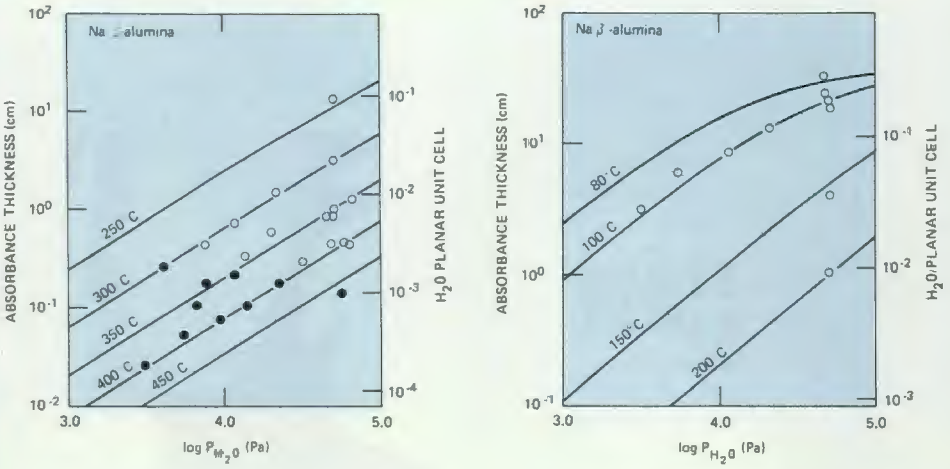


Fig. 5. Equilibrium concentrations of water absorbed by Na β- and Na β″-alumina as a function of the treatment temperature and water vapor pressure. The absorbance scale and the open vs closed symbols refer to the type of infrared measurements used to monitor the water content. The solid lines show the least-squares fit of the thermodynamic parameters to the data.

A family of aluminates commonly referred to as the β- and β″-aluminas is an interesting and important class of solid electrolytes in that they display remarkably high mobilities for a large variety of cations (alkali-metal ions, Ag^+, H^+, Pb^{2+}). The structures of the β- and β″-aluminas are similar: both consist of thick, densely packed layers of aluminum and oxygen ions separated by thin, loosely packed layers (conduction planes) that contain the mobile cations. This layered structure results in a high conductivity parallel to the conduction planes but essentially zero ionic conductivity perpendicular to these planes.

The sodium compounds of β- and β″-alumina are represented by the formulas $Na_{1+x}Al_{11}O_{17+x/2}$ ($x = 0.2$) and $Na_{1+x}Al_{11-x}Mg_xO_{17}$ ($x = 0.7$), repectively. These two compounds are primary candidates for the separator in the high-temperature sodium-sulfur battery. Recent research in the Solid Electrolytes Group at ORNL has focused on the reaction of sodium β- and β″-aluminas with H_2O and with H_2O in the presence of CO_2. These reactions have important consequences on the lifetime and performance of the electrolytes in the sodium-sulfur battery.

Both Naβ- and Naβ″-alumina readily absorb water from the atmosphere at room temperature. The water molecules occupy open spaces in the conduction planes. A recently completed study by Nancy Dudney and John Bates of the hydration of these compounds shows that large concentrations of water can be reversibly absorbed and desorbed. The water concentration at saturation is 75% of the sodium ion concentration in Na β-alumina and 18% of the sodium concentration in Na β″-alumina. The enthalpy and entropy of the hydration reactions were determined from measurements of the equilibrium water concentration in single crystals of Naβ- and Naβ″-alumina treated in a range of water vapor pressures at different temperatures (Fig. 5).

Sodium β- and β″-aluminas also have been shown to react rapidly with water vapor and carbon dioxide at room temperature. The reaction products form a scale on the surface of the electrolytes, as illustrated in Fig. 6. At high CO_2 pressures, the reaction product is $NaHCO_3$, whereas at low CO_2 pressures, a layer of hydrated Na_2CO_3 is formed. During these reactions, Na^+ ions in the electrolyte's surface region (up to 20 μm below the surface) are replaced by H_3O^+ ions. The fact that the net free energies of these reactions are negative means that the standard free energies of formation of hydronium β- and β″-alumina are lower (i.e., more negative) than those of the respective sodium compounds. The irreversible degradation of the exposed surfaces of commercial electrolytes resulting from the reaction with water vapor and CO_2 may well be an important factor in their electrolytic breakdown, which is often observed in the operation of the sodium-sulfur battery.

A new class of solid electrolytes has evolved in the last decade. These new electrolytes are composites that contain a dispersed second phase. An example is an ionic matrix (e.g., β-AgI or LiI) in which 10 to 40 vol % of submicron Al_2O_3 particles are dispersed. The ionic conductivity is substantially higher (>100 times) in the composite than in the pure matrix material. In general, it is assumed that the enhancement is caused by the existence of a high-conductivity layer surrounding each Al_2O_3 particle. This idea was recently incorporated by Jim Wang (in our group) into model calculations of the conductivity as a function of composition of a composite represented by a cubic array of insulating particles imbedded in an ionic matrix. When compared with published data, the calculated results suggest that the conductivity increases rapidly with distance from the particle, reaches a maximum, and then decays more slowly to the bulk value. Typical calculations are shown in Fig. 7.

Fig. 6. Electron micrographs showing growth of $NaHCO_3$ on a polished face normal to the conduction layers of a single crystal of Na β''-alumina after exposure to H_2O-saturated CO_2 at 25°C for (a) 0 h (1000×) and (b) 72 h (250×).

The high conductivity layer surrounding the insulating particles in a composite has been attributed by several researchers to an enhancement in the concentration of ionic charge carriers in a space-charge layer at the interface between the insulating particles and the ionic matrix. A study that tested this hypothesis was recently completed by Dudney. In an ionic material, interfaces such as free surfaces and grain boundaries will typically have a net charge that is compensated by a diffuse layer of lattice defects (e.g., cation vacancies) to maintain electrical neutrality. An example of a calculated distribution of lattice defects in AgCl near a boundary with a net positive charge is shown in Fig. 8. To test whether formation of a space charge could be responsible for the enhanced ionic conduction of the composite electrolytes, Dudney calculated the maximum expected contribution of the interfacial space-charge polarization to the total conductivity of the composite. This analysis revealed that interfacial space charge layers may give rise to a modest enhancement of the ionic conductivity but not to the 50- to 500-fold increases observed in the βAgI and LiI matrix composites. Current research focuses on identifying the additional factors contributing to the ionic conductivity of such composites.

Applications of ceramic electrolytes in various devices, as well as the measurement of their electrical properties, almost always require a metal contact with the ceramic. For electrical measurements, the metal-electrolyte junction or interface is often a so-called blocking contact across which neither ions nor electrons can pass. In these cases, ac or pulse techniques must be used to determine conductivity. The impedance of a "cell" consisting of a solid electrolyte sandwiched between two metal electrodes is dominated by the impedance of the metal-electrolyte junction below a characteristic frequency that depends on the resistance of the sample. Figure 9 shows an example of the impedance of the cell Pt/Agβ-alumina/Pt in which ~0.5 μm-platinum contacts were sputtered onto opposite ends of a single crystal of Ag β-alumina. The impedance can be accurately represented by the function

$$Z = R + 2B(j\omega)^{-n} , \quad (8)$$

where R is the resistance of the electrolyte, B and n are constants ($0 < n < 1$), and $j = \sqrt{-1}$. If the two metal-electrolyte junctions behaved as ideal capacitors, the n would equal 1 and B would equal the reciprocal of the interfacial capacitance. In this case, $Z = R - 2j/\omega C$, so that

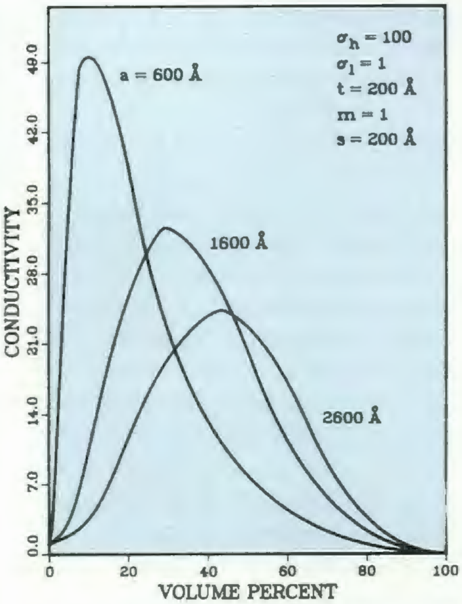


Fig. 7. Conductivity vs volume fraction of insulating particles for several particle sizes. The nonuniform high conductivity layer around each particle has a thickness of roughly $t + s$.

$Re(Z) = R$ is independent of frequency. However recent studies by Bates, Y. T. Chu, and Wang found that the frequency exponent n was <1 (typically, $n = 0.6$ to 0.9). In addition, n was dependent on the microstructure of the metal-ceramic interface in which n generally decreased as the interface was roughened. When $n < 1$, $Re(Z)$ is frequency dependent at low frequencies (Fig. 8). From Eq. (8)

$$Re(Z) = R + \frac{2B}{\omega^n} \cos(n\pi/2), \quad (9)$$

and

$$Im(Z) = - \frac{2B}{\omega^n} \sin(n\pi/2). \quad (10)$$

This behavior caused by the second term in Eq. (10) is characteristic of the so-called constant phase angle (CPA) impedance since $-Im(Z)/Re(Z) = \tan(n\pi/2) =$ a constant. Two models have been developed to account for the influence of the interface roughness on the observed CPA impedance. In one of them, developed by Wang, the rough interface is represented by a distribution of horn-shaped pores on the surface of the solid electrolyte. The resistance and capacitance of each pore varies with depth into the pore. Wang's results predict n values of the magnitude observed. A second model, developed by Sam Liu, Ted Kaplan, and Len Gray, is based on the representation of a rough interface by a self-similar or fractal structure known as a Cantor bar (Fig. 10). Their analysis indicated that the frequency exponent n is related simply to the fractal dimension $\tilde{d}$ of the Cantor bar: $n = 1 - \tilde{d}$. Their model, like Wang's, correctly predicts the dependence of n on the roughness of the interface. However, explicit quantitative agreement between predicted and observed behavior has not been achieved. The goal of current experimental and theoretical studies in the Solid Electrolyte Group is to further the understanding of the relationship between the CPA impedance of solid-solid and solid-liquid junctions and the interface structure.

Processing of Ceramics

To fabricate such toughened high-strength ceramics or ceramics having desired electrical or optical behavior, we must learn how to form dense ceramics from powders—the prime method for producing ceramics. This requires that we understand how to pack the powder particles to minimize the size and number of voids/holes. If we allow the particles to come together in a random array, both a significant number of large holes and a large range of hole/void sizes will result. If such a powder compact were heated, only a portion of these voids would be removed. We could eliminate still more voids if we heated the sample to a higher temperature because transport of material to the voids and vacancies from the voids to the exterior surface would be faster. However, the increase in mass transport will also allow the grains of the polycrystalline material to grow—an often undesirable feature. This is reflected in the influence of grain size on fracture strength and the crack-growth behavior of noncubic polycrystalline ceramics. In addition, the voids retained in the ceramic after firing can influence its fracture strength: depending on their size, the voids can act as cracks that cause fracture. One way to overcome the need to use high temperatures to make very dense ceramics is to allow the powder particles to arrange themselves in a more ordered packing and thus decrease the maximum void size and the number of voids. Lower temperatures can then be used to obtain fully dense ceramics.

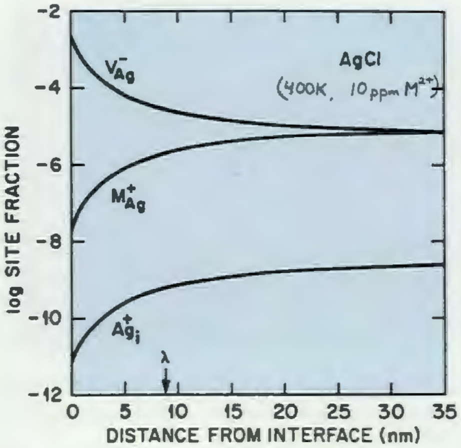


Fig. 8. Defect concentrations near an interface of extrinsic AgCl at 400 K. The charged lattice defects are vacant Ag lattice sites, Ag interstitial ions, and substitutional divalent cation impurities.

Another means to enhance densification of ceramic powders is to add small amounts of a second compound. This method is used extensively, but the mechanisms by which these methods promote densification are not well understood. It is thought that the additives increase mass transport rates or decrease the mobility of grain boundaries or that of the voids—both of which increase the probability that the voids remain at grain boundaries, where they are more efficiently removed. To determine the process that contributes to densification, it is important that we know where the densification aid is localized in the ceramic and how its effects are expressed in the system.

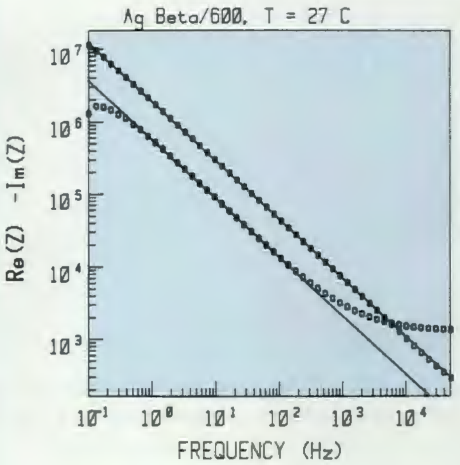


Fig. 9. Impedance of the cell Pt/Agβ-alumina/Pt. The solid lines through the data points [lower set is Re(Z)] are the real and imaginary components of the CPA impedance, $B(j\omega)^{-n}$, with $B = 8.37 \times 10^6$ ohm-rad^n and $n = 0.81$.

Behavior of Densification Aids

The production of ceramic components involves the heating of a powder compact to achieve the desired high density (i.e., to eliminate voids/pores) and shape. Experience has shown that often small amounts of intentionally added chemical compounds can promote densification (e.g., 0.5 wt % MgO to Al_2O_3, <1 wt % B in SiC) or that low levels of impurities can retard densification (e.g., >1 wt % oxygen in TiB_2).

Recently, Sunggi Baik of the Structural Ceramics Group initiated novel experiments to unravel the behavior of a densification aid

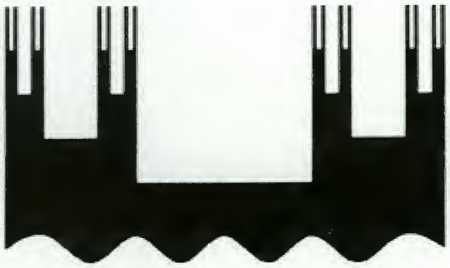


Fig. 10. Cantor bar model of a rough interface between an electrolyte (black) and an electrode (white). Each groove subdivides into two branches, and each branch is identical to the larger one when magnified by a factor A, where $A > 2$. This is the nature of the self-similar object, or fractal; in this case, the fractal dimension is given by $\bar{d} = \ln 2/\ln A$.

(i.e., does it segregate to grain boundaries, pore surfaces, or the surface of the particle; how fast does this occur; and what effect might it have on the structure?). In this regard, one should note that densification by mass transport is driven by the reduction of the free surface area of the powder compact because the particles have very high surface energy. Thus, we are determining the surface properties related to segregation of densification additives. This involves characterizing the segregation of this species to surfaces, changes in surface structure, and the surface diffusivity/mobility by Auger electron spectroscopy and low-energy diffraction techniques.

For example, a pure single crystal of alpha alumina is placed on an MgO-doped alumina crystal and the Mg^{2+} ions are allowed to migrate by heating to a desired temperature in a furnace that is part of the Auger system. The surfaces in contact are prepared to give the desired crystal planes in contact [e.g., both surfaces are parallel to the basal (0001) plane of the α alumina crystal structure]. These orientations can be altered to determine the influence of surface structure and lattice orientation on the diffusion/segregation processes.

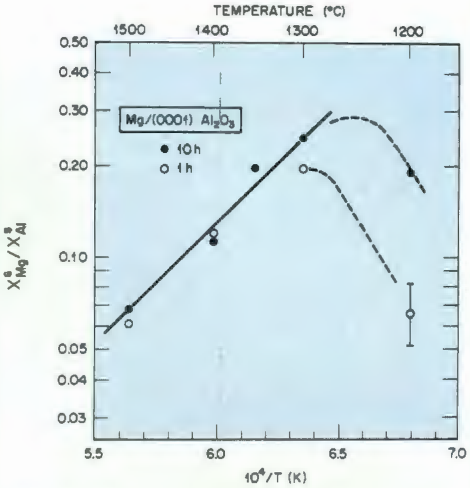


Fig. 11. The surface concentration of Mg measured as a function of annealing temperature and time. Magnesium atoms replace a quarter of Al surface atomic sites after annealing at 130°C. This corresponds to 1000 times higher concentration than bulk concentration.

After the sample is heated to the desired temperature, the surfaces are characterized.

Such studies show that the magnesium in a MgO-doped alumina single crystal is strongly concentrated on the (0001) free surface—it quickly segregates to the free surface. The amount of segregation increases as temperature increases until sufficient temperature is reached to evaporate the MgO faster than it segregates to the surface from the interior of the doped alumina (Fig. 11).

After the sample is heated to 1300°C, the magnesium replaces about one quarter of the aluminum sites on the first layer of the (0001) surface of the alumina. In fact, the magnesium segregation to the alumina surface results in a transformation of the surface structure of the alumina as shown in the LEED patterns in Fig. 12. These results indicate that the surface of the alumina (its chemistry and structure) is remarkably altered by the MgO dopant at temperatures at which densification occurs in MgO-doped alumina powders. Such segregation will alter the free surface energy of the alumina. This process is also observed to occur at the surfaces of model pore surfaces of alumina; thus, the MgO can influence the densification of alumina by altering pore mobility. Continuing studies are examining the segregation of other dopants and the effects of such segregation on grain boundary diffusion, mobility, and pore mobility, all of which can also be affected by segregation. Using these experimental approaches, we now have a means to understand the mechanisms by which dopants or impurities influence the densification process. This information will allow us to control the processing of ceramics and to determine which dopants to add or eliminate.

Colloid Science in Powder Processing

To control the ceramic's microstructure during densification, we must understand how to develop specific microstructure in the consolidated/compacted powders before they are fired. By far, the most promising approach is the use of powder suspensions. A fundamental understanding of processing must, then, focus on the controlled generation of powders, the behavior of solid-liquid suspensions, and the consolidation of ceramic powders as indicated in Fig. 13 and Table 1. These areas comprise an integral part of the research focus in the processing of ceramics in the Structural Ceramics Group. The approach is to join the disciplines of ceramic science and colloid and surface science to gain fundamental insight into the processing of ceramics with controlled microstructures.

First, we must consider how to generate "good" powders. Often, the desired powders are finely divided and described as colloidal. A colloid is a solid particle having a high

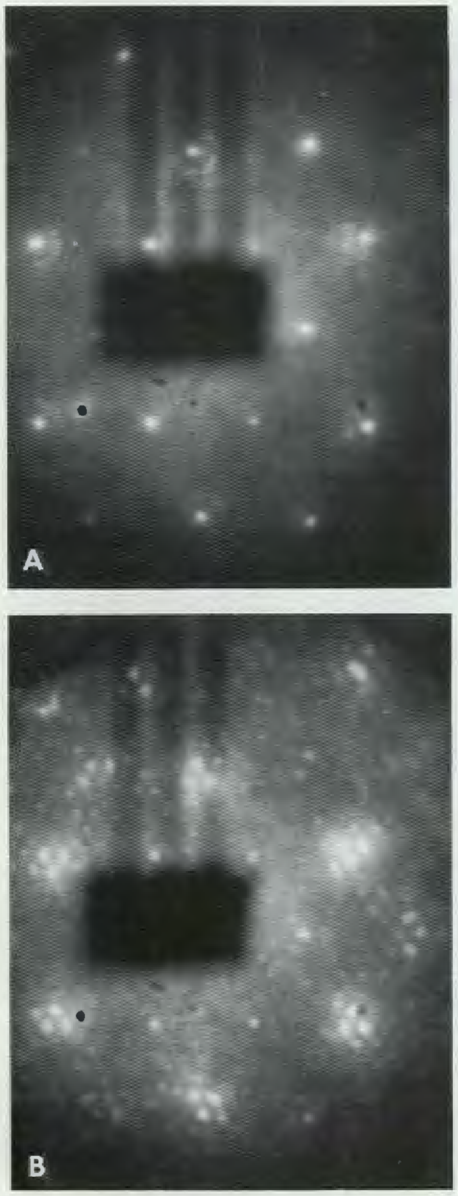


Fig. 12. Low-energy electron diffraction (LEED) pattern obtained with (001) surface plane of Al_2O_3 single crystal, sapphire. (A) Unreconstructed (001) plane obtained in the area in which Mg was not detected. (B) Reconstructed surface structure with quarter monolayer of Al atoms replaced with Mg atoms.

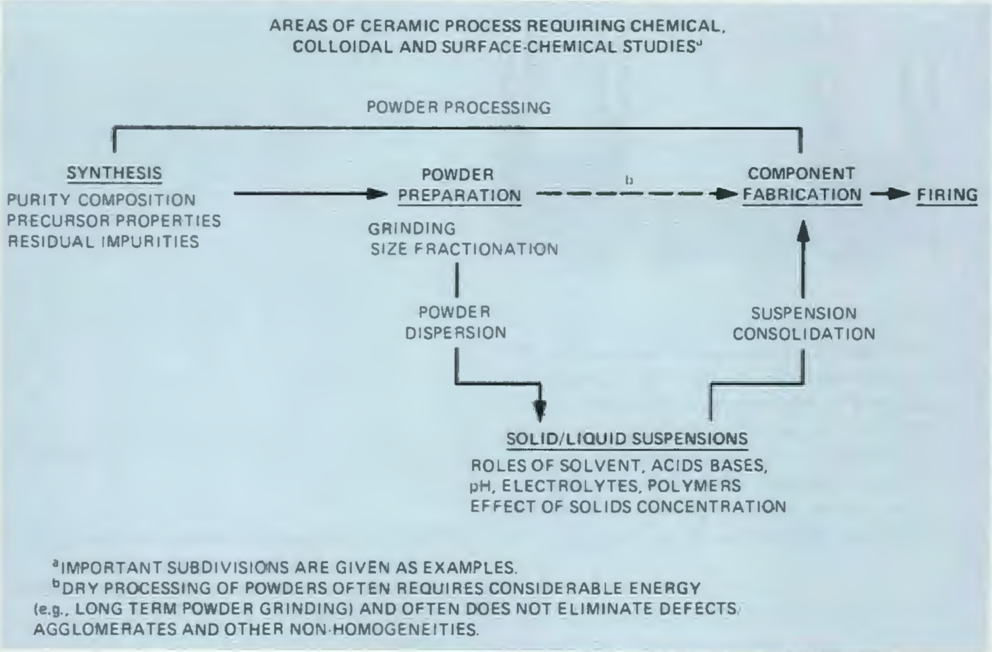


Fig. 13. Areas of ceramic processing that require chemical, colloidal, and surface-chemical studies.

surface area to volume ratio, which is characteristic of a submicrometer-sized particle. A good powder may be considered to be one that has the required chemical purity, phase composition, and desirable processing characteristics, including controllable packing density and sinterability. Other aspects of the powder to be considered are the particle size distribution, shape, morphology, type and degree of crystallinity, and reactivity with its processing environment.

Second, because we often use colloidal suspensions, an understanding of the interactions between powder particles and the liquid must be developed to control processing. Two general phenomena that contribute to these interactions are the liquid's ability to wet the powder and the powder's dispersibility—its ability to subdivide into individual particles. These contributions are critical to preventing the formation of irregular, porous arrays—known as agglomerates—that can affect the flow behavior of suspensions (see Fig. 14). Agglomerated suspensions exhibit greater flow resistance or

Table 1. Current processing needs and suggested research areas

Generation of powder
  Nucleation and growth mechanisms and effects on powder properities
  Manifestation of chemical precursor properties
  Development of amorphous, crystalline, and anisotropic particulates

Powder processing
  Inherent powder properties—effects on wetting, dispersion, stabilization, and consolidation of powder
  Role of surfactant, polymeric, and second-solvent additives
  Interparticulate and intraparticulate adhesional forces
  Role of surface roughness, elasticity, and plasticity
  Rheology—role of agglomerate structure

Consolidation (powder packing and compaction mechanics)
  Flow and collapse of agglomerated particulate structures
  Drying
  Particle packing structure

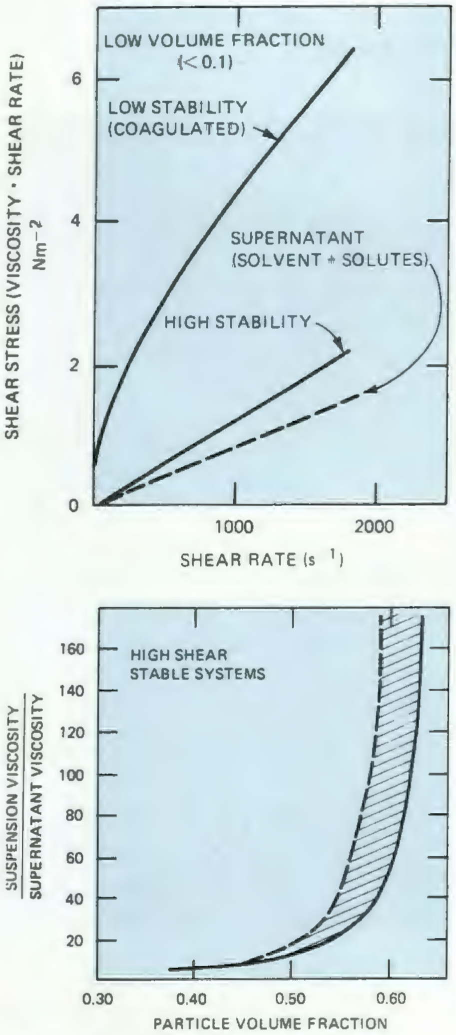


Fig. 14a. Highly stable suspensions approach viscosity of liquid phase whereas unstable ones are considerably more viscous. Note that shear rates may "break" agglomerate structures in unstable systems as manifested in a "flatter" curve at high rates. Fig. 14b. Effect of particle volume fraction on viscosity relative to that of liquid phase (solvent + solutes). Exact values within band depend on particle size and whether polymer dispersants are present.

viscosity when subjected to shear forces (as in mixing) than do well-dispersed suspensions. Particle interactions also influence, if not control, the packing arrangement of particles during consolidation. The packing structure depends on surface-interaction forces, which can lead either to ordered structures—like those of atoms in a crystal—or randomly arranged structures.

Fig. 15. Scanning electron micrograph of ZrO_2 packing. Note uniformity in particle characteristics and nearly ideal packing structures.

Powder that is uniform in size, shape, and composition is one requirement in achieving uniform packing during consolidation. Generation of ceramic powders by controlled chemical synthesis provides a means of achieving these features. Research by ORNL's Alan Bleier and Rowland Cannon of Lawrence Berkeley Laboratory on the reactivity of zirconium salts dissolved in water has led to an understanding of how to develop uniform, spheroidal, monoclinic zirconia powder. The scanning electron micrograph in Fig. 15 demonstrates the uniformity of packing and high density that can be achieved. The powder particles themselves are finely divided (typically 10 to 100 nm), depending on the specific synthesis conditions, and are polycrystalline with the ultimate crystallite size being ~3 nm.

The uniform ZrO_2 powder is easily dispersed in water and is stable as a colloidal suspension over a wide range of pH—where pH (i.e., concentration of H^+ vs OH^- ions in solution) is used to regulate the surface charge on the particles. These features provide for the formation of high-solids suspensions that readily flow and form the regular dense particle packing during consolidation seen in Fig. 15.

To stabilize the ceramic suspension, we establish an interparticle force that resists reagglomeration brought about by particle collisions. Collisions arise from diffusion (as in Brownian motion), shear waves within the liquid, and gravitational settling. One method of stabilizing particles is to promote the development of surface sites that possess ionic character (e.g., ZrO^- or $ZrOH^{2+}$ sites on zirconia and AlO^- or $AlOH^{2+}$ sites on alumina particles). This involves an electrostatic process, and the pH of the suspension is the factor that most influences the population density of charged sites for a specific oxide. Moreover, each oxide has a unique profile of surface charge vs pH (see Fig. 16). The presence of such charge sites on the surface of particles generates an electrostatic field that opposes the van der Waals forces that promote agglomeration.

Research by Bleier and Baik focuses on understanding the variety of interactions that occur in the processing of two-phase composite suspensions. Figure 16 demonstrates the nature of the agglomeration problem regarding composites of Al_2O_3 and ZrO_2. Al_2O_3 dispersions are unstable at pH 6.7 (see Fig. 17), and the sign of the Al_2O_3 surface charge is opposite that of the ZrO_2. Under such conditions, large agglomerate structures form and result in nonuniformly distributed ZrO_2. Under conditions in which both types of particles are highly charged and have the same type of charge (positive or negative) and, thus, form stable suspensions, nonuniformity in the distribution of the two phases can result from differential settling resulting from differences in particle size or density. The latter can be controlled by using smaller particles of the denser phase, which in this case is the zirconia.

An alternative to electrostatic stabilization based on particle surface groups is polymeric stabilization.

Industry Adopts ORNL's Ceramics and Ceramic Processing Technology

The lowly rice hull plays an important part in a sophisticated ceramic composite now being used for fast, long-lasting cutting tools. The composite, developed at ORNL, consists of an alumina matrix reinforced with microscopic "whiskers" of silicon carbide, which double the toughness of the normally brittle alumina. Rice hulls—among the few organic materials rich in both silicon and carbon, the necessary ingredients for silicon carbide—provide a cheap and plentiful source of the whiskers.

The microscopic whiskers help the normally brittle alumina resist cracking in much the way nails keep boards from being pulled apart. When a crack begins to develop in the matrix, the stronger SiC whiskers bridge the gap and stop the crack's growth. (For more technical details, see page 58.)

The patented composites, licensed in June to Atlantic Richfield's ARCO Chemical subsidiary, are being made into cutting tools and other wear parts. Cutting tools made of the composite can machine nickel-base superalloys up to ten times faster than tungsten carbide-tipped cutting tools, and they last up to seven times longer. The composite maintains its high strength and fracture toughness at temperatures up to 1000°C even when used at the higher speed.

ARCO has non-exclusive rights to this whisker technology. Other companies that make cutting tools, engine components, and other wear parts have also expressed strong interest in it.

An assortment of parts, including tubing and ceramic heat-engine components as well as cutting tools, can be made from ORNL's fracture-resistant whisker-reinforced ceramics.

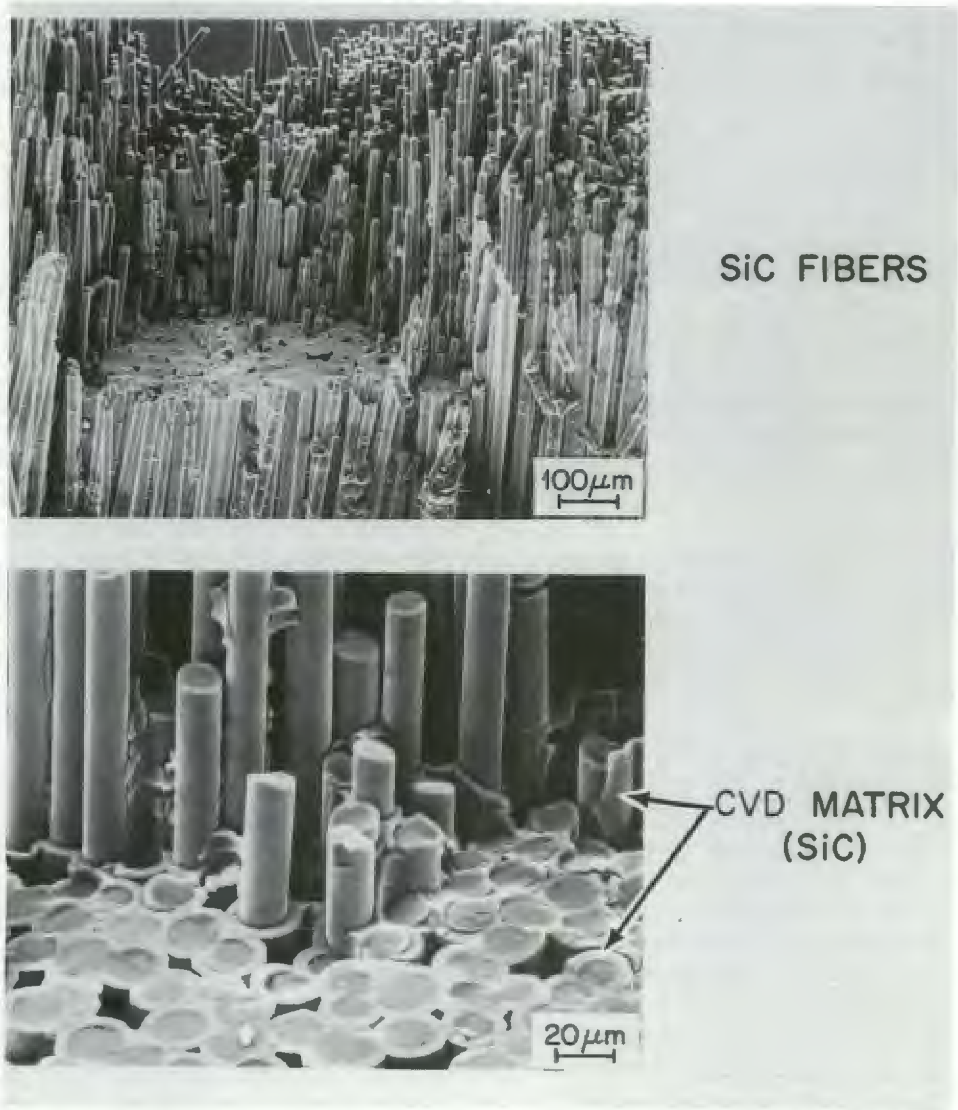
Chemical vapor deposition. Another ORNL ceramic technology being transferred to private industry is a technique for forming toughened ceramic composites by chemical vapor deposition (CVD).

In the CVD process, a shaped part is formed by winding filaments made of ceramic fibers onto a mandrel or by casting the part using a slurry of chopped fibers, as in the slip-casting method of forming ceramic greenwear. This shaped part of ceramic fibers or filaments is then placed in a furnace, and a reactive gas containing silicon and carbon is forced through the part. As the reactive gas is heated by the hot part, the gas decomposes and deposits silicon carbide on and between the fibers. This forms the matrix or binder phase of the ceramic fiber–ceramic matrix composite.

When composites produced by this technique are stressed, they deform and break gradually rather than fracturing catastrophically like most ceramics. This unusual fracture behavior is due to the fibers' pulling out of the matrix, thus absorbing energy and effectively stopping the crack.

Babcock and Wilcox Company is interested in using CVD to manufacture ceramic heat-exchanger tubes for recovering waste heat from industrial processes, such as steel soaking pits. ORNL and B&W entered into a collaborative research agreement two years ago to refine CDV technology.

Ceramic testing system. A third recent transfer is the licensing in August of a system for measuring tensile fatigue properties of ceramics. Because it is difficult to grip and pull ceramic test specimens in a manner that distributes the stresses evenly, the source of most data on ceramic strength is bend testing, in which a specimen is bent until it fractures. However, the values



Micrograph of ceramic composite formed by chemical vapor deposition. When the ceramic is stressed, some of the stress is absorbed by the "pullout" of individual silicon carbide fibers from the silicon carbide matrix. In the central region of this sample, the fibers were bonded too tightly to the matrix and failed to pull out, so a localized fracture occurred instead.

obtained by bend testing are controlled largely by near-surface properties and flaws, rather than by internal tensile stresses. More accurate information about cyclic tensile fatigue is vital to developers of advanced ceramic engines because of its potential for causing component failure. The tensile testing system—licensed to Instron Corporation—employs eight self-aligning hydraulic pistons to distribute stresses evenly throughout test specimens.

Instron and Atlantic Richfield paid licensing fees and advance royalties for rights to the ORNL-developed technologies; the companies will continue to pay royalties based on product sales. The money will be reinvested in programs for developing and marketing other Energy Systems technologies.

Ceramics Manufacturing & Engineering Center proposed. Transfer of ORNL-developed ceramic technology would receive an added boost from a planned R&D center for ceramics manufacturing and engineering. Proposed as a joint venture by ORNL and the University of Tennessee (UT), the Ceramics Advanced Manufacturing Development and Engineering Center (CAMDEC) would serve as a national test bed for innovative manufacturing processes for advanced ceramic components. Facilities would include prototype manufacturing lines for development of highly automated manufacturing and processing techniques.

The ORNL/UT Distinguished Scientist Program would support the Center's work by adding one or more distinguished scientists with expertise in advanced ceramic processing.

The Center would be initially supported by state and federal funds through UT and the Department of Energy; eventually, however, it would be financed by a consortium of industrial companies which, in exchange for membership, would share in patents and copyrights resulting from the Center's work.—*Jon Jefferson,* Review *associate editor, and Ron Bradley, Metals and Ceramics Division.*

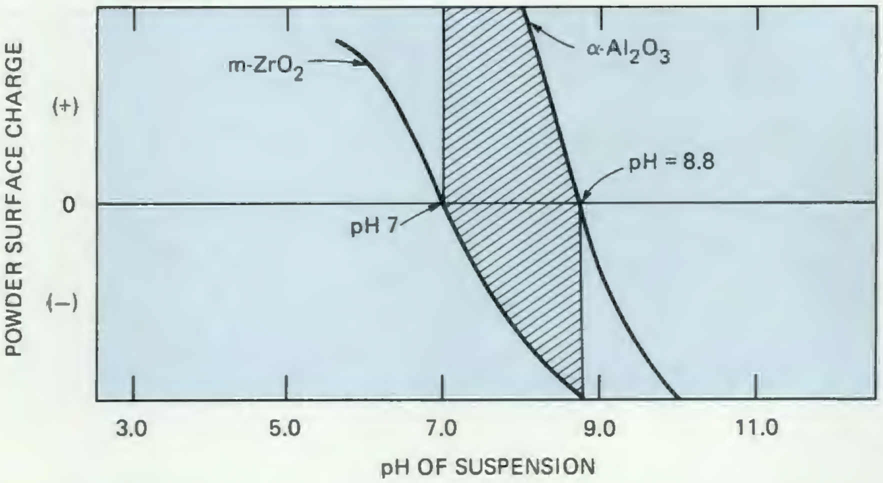


Fig. 16. Powder surface charge varies with pH. Each ceramic oxide has a unique profile. Processing of Al_2O_3-ZrO_2 composites under conditions represented by the shaded region results in extensive agglomeration between (+) Al_2O_3 and (-) ZrO_2. Both solids have a net (+) surface charge at low pH and a net (-) surface charge at high pH.

This mechanism, when applied to the dispersion of oxide particles in water, involves the introduction of a polyelectrolyte—a polymer such as polyacrylic acid that contains negative charge sites at various points along the molecular chain. When added to an oxide particle suspension, this polymer adsorbs onto the particle surface and imparts a negative charge. When sufficient amounts of this polymer are adsorbed on Al_2O_3 particles, the particles exhibit a highly negative charge in the pH range of 4 to 11 as opposed to that on the Al_2O_3 particles without the polymer (see Fig. 16). In this case, the particle surface is modified and it is the charge character of the adsorbed polymer that controls the repulsive forces between the particles. Because this approach can be used to regulate the surface charge of other oxides, it is of considerable interest in controlling the surface charge and the dispersion of two-phase systems.

The understanding and regulation of surface charge allows us to develop well-dispersed suspensions with controlled distributions of one or more phases. However, both the theoretical models and experimental studies are often based on low-solids suspensions. Such systems may not represent the interaction behavior of suspensions when they are consolidated by removal of the liquid phase. Thus, Bleier is conducting theoretical studies of the state of dispersion/interaction when the solids content is increased. These studies reveal that the electrostatic repulsion decreases significantly with increasing solids content because the surface charge on the particles is redistributed. This process can induce reagglomeration during consolidation of powders. The theoretical models allow us to identify conditions under which charge redistribution can occur and to suggest ways to appropriately control the surface charge to avoid reagglomeration.

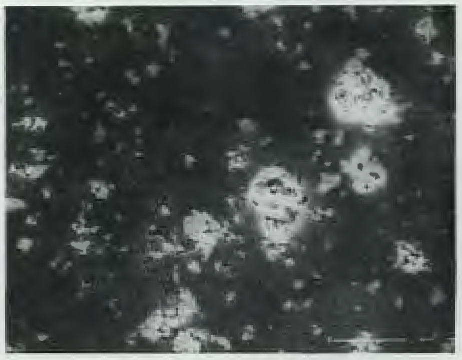


Fig. 17. Example of large agglomerates of ZrO_2 (white regions) produced in Al_2O_3-ZrO_2 two-phase composite when pH of mixed suspension is such that the surface change on the ZrO_2 is zero (pH ~ 7, see Fig. 16).

In summary, these advances in the fundamental understanding of the behavior of powder and suspensions provide us with a framework for developing principles that are useful in processing ceramic powders. For example, by characterizing the surface-charge behavior of powders and how it can be modified by adsorbed species, we can develop stable suspensions. In two-phase suspensions or those having differing particle sizes, we can account for and compensate for differential gravitational settling to design stable, uniform suspensions. Finally, by controlling surface-charge redistribution when the particles are consolidated, we can achieve uniformly and densely packed structures. As a result of our basic research, then, we can tailor the powders, the suspensions, and the consolidation process to achieve the uniform, high-density particle compacts which we desire for controlling the final microstructure that develops during heating, thus forming dense ceramics having the prescribed properties.

awards and appointments

Liane B. Russell has been elected to the National Academy of Sciences. She is the first woman from Tennessee to be so honored. She is also president-elect of the Environmental Mutagen Society.

Carl A. Burtis has received the 1986 National Lectureship Award of the American Association for Clinical Chemistry.

David E. Reichle has been named director of ORNL's Environmental Sciences Division, replacing **Stanley I. Auerbach**, who has been appointed senior staff advisor in the Environmental Sciences Division. Auerbach also has been appointed to the Executive Committee of the Science Advisory Board of the U.S. Environmental Protection Agency.

E. B. Harris has been named deputy director of the Strategic Defense Initiative Program at Martin Marietta Energy Systems, Inc.

Robert H. Gardner has received the 1985 Scientific Achievement Award of ORNL's Environmental Sciences Division.

Larry Barnthouse and **Barbara Walton** have been named members of the National Research Council's Committee on Pyrethroids and Ecological Risk Assessment.

Thomas J. Wilbanks has received the highest Honors Award of the Association of American Geographers.

W. C. (Bill) McWhorter has been named manager of the System and Equipment Maintenance Monitoring for Surface Ships Program for the Data Systems Research and Development Program of Martin Marietta Energy Systems, Inc.

The Council of the American Physical Society passed a resolution expressing gratitude to **Jack A. Harvey** for the "excellent service he has given the Society as secretary-treasurer of the Division of Nuclear Physics since its founding in 1966."

Jerry Elwood has been appointed to the Advisory Panel for Ecosystem Studies of the National Science Foundation's Division of Biotic Systems and Resources.

J. Lowell Langford has been certified for membership in the Institute of Certified Records Managers.

Edward L. Hillsman has been selected to receive a 1986 Applied Geography Project Citation Award for his paper "PARA: Population-at-Risk Analysis."

Michael Kuliasha has been named head of the Efficiency and Renewables Research Section of ORNL's Energy Division.

Gerald N. Case has received the Outstanding Technical Support to Researchers Award for 1986 from the Oak Ridge Chapter of Sigma Xi, the Scientific Research Society.

Susan Hughes, **Jeanne Dole**, and **Kathie McKeehan** have been elected president, secretary, and treasurer, respectively, of the East Tennessee Chapter of the Society for Technical Communication.

In the 1986 Battle of the Graphics Artists Competition sponsored by the Integrated Software Systems Corporation (ISSCO), seven Energy Systems employees won awards. They are **Margaret Susan Marsh**, gold, bronze, and honorable mention medals; **Morris L. Slabbekorn**, one silver, two bronze, and two honorable mention medals; **Alan R. Kerekes**, one silver medal; **Thomas R. Henry**, two honorable mention medals; **Robert Bruce Johnston**, two honorable mention medals; **LeJean M. Hardin**, honorable mention medal; and **Cynthia H. Johnson**, honorable mention medal.

David L. Greene has been named chairman of Committee A1FO1 of the Transportation Research Board of the National Research Council. This committee focuses on energy conservation and transportation demand for the 1986–1989·term.

Gene M. Goodwin has received the Airco Welding and W. H. Hobart Memorial Medal Awards of the American Welding Society. **R. K. Nanstad** also received a W. H. Hobart Memorial Medal Award.

Martin Marietta Energy Systems, Inc., honored its employees April 25, 1986, at the second annual dinner and awards presentation program at the Hyatt Regency Hotel in Knoxville. Of the 203 awards, 113 were given to ORNL employees. The inventor of the year was **Charles D. Scott**, and the author of the year was **Baha Balentekin**. Winners of other Energy Systems awards (excluding Community Service Awards) are given below.

Ten ORNL employees received Operational Performance Awards, which recognize outstanding, exemplary performance in management, business, personnel, manufacturing, and other similar functions. The winners were

Jeanette B. Berry, for project management, planning, and strategy development related to effective management and volume reduction of ORNL liquid waste streams; **Robert E. Bohanan**, for outstanding success in planning and coordinating installation of coils and equipment in the International Fusion Superconducting Magnet Test Facility, thus meeting an international commitment and DOE/Oak Ridge Operations milestone without sacrificing efficiency or quality; **Michael P. Farrell**, for managing personal computer (PC) procurement and operational essentials for DOE's China initiative to exchange PC technology for 1,000 years of weather data for the Carbon Dioxide Information Center; **William Fulkerson**, for outstanding leadership in building the Energy Division of ORNL into a national asset and a source of programmatic and financial strength for the Laboratory; **Andrew S. Loebl**, for organizing and managing the Data Systems Research and Development Program, which has become an important new initiative for Martin Marietta Energy Systems, Inc.; **Fred C. Maienschein**, for outstanding leadership in redirecting the Engineering Physics and Mathematics Division to a position of national prominence in parallel computing, intelligent machines, and human factors in reactor safety; **C. Phillip McGinnis**, for outstanding leadership of the Consolidated Edison Uranium Solidification Project (CEUSP), a program to convert a metric ton of fissile ^{233}U from a nitrate solution to an inert solid for safe, long-term storage; **George W. Oliphant**, for development and implementation of cost-effective, high-quality Plant and Equipment Division support and services to the ORNL research divisions and for guidance of a significant Laboratory Appearance Improvement Program; **Dennis C. Parzyck**, for outstanding leadership in ensuring that the Laboratory's programs in environmental monitoring, regulatory compliance, and radiation and occupational safety are being carried out in an effective and efficient manner; and **William K. Simon**, for project management and leadership in bringing the new ORNL Sewage Treatment Plant on-line and into regulatory compliance.

Twenty ORNL employees received Inventor Awards, which recognize innovative employee contributions to the activities of Energy Systems. The winners were **Jackson B. Davidson**, for invention and reduction to practice of the EIDEC Detection System for labeled molecules separated by electrophoresis or thin-layer chromatography, with improved speed, sensitivity, quantitation, and reduction of radioactivity; **Caius V. Dodd**, for the design and development of unique instruments to expand the technology of eddy currents for nondestructive inspection of various materials and structural components; **Christopher A. Foster**, for the invention of the SNAIL Cryopump, which is a cryocondensation type, high-throughput, all-metal-sealed, dry vacuum pump having a unique regeneration feature that allows it to operate continuously; **Donald M. Kroeger**, for innovative contributions to the development of microalloyed, iron-base, metallic glasses for use as core materials for electrical motors and transformers; **Robert J. Lauf**, for innovative contributions to the application of sol-gel technology to the development of improved zinc oxide varistors; **Kenneth C. Liu**, for the development and successful utilization of simplified, mechanical property test instrumentation for performing complex testing and evaluation of the behavior of metals and ceramics at elevated temperatures; **Arthur J. Moorhead**, for development of a series of filler metals that will directly braze a wide range of structural ceramics and ceramic-matrix composites for service in dirty, elevated-temperature environments; **Charles A. Mossman**, **R. L. Anderson**, **W. B. Jatko**, **D. R. McNeilly**, and **G. N. Miller**, for development of an inexpensive circuit that provides remote identification of all cables in complex electrical systems, such as power plants or safety and security systems; **John E. Mrochek**, for invention of a disc-type, four-port sampling valve for service with high-temperature, high-pressure, erosive process streams; **Horacio Perez-Blanco**, for continuing contributions to absorption heat pump technology, providing temperature-lift capability and improved efficiency while maintaining simple, workable system configurations; **Roswitha S. Ramsey** and **Richard A. Todd**, for designing the Pulsed Helium Ionization Detector Electronics System (PHIDELS) for gas chromatography; **Isidor Sauers**, for developing a technique that significantly improves by, three orders of magnitude, the sensitivity for the early detection of incipient faults in high-voltage systems insulated with compressed sulfur hexafluoride gas; **Charles D. Scott**, for the invention of a new class of immobilized biocatalysts containing microorganisms or enzymes in monodispersed beads that can be used in advanced bioreactor systems; **Robert J. Warmack** and **T. L. Ferrell**, for development of a unique microlithography technique for producing the best surfaces known for surface-enhanced Raman spectroscopy and many other applications.

Twenty-two ORNL employees received Technical Achievement Awards, which recognize the excellence of employee contributions of a scientific or engineering nature to the activities of Energy Systems. The winners were **Richard D. Cheverton**, for development and verification of fracture analysis methods used in assessing light-water reactor pressure vessel integrity under accident conditions; **Lynn D. Chitwood**, for outstanding technical support of nondestructive testing advancement through the development and field demonstration of eddy-current testing equipment; **John A. Clinard**, for outstanding contributions to the Large Coil Program through very large-scale, state-of-the-art structural analyses of the International Fusion Superconducting Magnet Test Facility; **Stephen K. Combs**, for outstanding contributions in the development, installation, and operation of an advanced plasma fueling device for the Tokamak Fusion Test Reactor; **Robert N. Compton**, for development of accelerator-based autodetachment spectroscopy for the study of metastable negative ions and for subsequent use of the technique in fundamental studies of "exotic" atomic and molecular ions and "particle beam" neutralization; **Elias Greenbaum**, for discovering that colloidal platinum precipitated onto the surface of thylakoid membranes interacts directly with the chlorophyll-driven photosystem I; **Dale W. Johnson**, for outstanding research on the role of biogeochemical cycling of forest nutrients and forest productivity in both natural and disturbed forest ecosystems; the late **Wallace C. Koehler**, for extensive innovative applications of neutron-scattering techniques in obtaining an understanding of many physical properties of materials and for administration of the NSF-DOE-ORNL National Center for Small-Angle Scattering Research. **Francis C. Kornegay**, for development of a real-time atmospheric dispersion modeling capability for Energy Systems facilities, which is important for predicting transport of airborne pollutants and evaluating ground-level concentrations; **Manfred O. Krause**, for continuing excellence in developing the photoelectric effect as a sensitive and specific probe of the electronic structure and dynamics of atoms; **James M. Leitnaker**, for innovative, significant, continuing contributions to the maintenance of barrier separative efficiency, operational safety, and improved system performance of the gaseous diffusion plants; **Steven E. Lindberg**, for quantifying the importance of dry atmospheric deposition of airborne contaminants and nutrients to forest vegetation and their influence on biogeochemical cycles within the forest; **Robert W. McClung**, for his major contribution in the repair of a multimillion-dollar, spacecraft, radioisotope-powered, thermelectric generator that contained several materials developed and fabricated at ORNL; **Carl J. McHargue**, for outstanding original research on the modification of the surface properties of ceramics by ion beams; **Sankar Mitra**, for outstanding contributions to the regulation and characterization of a protein that mediates the repair of chemically damaged DNA; **Masanori Murakami**, for outstanding contributions toward the international understanding of plasma confinement in tokamak devices; **Mark Rasolt**, for significant contributions to the theory of pulsed-laser annealing, the critical behavior of dilute Bose fluids, and the fractional quantum Hall effect; **Vinod K. Sikka**, for developing and advancing the commercialization of a new chromium-molybdenum (9 Cr:1 Mo) steel and advanced aluminide intermetallic alloys and for vigorous leadership in bringing the new Steel Initiative Program to ORNL; **G. Pedro Smith, Jr.**, for outstanding career contributions to the experimental determination of chemical structure and reactivity in molten-salt media; **G. Malcolm Stocks**, for outstanding, sustained, and innovative contributions to the development of a first principles theory to provide a microscopic understanding of the physical and metallurgical properties of metallic alloys; **Tuan Vo-Dinh**, for development of the simple, cost-effective, synchronous luminescence technique for screening important bioindicators—carcinogen-DNA interactions—in biological samples; **Alan J. Witten**, for advancing the state of the art in subsurface characterization methodology through the development of acoustical imaging techniques for both geophysical and medical applications.

ORNL employees received 58 Publication Awards, which recognize superior employee performance in the authorship of a paper, technical article, or book that represents a significant advance in the author's professional field. The winners were **B. K. Annis, R. L. Hahn,** and **A. H. Narten** for "Hydration of the Dy^{3+} Ion in Dysprosium Chloride Solutions Determined by Neutron Diffraction"; **T. C. Awes, R. L. Ferguson, F. E. Obenshain, F. Plasil,** and **G. R. Young**, for "Fission Decay of Reaction Products with $A \sim 150$"; **C. Baktash, I. Y. Lee, F. K.**

McGowan, **N. R. Johnson**, **M. L. Halbert**, and **D. C. Hensley**, for "Quasivibrational Bands at High Spins in Ytterbium-158"; **A. B. Balantekin**, **C. Bottcher**, and **M. R. Strayer**, for "Production of New Particles in Heavy-Ion Collisions"; **J. R. Beene**, for "Direct and Compound Gamma Decay of the Giant Quadrupole Resonance of Lead-208"; **W. H. Butler**, for "Theory of Electronic Transport in Random Alloys: Korringa-Kohn-Rostoker Coherent-Potential Approximation"; **J. F. Cooke**, for "New Interpretation of Spin-Wave Behavior in Nickel"; **C. C. Coutant**, for "Striped Bass, Temperature, and Dissolved Oxygen: A Speculative Hypothesis for Environmental Risk"; **H. L. Davis** and **J. R. Noonan**, for "Rippled Relaxation in the (110) Surface of the Ordered Metallic Alloy Nickel Aluminide (NiAl)"; **D. L. DeAngelis** and **W. M. Post**, for "The Influence of Naticid Predation on Evolutionary Strategies of Bivalve Prey: Conclusions from a Model"; **J. H. DeVan**, "A Perspective of the Corrosion Behavior of Lithium and Sodium"; **L. Garcia** and **B. A. Carreras**, for "Theory of Resistivity-Gradient-Driven Turbulence"; **G. S. Hurst**, **M. G. Payne**, **S. D. Kramer**, **C. H. Chen**, **R. C. Phillips**, **S. L. Allman**, **G. D. Alton**, and **J. W. T. Dabbs** for "Method for Counting Noble Gas Atoms with Isotopic Selectivity"; **J. Kao** and **J. Hall**, for "Skin Penetration and Metabolism of Topically Applied Chemicals in Six Mammalian Species, Including Man: An In Vitro Study with Benzo[*a*]pyrene and Testosterone"; **S. J. Kennel** and **P. K. Lankford**, for "Factors Affecting Passive Monoclonal Antibody Therapy of Moloney Sarcoma in BALB/c Mice"; **E. A. Lazarus**, for "Confinement in Beam-Heated Plasmas: The Effects of Low-Z Impurities"; **E. H. Lee** and **L. K. Mansur**, for "Evidence for a Mechanism of Swelling Variation with Composition in Irradiated Fe-Cr-Ni Alloys"; **S. H. Liu**, for "Fractal Model for the ac Response of a Rough Interface"; **R. E. Maerker** and **B. L. Broadhead**, for "Theory of a New Unfolding Procedure in Pressurized-Water Reactor Pressure Vessel Dosimetry and Development of an Associated Benchmark Data Base"; **S. B. McLaughlin**, for "Effects of Air Pollution on Forests: A Critical Review"; **D. G. Morris**, **C. B. Mullins**, and **G. L. Yoder, Jr.**, for "An Experimental Study of Rod Bundle Dispersed-Flow Film Boiling with High-Pressure Water"; **S. J. Pennycook**, for "Atom Location by Axial-Electron-Channeling Analysis"; **R. A. Popp** and **D. M. Popp**, for "Hematology of a Murine β-Thalassemia: A Longitudinal Study"; **J. H. Smith**, **C. V. Dodd**, and **L. D. Chitwood**, for "Multifrequency Eddy-Current Examination of Seam Weld in Steel Sheath"; **H. R. Witschi** and **R. C. Lindenschmidt**, for "The Many Faces of an Increase in Lung Collagen."

Douglas H. Lowndes has been named a member of the University Research Instrumentation Review Panel of the Department of Energy.

T. B. Lindemer has been named trustee of the Nuclear Division of the American Ceramic Society.

Carolyn Hunsaker has been appointed to the advisory board of the *Environmental Professional*, the journal of the National Association of Environmental Professionals.

Phil McGinnis has been appointed manager of the new Hazardous Waste Technology Program, which is part of ORNL's Waste Management R&D Programs. He also has been named Engineer of the Year by the Knoxville-Oak Ridge Chapter of the American Institute of Chemical Engineers.

John R. Noonan is chairman of the Publications Committee of the American Vacuum Society.

Ada L. Olins served as co-chairman (with **D. E. Olins**) of the Gordon Conference on Chromatin for 1986 and is serving on the Porgram Committee of the Electron Microscopy Society of America.

John B. Bates served as co-chairman of the Gordon Research Conference on Solid State Ionics for 1986.

G. N. Case has received the 1986 Outstanding Technical Support to Researchers Award from the Oak Ridge Chapter of Sigma Xi.

E. D. Collins has been named chairman-elect of the Knoxville-Oak Ridge Chapter of the American Institute of Chemical Engineers.

H. W. Godbee has been elected chairman of the Standards Working Group 16.6 of the American Nuclear Society. The group is concerned with the standard leach test for low-level radioactive waste.

Bill R. Rodgers is chairman of the Program Committee, Fuels and Petrochemicals, of the American Institute of Chemical Engineers.

Gary Sega is a member of the editorial board of *Environmental Mutagenesis.*

G. W. Strandberg has been appointed adjunct associate professor in the Department of Microbiology of the University of Tennessee, Knoxville.

J. L. Wendelken served as chairman of the Sixth Annual

Symposium of the Tennessee Valley Chapter of the American Vacuum Society.

Bob Wham is treasurer of the Oak Ridge–Knoxville Section of the American Institute of Chemical Engineers.

Susan Whatley is governor for the American Association of Engineering Societies.

H. R. Witschi has been named to the Complex Mixtures Committee of the Commission of Life Sciences of the National Research Council.

Dick Wood served as co-organizer of the Symposium on Excimer Laser Applications to Materials Processing, Fiber Laser '86 SPIE Conference in Cambridge, Massachusetts.

Curtis C. Travis has been appointed to the Food and Drug Administration Science Advisory Board.

The East Tennessee Chapter of the Association for Women in Science (AWIS) presented its first annual science achievement award to **Dorothy Skinner** for her research in developmental biology and genetics and a service award to **Mary Francis** for her service to AWIS.

Jerry W. Elwood has been named a member of the Advisory Panel for the Ecosystem Studies Program in the Division of Biotic Systems and Resources of the National Science Foundation.

Robert J. Luxmoore has been named to the editorial review board of *Tree Physiology*, a new journal dealing with theoretical and experimental research on woody species.

V. R. Tolbert and **James F. McBrayer** were recently recognized by the American Society of Surface Mining and Reclamation for "their dedicated service and professional insights in establishing the society's directory of members."

Ernest G. Silver has been appointed technical program chairman of the joint international meeting of the American Nuclear Society and the European Nuclear Society to be held in 1988 in Washington, D.C.

Dr. Daniel E. Conrad has been named medical director for Martin Marietta Energy Systems, Inc.

Lance J. Mezga has been appointed manager of a new Waste Management Coordination Office established by Martin Marietta Energy Systems, Inc.

William R. Hamel has been named chairman of the newly formed ORNL Robotics and Automation Council. The council will serve as a "technology clearinghouse" for ORNL, identifying opportunities for collaborative research with industry and universities and facilitating technology transfer to the commercial sector.

David Cole has been appointed associate editor of the *Journal of Geochemical Exploration.*

Gene M. Goodwin and **Joseph D. Hudson** have received the Airco Welding Award from the American Welding Society for their achievements in joining materials.

J. A. Horton and **E. A. Kenik** received first prizes in the electron microscopy class in the 1986 International Metallographic Exhibit sponsored by the International Metallographic Society and the American Society for Metals.

In ORNL's Solid State Division **Ralph M. Moon** has been named head of the Neutron Scattering Section and **James B. Roberto** has been named head of the Particle-Solid Interactions Section.

Johnnie Cannon has been named head of the Integrated Analysis and Assessment Section of ORNL's Energy Division, relacing **Bud Zittel**, who has retired.

The Physics Division now has two sections for experimental nuclear physics. Section heads are **Frank Plasil** (Nuclear Reactions) and **Fred Bertrand** (Nuclear Structure).

Michael S. Blair, **Tuan Vo-Dinh**, and **E. Jonathan Soderstrom** have received a Special Award for Excellence in Technology Transfer from the Federal Laboratory Consortium for Technology Transfer. The award was given for noteworthy contributions toward the commercialization of the fiber-optics luminoscope through a licensing agreement with Environmental Systems Corporation of Knoxville.

C. T. Liu, **Anthony Schaffhauser**, **Vinok Sikka**, and **E. Jonathan Soderstrom** have received a Special Award for Excellence in Technology Transfer from the Federal Laboratory Consortium for Technology Transfer. The award was given for noteworthy contributions toward the commercialization of nickel aluminide alloys through a licensing agreement with Cummins Engine Company.

Although activities classified as basic research in ceramics have attracted public attention, the other side of the coin, namely "ceramics in basic research," is often overlooked. One specific example of the important role that ceramics can play in solving basic research problems is the spectroscopic investigation of actinide ions that has long been carried out in ORNL's Solid State Division. Using electron paramagnetic resonance spectroscopy, ORNL researchers have determined the nuclear spins of several actinides.

Marvin Abraham (left) and Lynn Boatner check research results.

Ceramics in Basic Research

By LYNN A. BOATNER and MARVIN M. ABRAHAM

Ceramic materials are the subject of intensive research in numerous scientific laboratories in the United States and abroad. Fundamental studies of the basic properties of ceramic materials are aimed at understanding and ultimately tailoring them to reduce their brittleness. On the practical side, researchers eventually hope to develop new ceramic materials that can be used for structural applications in high-temperature and other hostile environments (e.g., components of highly efficient jet and automotive engines), in medical technology (e.g., prosthetic devices like artificial hip and knee joints), and in diverse high-technology areas (e.g., the packaging of semiconductor devices). Examples of some of the ongoing efforts at Oak Ridge National Laboratory in this topical field of "basic research in ceramics" are discussed in the preceding article.

Although activities classified as basic research in ceramics have attracted public attention, the other side of the coin, namely "ceramics *in* basic research," is often overlooked. One specific example of the important role that ceramics can play in solving basic research problems is the spectroscopic investigation of actinide ions that we have been carrying out for a number of years in ORNL's Solid State Division.

Actinides include the man-made elements heavier than uranium; in the actinide series, the inner 5*f* electron shell is progressively filled after the outer 7*s* shell has been filled and the 6*d* shell has begun to fill. We have applied the technique of electron paramagnetic resonance (EPR) spectroscopy (see sidebar) to basic studies of both the electronic and nuclear properties of actinide elements and the effects of the electric fields of ceramic crystals on these properties. Using this technique, we have determined the nuclear spins of several actinides.

Ceramic materials in the form of single crystals (or, in some cases, polycrystalline powders) have been critical to the success of these spectroscopic investigations by providing a stable medium in which the subject actinide ions could be isolated by adding them in the form of dilute impurities. Actinides doped into host ceramic single crystals in low concentrations (i.e., less than 1 at.%) can be studied with respect to the effects of the

Lynn Boatner has been the leader of the Research Materials Group in ORNL's Solid State Division since 1977. His research and development efforts at ORNL have been recognized in the form of an I•R 100 award in 1982 (shared with Marvin Abraham) and three more recent awards (shared with Brian Sales), including a DOE Materials Sciences Research Competition Award in 1984, a second I•R 100 award in 1985, and an award from *Science Digest* for one of the "100 most significant technological achievements in 1984–1985." The recipient of a Ph.D. degree in physics from Vanderbilt University, Boatner is a Fellow of the American Physical Society and an associate editor of *Materials Letters*. His research interests have centered on the Jahn-Teller effect, the application of crystalline ceramics and glasses to nuclear waste disposal, and electron paramagnetic resonance studies of actinide ions (described in the following article).

Marvin M. Abraham is a senior research staff member in ORNL's Solid State Division. He holds three degrees in physics, including a Ph.D. degree from the University of California at Berkeley. From 1958 through 1960 he was a Fulbright Fellow at Oxford University, where he studied at the Clarendon Laboratory. Before coming to ORNL in 1963, he worked at the Department of Energy's Lawrence Berkeley Laboratory and at the Institute of Physics in San Carlos de Bariloche, Argentina, on an International Atomic Energy Agency fellowship. At ORNL he has been co-recipient of two I•R 100 awards, one in 1975 with Yok Chen for growing single crystals of alkaline-earth oxides and one in 1982 with Boatner for developing a monazite process for stabilizing high-level radioactive waste. He helped organize a 1977 international conference on crystal defects and a 1980 DOE workshop on alternative nuclear waste forms. Abraham has served as a traveling lecturer for Oak Ridge Associated Universities. He is a Fellow of both the American Physical Society and the American Ceramic Society.

crystalline electric field on the electronic properties of the actinide $5f^{\,n}$ electronic configurations and can provide information concerning the coupling between the spins (i.e., magnetic dipole-dipole interactions) of the electrons and nucleus of each ion. These magnetic dipole interactions are responsible for the so-called "magnetic hyperfine" structure effects that are manifested as small splittings of the electronic energy levels. The purpose of diluting and isolating the actinide (or other paramagnetic) ions in a ceramic host crystal is to minimize cooperative effects such as spin-spin and exchange interactions that occur only when paramagnetic species (e.g., ions with unpaired electrons) are close together. Such cooperative effects lead to a loss of resolution in the electronic absorption spectra.

Early EPR Observations

EPR investigations of actinide ions at ORNL were initiated in 1963 by Marvin Abraham, who had joined the Solid State Division following postdoctoral research at Lawrence Berkeley Laboratory (LBL). While at Berkeley, Abraham had carried out EPR studies of actinide elements and performed the first magnetic resonance observation of curium (Cm, or element 96); in this work, he verified that Cm^{3+} had the $5f^{\,7}$ configuration and, therefore, was a half-filled shell; in other words, the $5f$ shell had 7 electrons, not its full complement of 14. Abraham began planning similar studies after arriving at ORNL and, in fact, the first experimental work to emerge from ORNL's Transuranic Research Laboratory (TRL) shortly after it opened in 1967 was an EPR study of Cm^{3+} diluted in the ceramic host crystals thorium oxide and cerium oxide.

Cabell Finch and Wayne Clark of ORNL's Metals and Ceramics Division collaborated with Abraham on these early EPR investigations of the actinides by growing the highly refractory ceramic host single crystals using a flux technique. (This and other techniques for the growth of refractory single crystals are discussed in an article by Lynn Boatner in the Fall 1983 issue of the ORNL *Review*.) In the case of Cm^{3+} in ThO_2, an extra unidentified EPR absorption was found, and speculation was that this absorption (i.e., electronic transition) was caused by the isotope plutonium-240 (^{240}Pu) that could be introduced as a decay product of ^{244}Cm. Additional crystals doped with the "odd" isotope ^{239}Pu were grown by Finch. Lynn Boatner and Bob Reynolds (at this time a graduate student from Vanderbilt University) joined Abraham in showing that the extra resonance was, indeed, caused by trivalent plutonium—that is, plutonium having five electrons in its *f*-electron shell. These researchers went on to study crystal-field effects on the $5f^5$ Pu^{3+} ion in strontium chloride ($SrCl_2$)—a host that is structurally similar to ThO_2. During this period they also made the first observation by EPR of the tetravalent state of americium (five electrons in the *f*-electron shell) by diluting both ^{241}Am and ^{243}Am in ThO_2 host crystals.

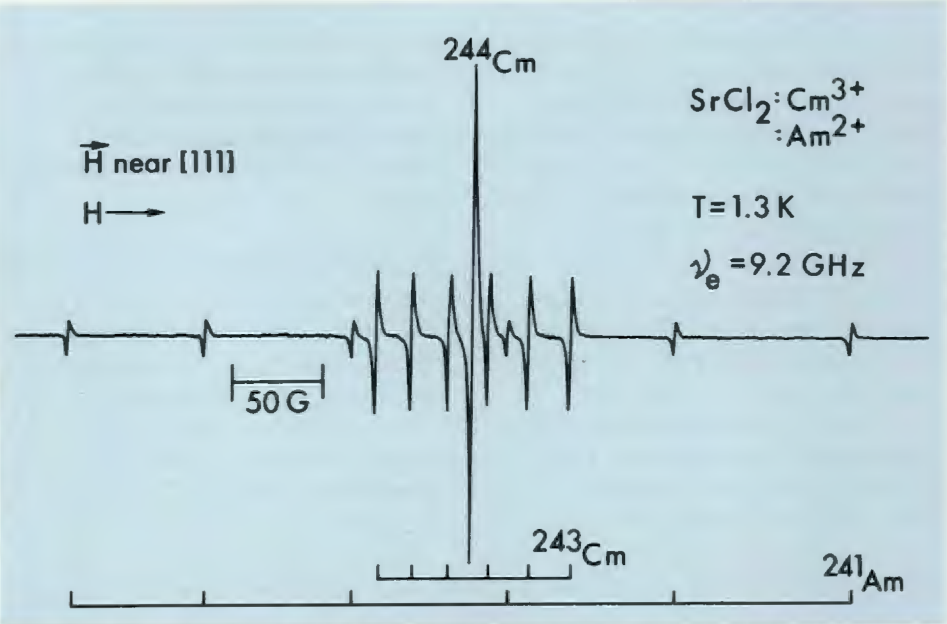


Fig. 1. Hyperfine patterns in EPR spectroscopy can provide a distinctive fingerprint of paramagnetic elements. In the case of rare isotopes such as those of some actinide elements, the observation of a hyperfine pattern in conjunction with a known resonance of another isotope of the same element can be used to determine the nuclear spin of the so-called odd isotope responsible for the hyperfine spectrum. (An odd isotope has an odd number of protons or neutrons. An even-even nucleus, on the other hand, has an even number of protons and an even number of neutrons and does not exhibit hyperfine structure in its EPR spectrum.) This figure shows a single intense line caused by the even isotope ^{244}Cm, which is flanked by a less intense 6-line hyperfine pattern caused by ^{243}Cm, whose nuclear spin is 5/2. A weaker six-line hyperfine pattern caused by ^{241}Am is also present. The spectrum is shown as a first derivative of absorption vs magnetic field.

Measuring Nuclear Spin

The nuclear spin of paramagnetic isotopes can be determined from EPR observations of the associated hyperfine structure. Coupling between the nuclear and electronic spins results in a characteristic spectrum in which each electronic transition is split into 2 I + 1 components,

Electron Paramagnetic Resonance Spectroscopy

Paramagnetism arises from the orbital and spin angular momentum of electrons. While one might expect all free atoms (unless their electrons form closed shells) to exhibit paramagnetism, most solids are not paramagnetic because their outer electrons, which are not in closed shells, interact strongly with each other to form bonds, or else they have important collective properties (as in metals). If the unpaired electrons belong to incomplete inner shells, however, the interaction with the surroundings is not as strong and paramagnetism may be exhibited. Paramagnetism may be considered as "weak magnetism" in contrast to the "strong magnetism" characteristic of ferromagnets.

To observe paramagnetic resonance absorption, we first incorporate the paramagnetic ions into a suitable crystal (magnetically dilute, to minimize spin-spin and exchange interactions). We then apply a steady, external magnetic field of a few kilogauss, causing the electronic energy levels to separate (an effect known as Zeeman splitting). Transitions (i.e., changes from one electronic state to another) are then induced between the Zeeman split levels by a small magnetic field oscillating at microwave frequencies. Because the probability for induced absorption and emission is the same, a difference in the population of the initial and final states is necessary to detect a net absorption of energy.

If the spin system is in thermal equilibrium with its environment, there will be a surplus population in the lower state in accordance with the Boltzmann factor, and a net microwave energy absorption is detectable. The excited spins "relax" by flipping down to the lower energy state and giving up energy to the lattice in a characteristic time called the spin-lattice relaxation time.

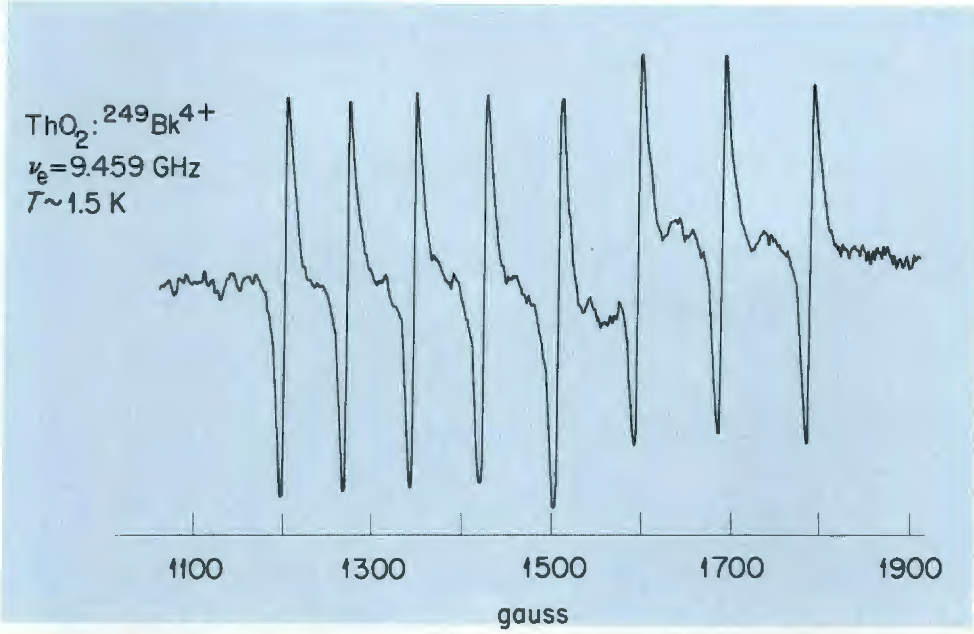


Fig. 2. A typical EPR spectrum obtained for a very nontypical ion—tetravalent berkelium. The spectrum is presented as a first derivative of the absorption vs applied magnetic field. The eight-line hyperfine pattern is the result of coupling with the $I=7/2$ nuclear spin of ${}^{249}Bk$.

where I is the nuclear spin and the total spread of this "hyperfine pattern" is proportional to the nuclear magnetic moment. Along with Reynolds, we used these spectroscopic features to make the first experimental determination of the nuclear spin ($I=7/2$) of the isotope ${}^{245}Cm$, again using $SrCl_2$ crystals grown by Finch. As luck would have it, these samples having a fluorite structure were intentionally doped with ${}^{244}Cm$ containing a very small amount of ${}^{245}Cm$, thus enabling us to make the nuclear spin measurement. Encouraged by this success, our team and W. P. Unruh, a visiting scientist from the University of Kansas, obtained the isotopes ${}^{243}Cm$ and ${}^{247}Cm$ and employed EPR spectroscopy in making the first direct measurements of their nuclear spins ($I=5/2$ and $I=9/2$, respectively). See Fig. 1. Again, a ceramic insulating host crystal grown by Finch was employed as the medium for diluting the actinide isotopes so that EPR spectroscopy could be used.

Our experiments continued to move up the periodic table and, in 1972, we used "Finch-grown" ThO_2 single crystals to make the first (and to this point, only) EPR observation of berkelium (Bk, or element 97). We observed that ${}^{249}Bk$ in the ThO_2 host is in the tetravalent state, confirmed that the nuclear spin of ${}^{249}Bk$ is $I=7/2$, and estimated the nuclear magnetic moment of this isotope. Our work also showed that tetravalent berkelium, which corresponds to a half-filled shell in the actinide series, is stable in the solid state in the oxide host (see Fig. 2).

By 1976 the ORNL team had used the EPR technique to study actinides up to element 99 (einsteinium-253, or ${}^{253}Es$), and our spectroscopic results showed that divalent einsteinium had the electronic configuration $5f^{11}$. Unfortunately, we were not the first to observe ${}^{253}Es^{2+}$ by EPR spectroscopy. We were "scooped" in this case by LBL's Norman Edelstein, who had used EPR to study einsteinium diluted in the fluorite-structure host crystal calcium fluoride (CaF_2).

In general, however, a close cooperative relationship has existed between ORNL's EPR spectroscopists and the actinide group headed by Edelstein. In fact, many of the samples investigated by EPR techniques at Oak Ridge have subsequently been studied at Berkeley using high resolution optical transmission spectroscopy. The complementary nature of EPR and the optical techniques usually employed by Edelstein has resulted in a much clearer picture of the electronic properties of the actinide ions and the alteration of these properties by crystal-field effects.

Clearly, the study of actinide elements by EPR and other spectroscopic techniques is a highly specialized and somewhat esoteric field. These man-made elements are often produced in only minute quantities and represent the output of significant expenditures of human and monetary resources. Additionally, because these transuranium elements are radioactive, only facilities that are appropriately equipped can be used in studying their properties (see Figs. 3 and 4). Fortunately, for the EPR spectroscopists at ORNL, the heavier actinides are produced in a Laboratory facility designed specifically for this purpose—the High Flux Isotope Reactor (HFIR). The actinide isotopes resulting from irradiations in the HFIR core assembly are processed and separated in the Transuranium Processing Plant (TRU) at ORNL and are then made available in a pure, isolated form for researchers at ORNL and elsewhere. Obviously, behind every actinide study, spectroscopic or otherwise, lies a long line of support facilities and

Fig. 3. A platinum crucible is removed from a high-temperature furnace in ORNL's Transuranium Research Laboratory. The crucible contains actinide-doped single crystals that have formed in a molten flux.

Fig. 4. Cabell Finch works in a controlled-atmosphere glove box where actinide-doped single crystals are grown.

personnel. Without the contributions of John Bigelow of TRU and ORNL health physicists Bill Carden (TRL), L. C. Johnson, and Ray Cooper, work of this type would simply not be possible.

Nuclear-Waste Application

In spite of the fundamental nature of much of the information obtained by investigating actinide ions as dilute impurities in ceramic hosts, work of this type has a practical side. Some of the actinides are produced in significant amounts in nuclear reactor fuels during the operation of nuclear reactors. Consequently, actinides constitute a significant part of the radioactive waste material that eventually must be permanently isolated. Much of the basic information obtained throughout the course of ORNL's EPR studies of actinides was applied to the characterization of polycrystalline ceramic nuclear waste forms that are potential candidates for the disposal of radioactive actinide wastes. In particular, we have studied the properties of elements such as neptunium, plutonium, and curium in lanthanide orthophosphate ceramics (i.e., synthetic monazites).

We hope someday to carry out EPR studies of fermium-257 (element 100), which has an 80-day half-life, or mendelevium-258 (element 101), which has a half-life of about 54 days. Again, one prospect of such work would be the opportunity to directly determine the nuclear spins of these isotopes through their hyperfine structure.

We are still using EPR techniques to study the basic properties of actinides as dilute impurities in ceramic hosts and, most recently, have observed excited-state resonances of the trivalent curium ion in a refractory oxide, lutetium orthophosphate. We have used these results to predict the position of other energy levels, and these predictions have recently been verified by optical measurements performed by Edelstein and his LBL collaborators. In all of this work, the fundamental properties of the insulating ceramics used as host media for the incorporation of the actinide ion of interest are critical to the success of the experiments, thereby providing only one small example (albeit an unusual one) of the role of ceramics in basic research.

Alex Zucker has been ORNL's Associate Director for Physical Sciences since 1973. He came to ORNL in 1950 after earning a Ph.D. degree in nuclear physics from Yale University. From 1960 to 1970 he served as associate director of the Electronuclear Division (now part of the Physics Division). He was Ford Professor of Physics at the University of Tennessee from 1968 through 1972. From 1970 to 1972 he was executive director of the Environmental Science Board of the National Academy of Sciences in Washington. From 1972 to 1974, he was director of ORNL's Heavy-Ion Accelerator Project. He is a member of the American Physical Society Panel on Public Affairs, the White House Steel Industry/National Laboratories Initiative, and the Council on Energy Engineering Research of the U.S. Department of Energy. He has served on a number of committees for DOE, the National Research Council, and the Congressional Office of Technology Assessment. He was a member of the editorial board of *Science*, the National Academy of Sciences Nuclear Physics Delegation to the People's Republic of China, and the the U.S. delegation to the U.S.S.R. on peaceful uses of atomic energy. In 1966–1967 he spent a year at the Rutherford Laboratory in England as a John Simon Guggenheim Fellow and Fulbright-Hays Research Scholar. He is a Fellow of the American Association for the Advancement of Science and the American Physical Society.

Users, Users Everywhere

By ALEX ZUCKER

Some of our best things we give away.

I am speaking about the neutrons, ions (light or heavy), photons, electrons, and positrons available at the user facilities of Oak Ridge National Laboratory. In 1985, 400 scientists came to ORNL to use the seven physical sciences user facilities. Next year we are adding three more: the High-Temperature Materials Laboratory, the Low-Temperature Neutron Irradiation Facility, and the Ceramic Powder Characterization Laboratory. All this activity is part of a deliberate plan to make the large or unique facilities at ORNL available to the academic and industrial scientific communities. The Laboratory holds these installations in trust for the country's scientists and has the responsibility of providing to these individuals not only access to various instruments, but also professional help and guidance, logistic support and computers large and small, and more often than not assistance in housing and transportation.

Users normally begin by collaborating with Laboratory staff members on research projects of mutual interest. In this way users get to know the facility, find out

The Holifield Heavy-Ion Research Facility is the nation's premier facility in heavy-ion nuclear physics.

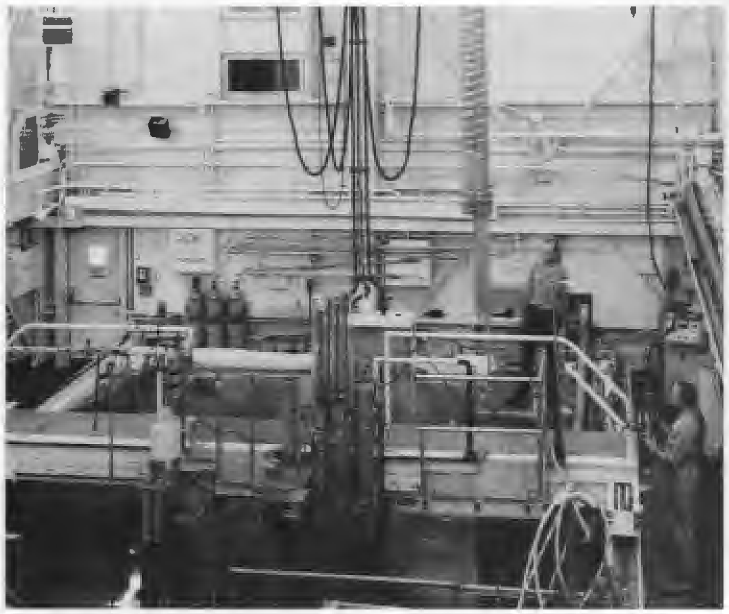
ORNL's user facilities for the physical sciences are a national resource. They provide the nation's scientists with access to valuable instruments, professional guidance, and logistic support. In return for using ORNL's accelerators, lasers, electron microscopes, and reactor-neutron-scattering apparatuses, some 400 outside scientists each year offer ORNL researchers fresh ideas and new opportunities for collaboration, and some institutions from which the users come provide financial support.

what kind of support they can expect, who is helpful, and what is expected of them. Many users remain in this collaborative mode forever, but others eventually graduate to what we call freestanding users. Users often appear as a team: a senior investigator, perhaps a postdoctoral candidate, and some graduate students. It is not uncommon for the postdoc or a graduate student to be in residence at the Laboratory for a year and thus become a de facto staff member. The rest of the team may come back to the Laboratory three or four times a year, but the resident member of the team is responsible for most of the on-site preparation. In yet another category is the industrial user who wants to do proprietary work at a facility. Although a freestanding user, this individual is not obliged to divulge research plans or results. Beyond ensuring the safety of personnel and the integrity of the facility, ORNL asks no questions. In return the proprietary user must pay full cost recovery for the facility, whereas the service is free to others.

User facilities vary in size, number of users, and the amount of formality required for obtaining time. The most popular facilities, the Holifield Heavy-Ion Research Facility and the National Center for Small-Angle Scattering Research, each serve over 100 users annually. They have their own user organizations, develop their own bylaws, and elect officers. Because the pressure for time is high, both of these facilities require outside review and approval for proposed experiments, and time is assigned in a formal way. At Holifield, for example, about one-third of the proposed experiments fail to receive accelerator time. The High Flux Isotope Reactor user operation also has a user organization and is just now beginning to require outside review of proposed research.

The smaller user centers have less formal arrangements. Approval for an experiment is given by the manager of the facility, who in turn

Electron microscopes at the Shared Research Equipment facility in ORNL's Metals and Ceramics Division.



Researchers C. E. Klabunde and H. D. Atkins guide the new Low-Temperature Neutron Irradiation Facility irradiation cryostat to its baptism in the Bulk Shielding Reactor pool. See the discussion of this development on page 102.

Wally Koehler (who died early in 1986) was the driving force behind the establishment of the National Center for Small-Angle Scattering Research at ORNL. The new director of the center is George Wignall (right). In the background is the Small-Angle Neutron-Scattering Facility.

Steve Withrow checks equipment at the Surface Modification and Characterization Collaborative Research Center, which has been responsible for the development of a wear-resistant hip-joint replacement, prototypes of which are now being tested by Johnson & Johnson.

may wish to seek outside advice. Also, in these facilities the collaborative mode of operation is pretty much the rule. Time assignment is flexible and informal.

Now for a lightning tour of the user facilities. What are they, what do they do, and who uses them?

The Holifield Heavy-Ion Research Facility is currently the nation's premier facility in heavy-ion nuclear physics. It consists of a 25-MV tandem accelerator coupled to an isochronous cyclotron. It produces heavy-ion beams of 54 elements having energies ranging from 25 MeV/amu down to 3 MeV/amu for the heaviest elements. Holifield is a very lively place, in part because of its excellent research facilities and in part because of its two buildings set aside exclusively for user activities. One of these buildings was, in fact, funded by the State of Tennessee expressly for this function. The user research at Holifield deals with the structure of very high-spin nuclei, the reaction mechanisms following the collision of heavy nuclei, and the production of nuclei far from the stability line.

The High Flux Isotope Reactor supports two separate user operations. One is the National Center for Small-Angle Scattering Research whose operation is funded by the National Science Foundation. Because it is by far the most powerful facility for small-angle neutron scattering in the United States, it attracts a large number of polymer scientists from industry and universities. Some biology and materials science research is also performed there. The popularity of the instrument is enormous; there is currently a four-month waiting time to get on the machine. It is also our most user-friendly facility. We have five full-time people whose primary job is to support the users.

Construction was completed on the High-Temperature Materials Laboratory in 1986.

The other user operation on the High Flux Isotope Reactor is the Neutron Scattering Facility, which is funded by the Department of Energy's Materials Sciences Division. It too is heavily booked, but because its experiments are usually longer and more complex than the small-angle ones, the limited number of instruments holds down the number of users. The most popular instruments are triple-axis spectrometers, together with their ancillary equipment such as superconducting solenoids and low-temperature target chambers. The research deals with a wide variety of solid-state physics, but magnetism and rare-earth compounds are perhaps the most prominent areas of research. The neutron-scattering facilities attract scientists from all over the world. A formal agreement now exists between the United States and Japan whereby Japanese scientists have underwritten some instruments in return for significant amounts of time for research. This bilateral exchange agreement has worked to the benefit of both parties. It runs smoothly and has produced much valuable scientific information.

The Surface Modification and Characterization Collaborative Research Center centers around two accelerators and two ion implanters. The surfaces to be modified are implanted with various ions, then perhaps laser annealed or treated in other ways while the accelerator-produced beams are used to diagnose the surface by channeling or Rutherford backscattering. This laboratory has enabled users to prepare surface and near-surface regions to give them unique physical properties of potential use for the semiconductor industry. Other properties can also be altered; for example, resistance to wear and corrosion can be greatly enhanced by ion implantation. One

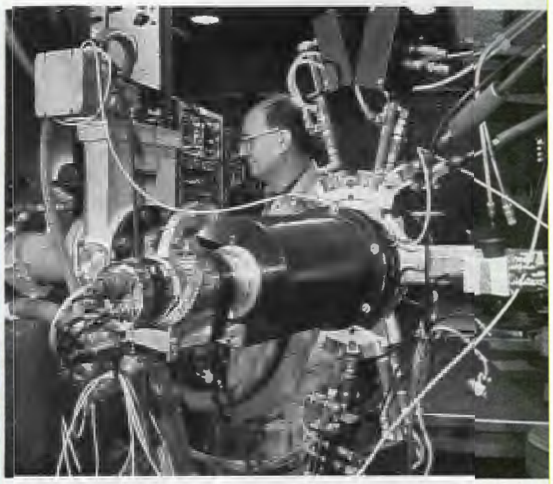
Information on ORNL user facilities is available in these brochures.

highly visible result in the last few years has been the development of a wear-resistant hip-joint replacement that resulted from the collaboration between scientists from the University of Alabama and ORNL.

The Shared Research Equipment facility is a user facility of a different order. It is not centered around one particular installation but rather a collection of modern, up-to-date analytical electron microscopes. These are expensive devices and most universities and industry laboratories are not as well equipped as ORNL. Research here is done principally in a collaborative mode and is focused almost exclusively on problems in metallurgy and ceramics. The recent acquisition of a state-of-the-art imaging atom probe has added another dimension to our ability to study structures of alloys.

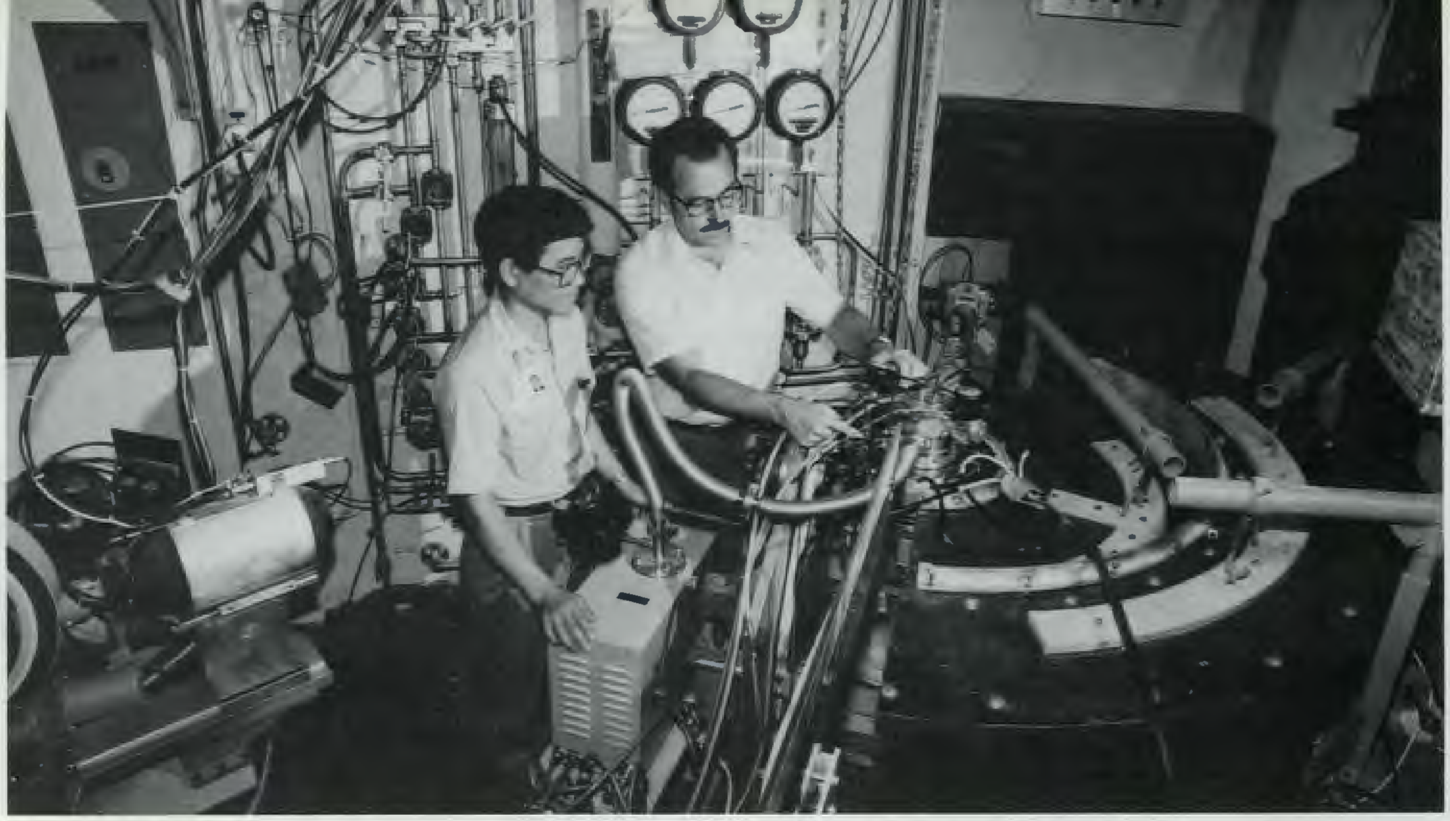
The EN Tandem Van de Graaff Accelerator has fewer clients than most of our other facilities. This accelerator, which was originally used for pioneering nuclear physics research, is now totally devoted to the study of accelerator-based atomic physics. This is a branch of atomic physics that uses highly charged atoms produced by the Van de Graaff to study ion-atom collisions, electron capture and loss, channeling, etc. A number of universities base a significant fraction of their experimental capability on this accelerator and its ancillary equipment.

The Oak Ridge Electron Linear Accelerator is the world's most powerful tool for the study of neutron interactions with nuclei. It is used almost exclusively to measure cross sections related to fission and fusion power reactors. The users are therefore usually limited to those scientists who are engaged in this field of research. Occasionally, more basic experiments are undertaken to explore the fundamental interactions between neutrons and nuclei.



This neutron capture detector at the Oak Ridge Electron Linear Accelerator has provided data essential for the understanding of the buildup of elements in stars. See Jack Harvey's article on ORELA on page 242.

The 400 scientists who use the physical sciences facilities form a most important ingredient in our overall research. Their interactions with our staff are stimulating and often result in exceptionally fruitful research. The presence of so many scientists in itself serves as a kind of leaven for ORNL programs, and the needs of our visitors make the Laboratory more aware of our own need for state-of-the-art instruments including new accelerators, reactors, microscopes, and surface-modification tools. If your instruments are not at the frontier in a discipline, your users are quick to let you know. However, user operation also places burdens on the Laboratory. Some ORNL scientists are spending more time helping users and, consequently, less time on their own research. Also, user operation adds to their frustration and forces them to be involved in the more bureaucratic aspects of science. On balance, however, there is no question. Users are good for us.



Bob Nicklow is group leader of the Neutron Spectrometry Group in ORNL's Solid State Division and the director of the Neutron Scattering User's Program. He received a Ph.D. degree in physics from Georgia Institute of Technology. He joined the ORNL staff in late 1963. Since then he has been conducting neutron-scattering studies on lattice dynamics, defect properties, and magnetic excitations. A Fellow of the American Physical Society, he is the author of three book chapters. Here, Nicklow (right) and Yukio Morii of the Japan Atomic Energy Research Institute (JAERI) in Tokai, Japan, discuss the performance of a wide-angle neutron diffractometer that was recently installed at ORNL's High Flux Isotope Reactor. The diffractometer, funded by JAERI through a collaboration with ORNL on neutron scattering, provides a unique capability for studying the real-time changes of structural properties of materials caused by time-dependent external perturbations. The furnace seen here can produce a rapid change in the sample temperature of up to 1000°C/min.

Probing Materials Using Low-Energy Neutron Beams

By ROBERT M. NICKLOW

It is now widely recognized that beams of low-energy neutrons can be uniquely powerful probes of certain microscopic properties of solids and liquids. The reason for this, as discussed extensively in previous issues of the *Review*, is that the neutron possesses several properties (short wavelength, low energy, magnetic moment) that even separately would make it extremely valuable. In combination, these properties provide a truly remarkable research tool capable of giving information on crystal structures, magnetic structures, vibrational and magnetic energy levels, liquid properties, superconductivity, polymers, and phase transitions, to name a few examples.

In this article I will briefly describe the variety of research activities involving neutron scattering that are currently being pursued at Oak Ridge National Laboratory. In almost all cases, the quality or the completeness of the results obtained are limited by the low intensity available at the neutron source. Consequently, a large effort at ORNL is now aimed at constructing the highest-intensity neutron source in the world.

Magnetism Studies

The study of magnetic materials has always been an important

The neutron possesses several properties (short wavelength, low energy, magnetic moment) that make it a truly remarkable research tool. At ORNL it has provided information on crystal structures, magnetic structures, vibrational and magnetic energy levels, liquid properties, superconductivity, polymers, and phase transitions. ORNL hopes to improve neutron-scattering research by building the Center for Neutron Research, which would be the highest-intensity neutron source in the world.

application of neutron scattering. Because the neutron has a magnetic moment, a magnetic interaction exists between the neutron and the atomic magnetic moments (electron spins) existing in a magnetic material. Consequently, the spatial arrangement of the atomic moments are revealed by the intensities and locations of the "magnetic" peaks occurring in the neutron diffraction pattern. In such studies, it is necessary to distinguish magnetic scattering from the scattering arising from the interaction between the neutron and the atomic nuclei (nuclear scattering), which can be used to determine the spatial arrangement and positions of the atoms in a material. A clear separation of the magnetic and nuclear scattering may occur naturally if the peaks in the magnetic and nuclear scattering patterns do not overlap. Otherwise, it may be necessary to use a polarized neutron beam and analyze the polarization after scattering. Polarization analysis, which was pioneered at ORNL, is widely used for such studies. Recently at ORNL, however, polarization analysis has been used in somewhat unconventional investigations.

One area of research that makes use of the unique properties of the neutron and polarized beams in a novel way is the study of nuclear magnetism, the long-range alignment of nuclear magnetic moments in crystals at very low temperatures. In "conventional" magnetic materials, the magnetism arises from the electrons. That is, the atomic magnetic moments arise from the magnetic moments of the atomic electrons. The atomic moment is the "excess" moment that results from the number of unpaired electrons. Recall that the electrons in atoms tend to organize themselves in pairs such that the magnetic moment of one member of the pair cancels that of the other. A similar situation occurs in the nucleus of an atom: the nuclear magnetic moment results from unpaired neutrons and protons.

The sensitivity of neutrons to the magnetic ordering of nuclear moments is not solely the result of magnetic interactions, however. In fact, the principal interaction is a nuclear interaction between the neutron and a nucleus that depends on the spin-quantum states of each. (The magnetic moment is proportional to the spin-quantum number.) When the neutron, whose spin is ½, interacts with a nucleus of spin I, it can lead to states of the neutron-nucleus combination having total spin $I \pm \frac{1}{2}$; in general, the neutron scattering strengths associated with these two states, b^+ and b^-, are different. Because of the difference between the interaction of the neutron with electrons and with nuclei, it is possible to study electronic magnetism and nuclear magnetism separately when they occur simultaneously in the same material—as they usually do.

The simultaneous long-range magnetic ordering of nuclei and unpaired electrons is a particularly challenging problem requiring the understanding of ordering phenomena in separate but coupled or interacting systems. Several key questions require the attention of researchers: Do the nuclear system and electronic system order simultaneously at the same temperature, or does one order first, inducing the ordering of the other? What forces cause the ordering? Is the periodicity of the magnetic order the same as that of the crystal structure? In what direction in the crystal are the magnetic moments pointing? Do the nuclear and electron moments point in the same direction? Only by doing experiments with polarized neutron beams can all of these important questions be answered.

A typical example is the recent study of a praseodymium-copper compound ($\mathrm{PrCu_2}$) by John Arthur of ORNL and Shuzo Kawarazaki of the University of Osaka in Japan. Previous studies of the bulk magnetization of $\mathrm{PrCu_2}$ had revealed that a magnetic phase transition occurs at 58 milli-Kelvin (mK). This very low ordering temperature is typical for materials that display nuclear ordering, but no other corroborative evidence existed. The neutron scattering experiment was particularly illuminating (see Fig. 1). The results showed that the nuclear moments did indeed order at 58 mK and that that ordering also induced an electronic ordering. However, the nuclear and electronic moments on the *same* atom were found to be antiparallel and aligned parallel to the C-axis of the crystal structure. Most surprising was the discovery that the ordering periodicity was not the same as that of the crystal chemical order, but rather was incommensurate. That is, the periodicity is described by a magnetization wave having a wavelength that is no simple multiple of the repeat spacing of the chemical lattice. One possible conclusion is that the magnetic interaction between nuclei must be mediated through the conduction electrons because no other interaction mechanism will provide the long-range magnetic force necessary for such an unusual structure—that is, a force having alternating positive and negative signs as the separation distance of the magnetic moments increases.

Magnetic Spin Waves

Another challenging problem in the field of magnetism for which the scattering of polarized neutron beams is providing new discoveries is that of magnetic spin-waves at high temperatures. At very low temperatures in a ferromagnet, for example, the magnetic moments of all the atoms are parallel to each other. However, as the temperature increases, this perfect alignment begins to break down as the thermal energy causes oscillations in the moment directions. These disturbances in the moment directions are best described in terms of a superposition of oscillation waves, called spin-waves. At low temperatures, a spin-wave has a single energy that depends on its wavelength and on the magnetic forces existing between the moments on different atoms. A major triumph of neutron scattering research has been the direct experimental determination of magnetic forces through measurements of the spin-wave energy spectrum for numerous materials.

As the temperature is raised, the amplitude of the magnetic-moment oscillations increases until a temperature is reached—the magnetic-ordering temperature T_c—above which the magnetic moments are no longer aligned and the material loses its ferromagnetic properties. The temperature evolution of the spin-wave spectrum from low temperatures through T_c has been a difficult problem for many years, both theoretically and experimentally. It has been a very important problem because of its relationship to our understanding of magnetic phase transitions.

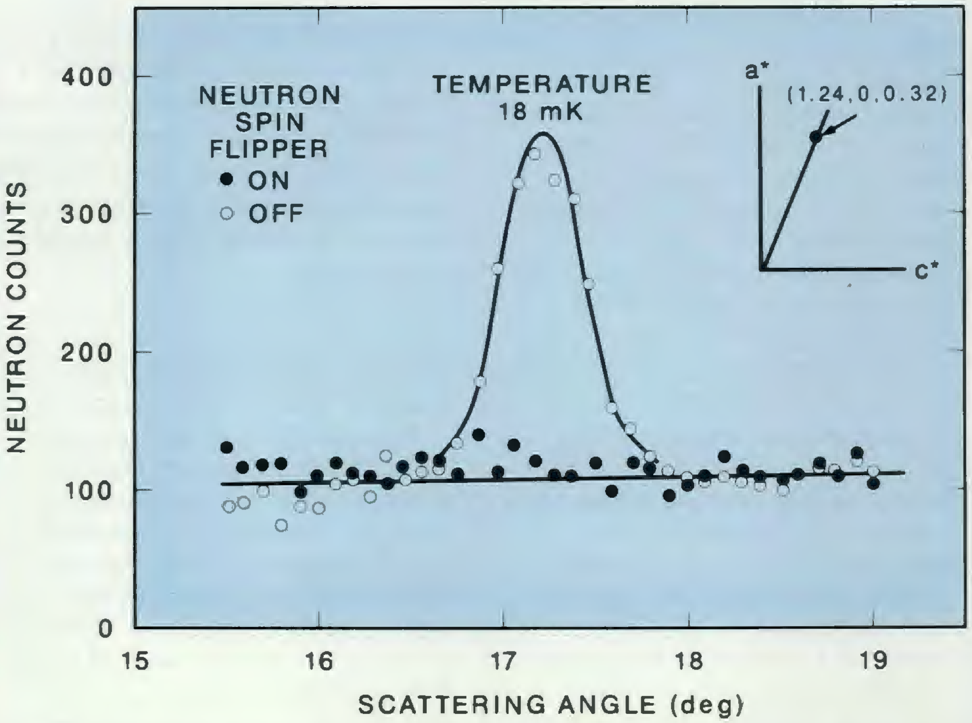


Fig. 1. A polarization analysis of the neutrons measured at the (1.24, 0, 0.32) magnetic Bragg position of $PrCu_2$ shows that the scattering produces a complete polarization reversal of the incident beam. This result indicates that the magnetic moments are aligned in the a^*-c^* plane of the $PrCu_2$ crystal. The observation that the magnetic peak is located at nonintegral values of a^* or c^* shows that the magnetic periodicity is not commensurate with the crystal chemical periodicity.

Previous theoretical work on simplified models had led to the conclusion that when the temperature is increased, the spin-wave energies decrease and their energy widths increase. Then as T_c is approached, the spin-wave energies become zero for all wavelengths and the widths are very wide, thus giving a continuous and broad energy spectrum for the scattered neutrons for all temperatures above T_c. The results of previous experimental investigations have been difficult to interpret unambiguously because as the spin-wave spectrum broadens in energy, the magnetic scattering begins to overlap the normal nuclear inelastic scattering caused by the motions (or vibrations) of the atoms. The only way to separate the magnetic and nonmagnetic neutron scattering is to use an incident beam of polarized neutrons and to carry out a polarization and energy analysis of the scattered beam. Because of the inefficiency of polarization devices, resulting in an intensity loss of a factor of 10 or more, such experiments have been impractical until now.

In a recent experiment, Herb Mook (ORNL) and Jeff Lynn (University of Maryland) have used new higher efficiency iron-57 polarizing devices for studies of the spin-wave spectrum of nickel at high temperatures. Their measurements revealed that the spin-waves having long wavelengths behaved as predicted by the simplified theories—that is, they have a broad energy spectrum centered on zero energy. However, the spin-waves having short wavelengths behaved quite differently (see Fig. 2). The energy spectrum for these spin-waves continued to possess a rather well-defined peak at finite energy for temperatures above T_c. The results

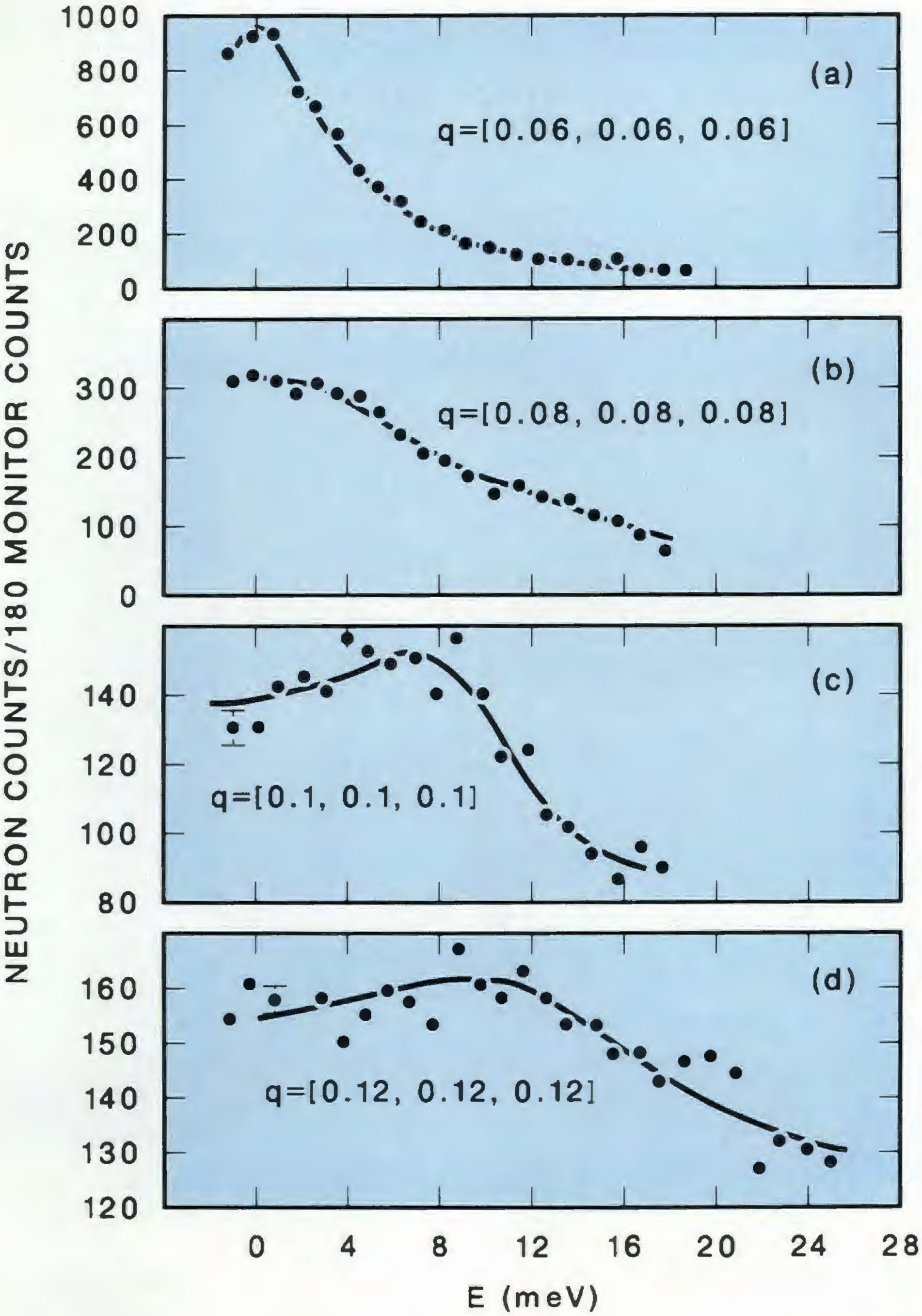


Fig. 2. The energy dependence of the neutrons that have undergone a polarization change as a result of interactions with spin oscillations in nickel for a temperature above the magnetic-ordering temperature T_C. The observation that a peak in the intensity distribution occurs at $E > 0$ for short-wavelength spin waves (larger values of q) as seen in scans (c) and (d) is at variance with simple theories that predict a peak at $E = 0$ for all q, such as seen in scans (a) and (b).

will stimulate additional theoretical work.

Structural Changes in Materials Examined

In another general and growing area of application, neutrons are being used at ORNL to investigate the real-time changes of structural properties on an atomic scale caused by external perturbations applied to a sample, such as temperature, stress, or magnetic fields. The study of structural changes during processing of alloys and ceramics is an area of great potential. Many such studies rely on the penetrating power of neutrons to probe bulk rather than surface properties and to perform scattering studies on samples within furnaces, cryostats, and high-pressure cells. Position-sensitive detectors, which cover a large range of scattering angles, are very useful for such studies because, for example, they allow the simultaneous measurement of the time dependence of many parts of the diffraction pattern.

Through a collaboration on neutron scattering research between ORNL and the Japanese Atomic Energy Research Institute in Tokai, Japan, a unique wide-angle neutron diffractometer has been constructed at ORNL for such real-time investigations. The position-sensitive detector for this spectrometer was designed by Manfred Kopp of the Instrumentation and Controls Division.

An example of a recent investigation using this apparatus is the study of the order-disorder phase transition occurring in a nickel-manganese alloy (Ni_3Mn) at the critical temperature T_c = 510°C. Above 510°C the Ni and Mn atoms are distributed randomly on the allowed atomic sites in the crystalline lattice of this material. When the temperature is rapidly lowered through T_c, the Ni and Mn somehow reorganize themselves to produce a new distribution that is no longer random, but rather is precisely ordered to give, for example, a Ni-Ni-Ni-Mn repeating pattern. The ordered pattern leads to new (superlattice) diffraction peaks in the neutron scattering pattern.

By measuring the changes of the widths and intensities of these peaks with time, scientists can determine how long it takes for the ordered structure to evolve from the random structure. The intensity is determined by the total fraction of the sample that is ordered, and the width is determined by the average size of the ordered "droplets" within the disordered matrix. This ordering process requires many seconds to develop, and the actual time depends on the temperature differences between the initial and final temperatures (T_i and T_f) and the critical temperature T_c.

For example, if $T_i = 600°C$ and $T_f = 470°C$, it takes about 60 min before Ni and Mn reorganize sufficiently to give a sharp superlattice peak indicative of long-range order (see Fig. 3). The peak continues to sharpen for another 30 h. One discovery in this study is that no matter what the values of T_i and T_f, the time required for the growth of the order phase is describable by the identical mathematical formula. Studies of such "scaling" laws in alloy structure studies will provide new tests of theoretical models for the kinetics of order-disorder phenomena.

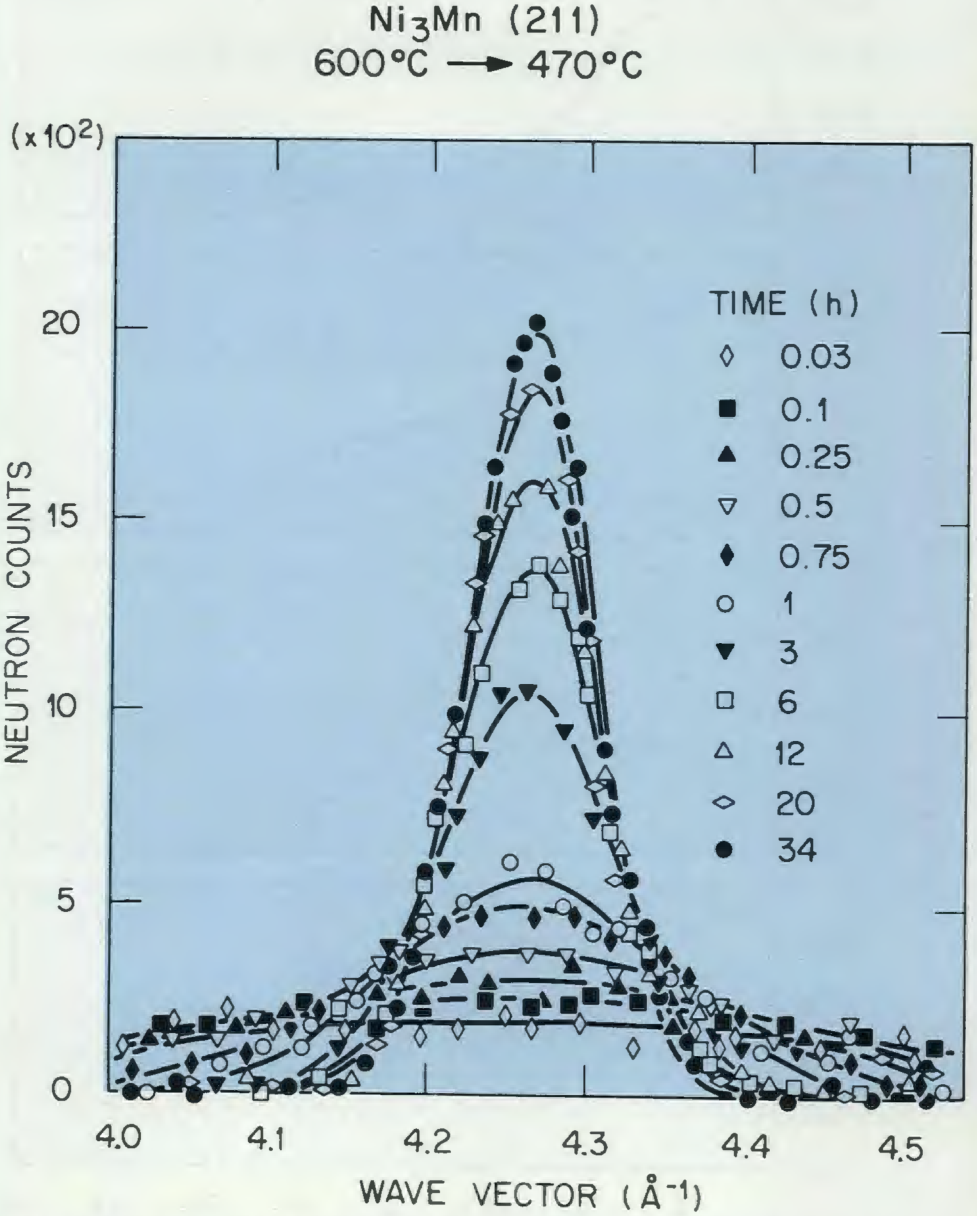


Fig. 3. Neutron-scattering data showing the time dependence of a diffraction peak for Ni$_3$Mn after rapid cooling from a high temperature. One obvious conclusion is that the evolution of an ordered structure from the random structure requires many hours.

Small-Angle Scattering

One of the fastest growing applications of neutron scattering in the United States, and particularly at ORNL, is small-angle neutron scattering (SANS). Research at ORNL is carried out at the facilities of the National Center for Small-Angle Scattering Research (NCSASR), which was directed by Wallace C. Koehler until his death in April 1986. (It is now directed by George Wignall.) The Center is sponsored jointly by the National Science Foundation, the Department of Energy, and ORNL. One of the instrumentation innovations that led to the great expansion of SANS research is the large (100-cm diameter) area detector based on a concept originated by Cas Barkowski and Kopp of ORNL's Instrumentation and Controls Division. Position-sensitive detectors based on the ORNL design make it possible to measure the scattered neutrons at all (small) angles simultaneously, thus speeding up experiments by a factor of more than 100.

The signal observed in small-angle scattering experiments depends on the contrast in scattering density between the structural entities being investigated and the matrix in which they are embedded. Typically, the dimension of these entities are in the range from several tens to several thousands of angstroms (1 Å = 10^{-10} m = 0.1 nm). Thus, the technique is ideally suited for studies of large molecules in solution and in solids (biological molecules, polymers, and liquid crystals).

Submicron or colloidal systems have long been an area of industrial

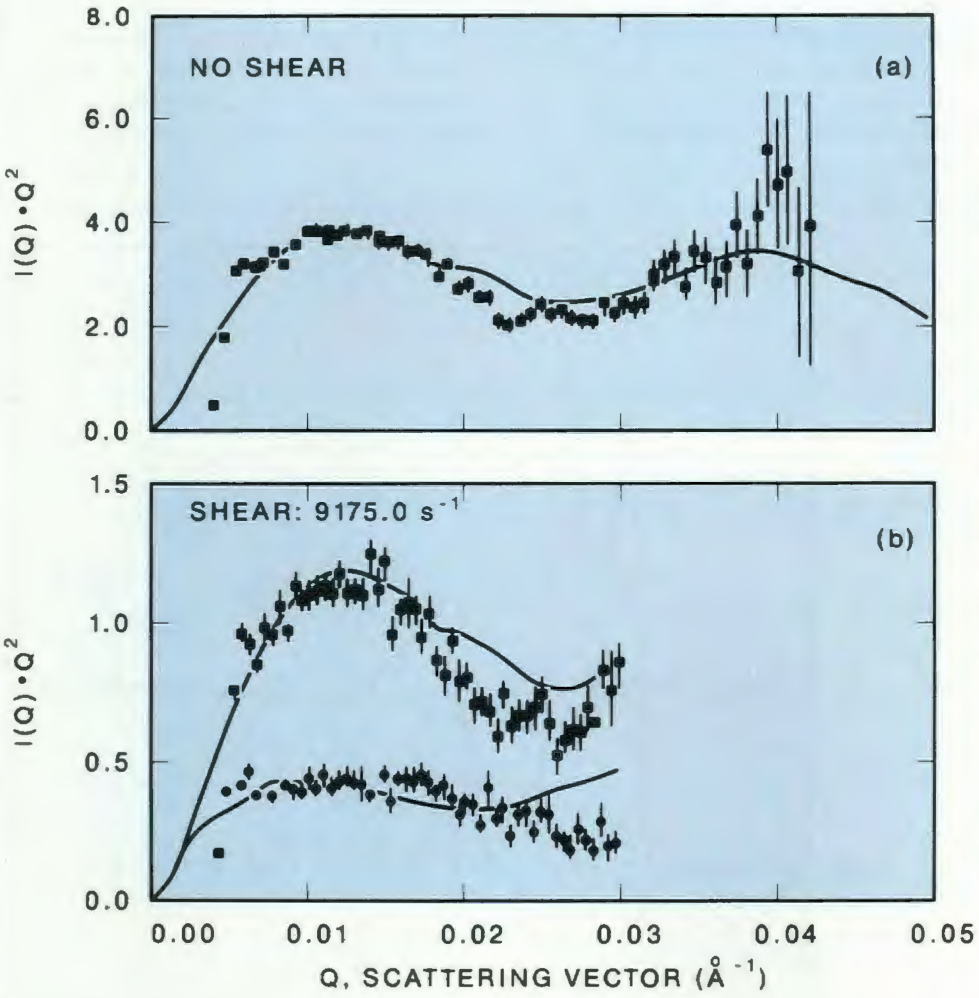


Fig. 4. Small-angle, neutron-scattering patterns from a solution of cylindrical micelles. The scattered intensities in two directions orthagonal to the beam are plotted on each graph. When the solution is stationary (a), the scattering in the two directions is indistinguishable. When the liquid is flowing (b), the shearing force aligns the micelles, and the intensities in the two directions are different. The value of Q is proportional to the distance from the beam axis (up or sideways) at which the intensity is measured. More detailed study of these results can show that the micelle cylinders have 180° bends.

importance, and traditionally most research has concentrated on their macroscopic behavior. In recent years SANS has proven to be remarkably useful in studying the microscopic properties of such systems. Not only can details of the intraparticle structure be studied, but interparticle correlations in position are revealed. In fact, these systems form three-dimensionally ordered arrays of particles. Surfactant solutions form a rich variety of submicron structures that vary with temperature and concentration. Spherical and cylindrical micelles, lamellar, cubic, and hexagonal structures, and liquid crystalline phases form a partial list. Advances in liquid theory have permitted a quantitative description of scattering from spherical micelles or colloids in concentrated solution that have excluded volume, coulombic, or magnetic dipolar interactions between the particles. Attention is now turning to the anisotropic phases. Anisotropic SANS scattering from cylindrical micelles aligned by viscous shear has been recently observed and analyzed at ORNL by John Hayter (see Fig. 4).

New Opportunities

I have tried to highlight neutron scattering research at ORNL using a few specific examples. In many cases, the materials themselves provide the novelty and excitement. The actual neutron scattering techniques are becoming rather standardized and routine. On the other hand, there is room for significant advances. For example, the most copious sources of thermal neutrons are fission reactors. However, much of the work described above, especially that requiring polarization analysis or time-dependent measurements, is severely limited because of the very low intensities of neutrons available at the best, highest-flux sources, such as the High Flux Isotope Reactor (HFIR) at ORNL.

Furthermore, the most powerful reactors in the United States, the HFIR and the High Flux Beam Reactor at DOE's Brookhaven National Laboratory, are more than 20 years old and do not possess neutron-energy-spectrum tailoring devices (hot and cold sources) as advanced as those used at some European neutron sources. Also, although neutron scattering techniques provide unique capabilities for unraveling many problems in studies of condensed matter and have become refined and standardized in many fields of research, the number of scientists in the United States who can use neutron scattering routinely is limited (though growing rapidly) because of the small number of facilities.

Consequently, ORNL, under the leadership of Colin West of the Engineering Technology Division and Mike Wilkinson and Ralph Moon of the Solid State Division, is proposing the design and construction of a Center for Neutron Research (CNR), which will house a fission reactor that would have the world's highest neutron flux. This reactor is planned to have a flux at the beam tubes 5 to 10 times as great as that at the HFIR. By incorporating recent developments in neutron

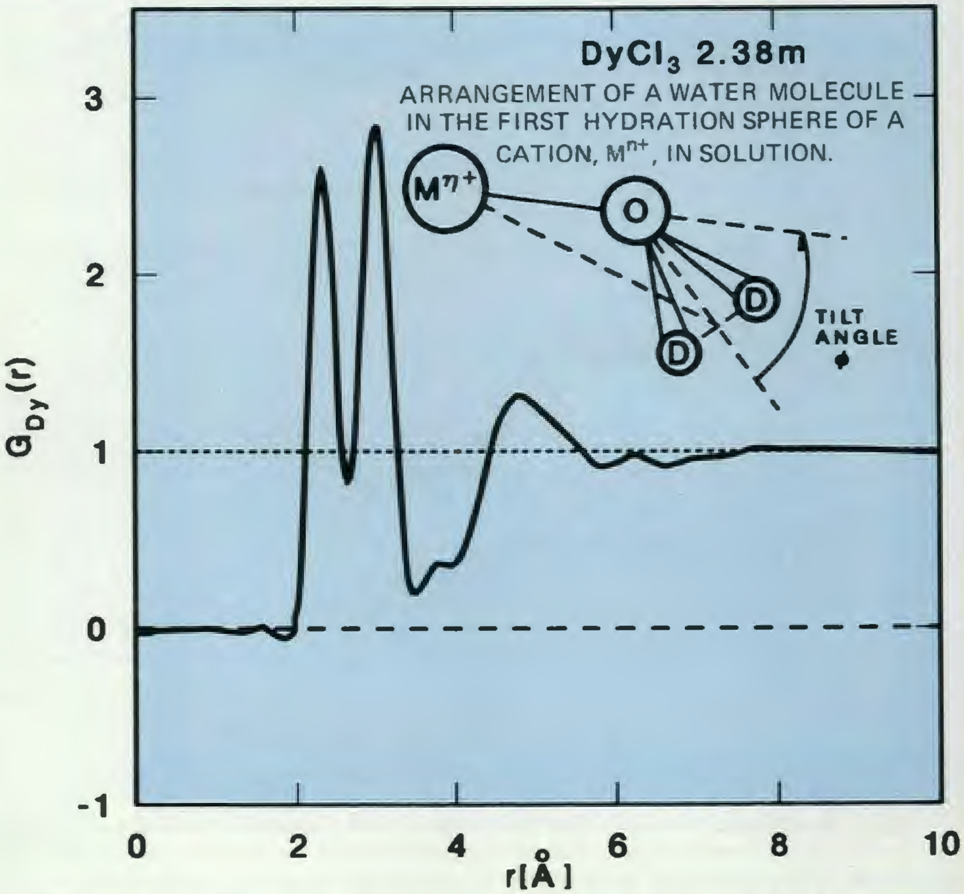
Chemical Applications of Neutron Scattering

More than ever before, understanding the chemical nature of materials requires a knowledge of the structure and dynamics of molecules in solids and liquids—information that can be obtained by neutron scattering. At ORNL neutron-diffraction studies of condensed phases have been performed for 20 years at the High Flux Isotope Reactor (HFIR). Neutron-scattering experts are now anticipating the studies that could be done if the proposed Center for Neutron Research (CNR), including a reactor having the world's highest neutron flux, is built at ORNL in the 1990s.

For crystalline materials, neutron-diffraction studies have already provided a wealth of structural information. Much of this information was made possible by the many advances in crystal structure determination by Bill Busing, George Brown, Ray Ellison, Carroll Johnson, Henri Levy, and Pete Peterson of ORNL's Chemistry Division. These advances include the first single-crystal neutron diffraction study and the development of the first minicomputer-controlled diffractometer.

Computational methods and computer programs developed by the ORNL crystallographers are used in many laboratories throughout the world. The ORNL work forms the basis of commercial programs for correcting and processing experimental measurements, analyzing and refining crystal structures, generating pictures of the resulting atomic arrangements (e.g., in new synthetic materials), and interpreting them in terms of intermolecular forces.

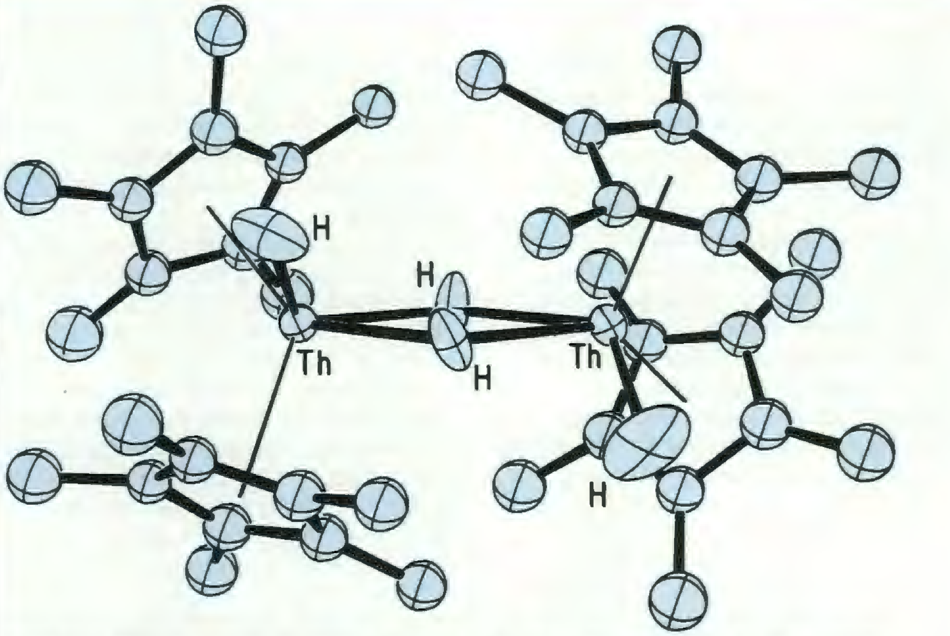
Busing is now working on methods for interpreting diffraction data from partially oriented fibers used in advanced polymeric materials such as Kevlar. The CNR's increased neutron flux would greatly facilitate this work by permitting the study of very small crystals. Such an advance will also open up this field to analysis of materials produced in minute amounts such as hydrogen-containing transplutonium compounds.



Radial distribution function G(r) for the relative position of oxygen and hydrogen atoms in the water molecules around a dysprosium cation in solution. The arrangement shown in the insert follows directly from this curve, derived from neutron diffraction using different dysprosium isotopes.

The vast bulk of materials chemistry, however, is concerned with noncrystalline solids and hydrogen-containing liquids. The structure of these materials is not the same as the structure of crystalline solids. Atoms in crystals are arranged in a periodic order. The structures of liquids and amorphous solids, however, are specified by the average relative locations of atoms and molecules, described by "radial distribution functions." These structures can be determined by X-ray and neutron scattering

ORNL has a long and distinguished history of work on the structure of liquid water. At the Graphite Reactor in 1946, Ernie Wollan and Cliff Shull made the beam transport devices, neutron intensities on a sample could be up to 50 times that now available at the HFIR. These improvements, together with an increased number of instruments (e.g., 30 neutron spectrometers at CNR vs 9 at HFIR) would yield a scientific productivity up to 30 times higher than that of our best current neutron sources. Such a facility would put ORNL—and the United States—at the forefront of neutron scattering research.



Structure of the thorium compound $\{Th[(CH_3)_5C_5]_2H(\mu-H)\}_2$ *as determined by single-crystal neutron diffraction analysis, showing the bridging and nonbridging hydrogen atoms attached to the thorium atoms. For clarity, the methyl hydrogen atoms are not shown.*

first measurement of the neutron diffraction pattern of water. In 1966, Dan Danford, Henri Levy, and I obtained the radial distribution function for oxygen atoms from X-ray diffraction. This work confirmed the open tetrahedral arrangement of the oxygen atoms in water and has provided a crucial test of proposed water models. In 1981, Bill Thiessen and I completed a long and difficult neutron-diffraction study of mixtures of light and heavy water. This work has yielded the H-H and O-H radial distribution functions—that is, the interatomic distances between two hydrogen atoms and between an oxygen and hydrogen atom in the same molecule or in neighboring molecules of water (H_2O). This structural information should lead to a realistic statistical mechanical theory of liquid water.

Structural chemistry of ionic solutions (ions dissolved in water) has been revolutionized by the isotopic substitution method in neutron diffraction. In this case, one measures the diffraction patterns of two solutions that are identical in every respect except for the isotopic composition of one of the ions. The difference between the two sets of measurements then yields directly and unambiguously the arrangement of the nearest-neighbor water molecules around this ion.

Brian Annis, Dick Hahn, and I have applied this method to several isotopically substituted lanthanide solutions, that is, solutions containing different isotopes of lanthanides (a series of elements beginning with lanthanum—element 57—and ending with lutetium—element 71). Our results confirm the hypothesis that the number of water molecules in the first hydration sphere of the heavier lanthanide ions is one less than that in the sphere of the lighter lanthanide ions because the heavier ions each have smaller ionic radii than the lighter ones. As a result, less space is available for water molecules neighboring the heavier ions in a given sphere.

The enhanced neutron flux of the CNR reactor would permit the extension of this method to pairs of nuclides having small differences in scattering length, such as carbon (^{12}C and ^{13}C) or nitrogen (^{14}N and ^{15}N).

An important advantage of the CNR for materials chemistry would be the availability of "hot" neutrons having an energy spectrum extending into the region of ~0.5 eV. This capability will permit the characterization to very high momentum transfers (~50 $Å^{-1}$) of amorphous solids such as semiconductors, switching materials, optical materials, magnetic glasses, and polymers. Molecular vibrations can be studied in the solid and liquid state to obtain information on molecular motion that cannot be determined by optical spectroscopy.

Reaction kinetics in hydrogenous materials—in particular, the kinetics of very fast, diffusion-limited chemical reactions—can be studied by incoherent inelastic neutron scattering. This method gives unique information on the microscopic aspects of diffusion of molecules in liquids because of the large and controllable momentum transfer possible in these experiments. Because of the recent advances in the understanding of the structure of proteins and polymers, it will be possible to interpret the specific role of water in solutions of these materials. Neutron scattering from selectively deuterated materials can "zero-in" on the motions of specific protons in these macromolecules. Because of its increased neutron flux, the CNR will offer advantages for this type of study.—*Al Narten, Chemistry Division.*

ORNL's X-Ray Facility at the National Synchrotron Light Source

Much progress in designing materials has come by trial and error. In more recent years, the science of materials has advanced rapidly, largely because of structural characterization techniques that provide information on the chemical identity and geometrical arrangement of atoms. Yet modern technology requires improved characterization techniques to provide materials that have physical and mechanical properties that allow them to perform under the most adverse environments of high temperatures, corrosive atmospheres, and intense radiation fields. Better material performance is achieved by careful control of manufacturing, impurity levels, structure and compositional variations, minor phases, and interfaces. The basis for this control is the information provided by structural and chemical characterization techniques.

Of the several new probes available to study matter, X-ray synchrotron radiation has advantages that researchers find compelling. The most attractive property—the unique resonances that X rays have with specific electron energy levels of atoms—is not available with other probes. Another enticement of synchrotron radiation is its broad and intense energy spectrum, which is pulsed and nearly linearly polarized.

Synchrotron radiation provides a continuous spectrum from which an energy can be selected that is very near the binding energy of a bound electron. X rays at this energy can excite large resonances. We can choose an energy approximating that required to photoeject a particular electron in a specific element, thus highlighting any of the atoms in the periodic table. In this way, we enhance the X-ray scattering, photoelectron, Auger, and fluorescent signals to study the crystal structure, chemical valence, interface preference, and concentration of elements forming the materials of interest. This information provides clues to help us understand behavior of materials.

To exploit the special properties of synchrotron X rays to probe the structure of materials, Gene Ice, Tony Habenschuss, and I have developed a beam line and installed it at the National Synchrotron Light Source at Brookhaven National Laboratory. Our advanced X-ray optics using crystal monochromators, which won an I•R 100 award from *Research & Development* magazine in 1983, permits us to select and focus single wavelengths of X rays continuously over the energy range of 3 to 40 keV. This energy region was chosen to excite the deeper electron energy levels of the elements most common to metals and ceramics that are important to the basic physical and chemical behavior of these materials. Our beam line, which focuses synchrotron X rays, increases the intensity at the sample up to 200 times and is as intense as any bending magnet X-ray source in the world. So-called "insertion devices," currently being installed at Brookhaven, will give us another factor of 1000 in intensity.

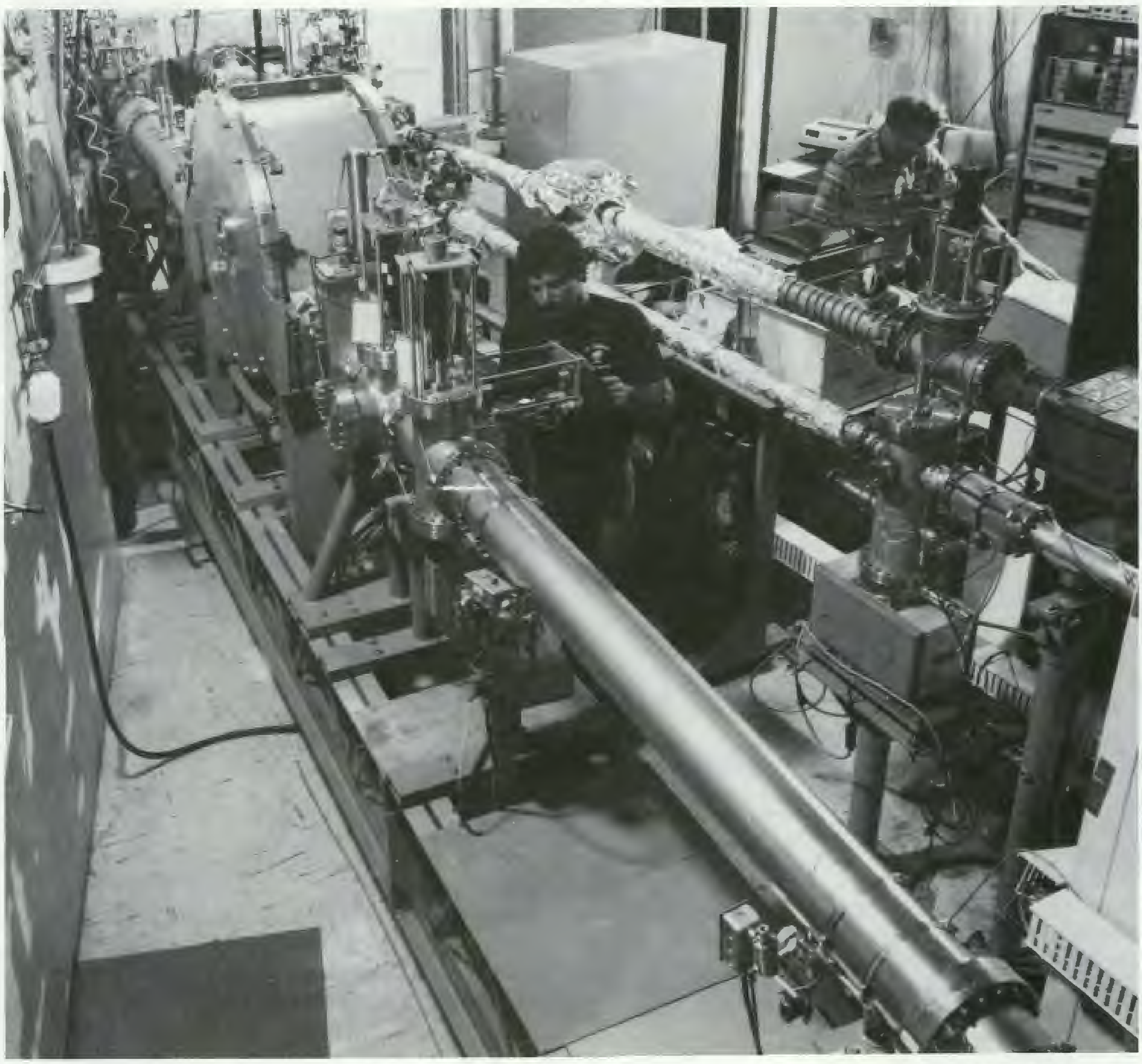
Other ORNL researchers in the Solid State, Health and Safety Research, and Chemistry divisions are involved in both using and instrumenting research facilities having synchrotron sources that emit lower-energy vacuum ultraviolet radiation, which is more widely used for studying surface properties than for studying bulk properties.

Our X-ray beam line at the NSLS is now fully operational and our X-X-ray optics perform well. The high X-ray intensity available permits us to measure the weak X-ray scattering associated with the small fraction of atoms that are at the surface. Measurements of surfaces of single crystals of aluminum oxide (a ceramic) and those covered by a few hundred atomic layers of nickel (a metal) are giving us insights into the structure of atomic layers that form the boundary between the metal and the ceramic in a composite.

We have made precision lattice parameter and diffraction line width measurements of nickel aluminide (Ni_3Al). These measurements, which are sensitive to fluctuations in lattice parameters, reveal the kinds of defects that exist as the composition is varied about the stoichiometric Ni_3Al. Such measurements indicate the variations in the distances between atomic layers and the arrangements of atoms on the atomic planes. Others in the Solid State and Chemistry divisions are conducting dynamic experiments on surface melting, ion-implanted materials, and polymers.

Although advances are being made, materials scientists find it difficult to theoretically predict the properties of materials (see the article by William H. Butler on page 54). Thus, we must use experimental information about the geometric arrangements of atoms and molecules in synergistic relationships in matter and on surfaces to help test and refine our theoretical understanding. Experiment and theory together stimulate new insights on ways to improve materials. Property measurements of the 90-odd naturally occurring elements are relatively easy. However, because alloys, which constitute most materials of technological interest, consist of several elements in varying concentrations, the number of conceivable combinations makes such measurements of every property an incredible task. One of our goals is to synthesize experimental results and theoretical calculations to help identify ways of tailoring materials for specific needs without having to make and test every conceivable combination.

With the aid of the Oak Ridge Associated Universities, we formed a consortium of university and industrial scientists to collaborate in research using the ORNL synchrotron X-ray beam line. Examples of collaborating organizations include small companies like Energy Conversion Devices and giants like AT&T, government laboratories, and universities (e.g., Harvard, University of Chicago, Massachusetts Institute of



Gene Ice works at ORNL's X-ray beam line, which was recently installed at the National Synchrotron Light Source at Brookhaven National Laboratory. The I·R 100 award-winning beam line contains advanced X-ray optics using crystal monochromators. By selecting and focusing single wavelengths of synchrotron X rays continuously over the energy range of 3 to 40 keV, the ORNL beam line increases the intensity at the sample up to 200 times, which is as intense as any bending magnet X-ray source in the world. So-called "insertion devices," currently being installed at Brookhaven, will provide another factor of 1000 in intensity.

Technology, Georgia Institute of Technology, and the universities of Kentucky, Oregon, and Washington). We expect this interdisciplinary interaction will produce new scientific insights into materials.—*Cullie Sparks, Metals and Ceramics Division.*

Louis K. Mansur is group leader of the Defect Mechanisms Group in ORNL's Metals and Ceramics Division. Before joining ORNL in 1974 he spent five years with the Atomic Energy Commission (now part of the Department of Energy). He received a bachelor's degree in physics from the University of Lowell and a Ph.D. degree from Cornell University, where he specialized in engineering physics and materials science. His research at ORNL has emphasized the theory and mechanisms of radiation effects and defect behavior in materials. In 1983 his group received DOE's Materials Sciences Award for research having significant implications for energy technology, for work on helium effects and pulsed-ion bombardments. Mansur has received Martin Marietta Energy Systems, Inc., technical achievement and publication awards and is a Fellow of the American Nuclear Society and of the American Society for Metals.

The Science and Engineering of Irradiated Materials

By LOUIS K. MANSUR

Irradiating materials with energetic neutrons or ions can lead to profound changes in their properties. Some of the atomic and microstructural mechanisms by which these changes occur are unknown in "classical" materials science. As a result of combined theoretical and experimental research at ORNL, our understanding of the underlying physical mechanisms has increased rapidly as has our ability to design alloys and predict their behavior for technological applications.

Irradiation can produce remarkable changes in the structure and properties of materials. The study of these effects, which dates back to the earliest days of Oak Ridge National Laboratory, continues to be a major activity at ORNL. The scope of this research perhaps can be appreciated by contrasting it with traditional subfields of materials science, such as the study of mechanical properties or of phase transformations. While these subfields center on groups of conceptually similar phenomena, the study of radiation effects represents an extension of the entire field of materials science. Irradiation adds a new dimension because all processes are potentially affected. In this sense, the science is somewhat akin to that of high-temperature materials, in which a high level of thermal activation is the common denominator.

The wide scope of the field is well represented by the range of efforts at ORNL. The work generally follows two main lines: (1) characterizing and understanding the effects of radiation and (2) using irradiation as a tool to explore the behavior of materials. Scientific questions and technological needs motivate the work. Some basic questions are: What physical principles underlie radiation effects? What can be learned about induced defects and

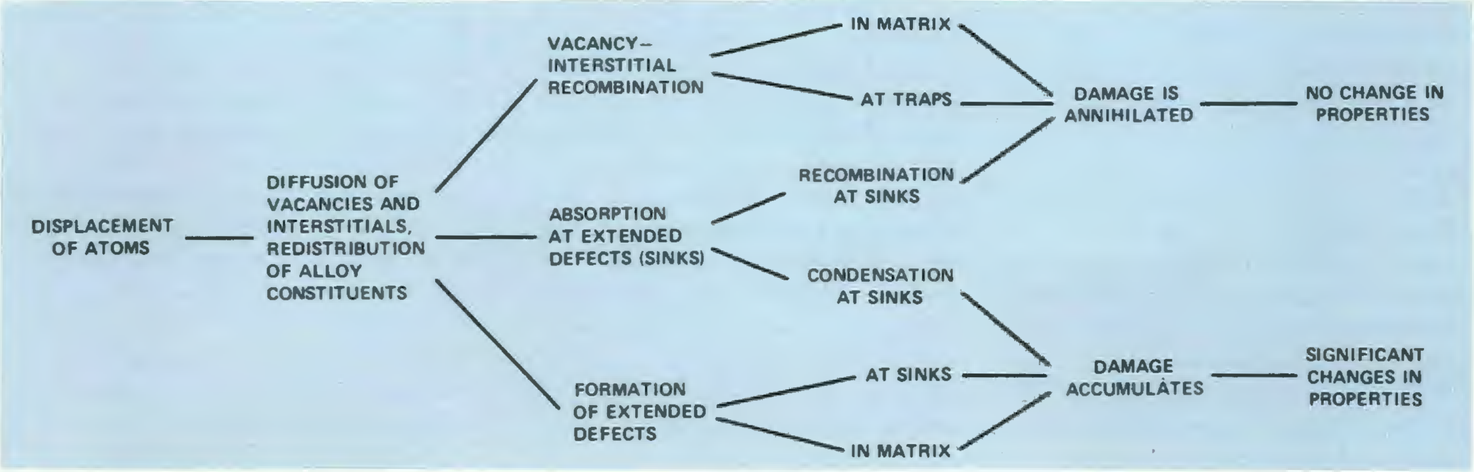


Fig. 1. A flow diagram showing the possible fates of point defects generated by irradiation. By various paths, the defects following the upper branch recombine, leaving an atom on a lattice site and producing no permanent change. This is the fate of most of the defects. Defects following the lower branch accumulate in the material and produce changes in structure and properties.

their host materials? Some questions related to technological needs are: How can we develop radiation-resistant materials for fusion and fission reactors? What applications can most benefit from the altered states of materials produced by irradiation?

We are interested mainly in the effects of energetic neutrons and charged particles because such radiations displace atoms from their lattice sites, creating vacant lattice sites (vacancies) and atoms in the interstices between normal lattice atoms (interstitials). Both vacancies and interstitials are called point defects. Point defects diffuse by thermal activation—that is, their positions change by atomic jumps stimulated by thermal vibrations. In diffusing they may interact with each other and with other lattice imperfections. Ultimately, significant changes in structure, local composition, and properties result. Thus, radiation effects research is often divided into three interconnected topics: damage production, kinetics of defect processes, and property changes.

One energetic projectile can impart to a lattice atom (the primary knock-on atom) enough energy to cause its displacement and the subsequent displacement of numerous secondaries. This process and the resulting local region rich in point defects is termed a cascade. Vacancies can be formed also by thermal processes, but interstitials are formed virtually only by irradiation. Nearly all the information available about structure and transport properties of interstitials comes from irradiation studies. In turn, an understanding of these properties is essential to understanding the effects of irradiation in reactors and in materials bombarded by ion beams. Characteristics such as diffusional migration and interaction energies link defect production to more permanent changes in structure and composition.

Point defects may have several fates (see Fig. 1). Vacancies and interstitials may recombine with each other, leading to no permanent change. Maximizing this process is the goal of designers seeking to make alloys resistant to radiation effects. However, some defects may self-cluster to form "dislocation loops" or may be absorbed at pre-existing or newly formed sinks such as "dislocations" or "grain boundaries." A grain boundary is the interface between crystallites, or grains, in a polycrystalline material. A dislocation loop is the line bounding the extra plane of atoms that make up a platelet of clustered interstitials. Similarly, some dislocations bound extra planes of atoms in the crystal. Dislocations can be formed both during thermomechanical processing and during irradiation. Some types of dislocations absorb interstitials preferentially, leaving a small excess of vacancies. These vacancies may cluster to form "cavities" ranging in diameter from 1 nm (currently the smallest size observable in the electron microscope) to over 100 nm. Cavities can be effectively stabilized by the insoluble rare gas helium, which is produced unavoidably during neutron irradiations by (n, α) transmutation reactions in which a neutron is absorbed by an atom of the alloy, which then emits an alpha particle (helium nucleus). Helium is often deliberately injected during ion irradiations to study its effects on defect processes in order to gain insight into its possible effects during neutron irradiations.

Besides these changes in microstructure, drastic changes in local composition can be produced. In an alloy, atoms of one type may preferentially exchange or couple with a diffusing point defect. Demixing (i.e., separation of the alloying constituents) of the alloy on a local scale can result from many events of this type. For example, the vicinity of a point-defect sink like a dislocation, grain boundary, or cavity, may be significantly enriched or depleted in certain elements. This phenomenon is termed "radiation-induced solute segregation." Consequently, "radiation-induced precipitation" of a new phase having a composition, structure, or properties different from that of the host matrix may occur, even though the alloy has the wrong bulk composition to undergo such a reaction under thermal conditions. Drastic changes in properties can be produced as a result of these microstructural changes.

The cavities resulting from the agglomeration of vacancies corresponding to the atoms that have been knocked out as interstitials and subsequently absorbed at dislocations to form new planes of atoms make up a volume that shows up as macroscopic "swelling" of the material, one of the most significant radiation effects. Swelling levels of several tens of percent can result from high-dose irradiations of structural materials like stainless steels. The cavities responsible for swelling are essentially empty, requiring only enough gas to stabilize them in their initial growth stages. However, cavities that are helium-filled bubbles are formed on grain boundaries, weakening the latter. In addition, the hardening of grain interiors against plastic deformation by radiation-produced defects and the simultaneous weakening of grain boundaries by solute segregation may lead to "embrittlement." Alloys irradiated to high doses can become so brittle that ductilities (elongations in a tensile test) may be reduced from tens to only tenths of a percent.

"Irradiation creep" generally occurs in materials that are stressed during irradiation. This volume-conserving, stress-directed shape change can exceed by orders of magnitude normal thermally activated creep. Its driving mechanisms are reminiscent of that responsible for swelling. A preferential partitioning of point defects again occurs. Dislocations having different relative orientations to the stress axis absorb slightly different ratios of interstitials to vacancies. Also, dislocations in groups absorb defects at different rates than do isolated dislocations. Thus, even though interstitials and vacancies are created by displacement in equal numbers, this asymmetric absorption can lead to net dislocation motion ("climb"), which in turn results in creep either directly or by enabling dislocations to slip from an obstacle.

Alloys not designed to resist these effects of neutron irradiation are generally inadequate for use in fusion and fission reactors. Large-scale efforts have, therefore, been mounted to design alloys for irradiation performance. The principles applied to obtain improvements in alloy design have been derived largely from basic studies of the physical mechanisms and kinetics of irradiated materials.

Historical Perspective

Some effects of irradiation on solids were first observed in the 19th century. Certain minerals known to have externally crystalline shapes were found to be internally glass-like, or amorphous. These anomalies were later explained as the result of irradiation over geological times by decay products of the naturally radioactive elements uranium and thorium contained in the minerals.

The radiation effects field got its real start, however, in the 20th century during the Manhattan Project. Some 40 years ago, Eugene P. Wigner at the Metallurgical Laboratory at the University of Chicago realized the theoretical possibility of displacing atoms by radiation with neutrons. Colleagues at Clinton Laboratories (later ORNL) carried out experiments in the graphite pile to test the theory. A quote from Wigner's 1946 paper "Theoretical Physics in the Metallurgical Laboratory of Chicago," (*Journal of Applied Physics 17*) marks the beginning of the field at ORNL: "The matter has great scientific interest because pile irradiation should permit the artificial formation of displacements in definite numbers and a study of the effect of these on thermal and electrical conductivity, tensile strength, ductility, etc., as demanded by the theory." Wigner, now an ORNL consultant, was director of Clinton Laboratories in 1946–1947.

In 1946 ORNL's Metallurgy Division was formed and staffed by metallurgists and physicists. In 1950 its radiation effects group led by the late Doug Billington became the Solid State Division, whose main purpose was radiation effects research. A fresh postdoctoral member of this group was Fred Young, now associate director of the division. From his early work on very high purity copper crystals to the present time, Young has influenced fundamental studies in the field and is a source of information about the diverse radiation effects on materials that were explored in those years, including changes in specific heat, electrical resistivity, corrosion, internal friction, and creep. Metals, plastics, ceramics, and semiconductors were studied. Understanding was at a very elementary level; much of the work involved probing various properties by all available measurement techniques. Irradiations were carried out at ORNL's Graphite

Reactor, Bulk Shielding Reactor (BSR), and Oak Ridge Research Reactor (ORR).

The Metals and Ceramics (M&C) Division (name changed from Metallurgy in 1962) re entered the field because of the emerging technological need for reactor materials that are resistant to neutron irradiation. It has since been involved in developing structural and fuel materials with appropriate irradiation properties for about one and a half dozen different reactors.

In 1953 work at ORNL was started on the aircraft propulsion nuclear reactor, where high-temperature performance was required. Very large reductions in the stress rupture life of the high-temperature structural alloy Inconel 600 were found after irradiation. It was later shown that this lowered resistance to stress rupture results from helium produced by transmutation reactions involving boron-10 in the alloy; the gas accumulated at grain boundaries and weakened them. The problem was solved by alloying with small amounts of titanium, which tied up the boron in the matrix and kept helium out of the boundaries. Jim Weir was prominent in these efforts to improve mechanical properties by microalloying; for his work, he received the Department of Energy's E. O. Lawrence Memorial Award in 1972. After he became division director in 1973, a very large effort in radiation effects was built up.

In the 1970s, the division developed aggressive programs for research in radiation effects under Jim Stiegler and Everett Bloom. These programs covered the three areas of alloy development for liquid metal cooled fast reactor structures, alloy development for fusion reactor applications, and basic research on the physical mechanisms of radiation effects. These efforts were in response to national needs and epitomize ORNL's response to its mission. At the same time, national efforts were mounted in other countries, especially England, France, Japan, Germany, and the Soviet Union.

Today the main efforts in radiation effects in the Metals and Ceramics Division are centered on microstructural and microcompositional changes and on their relationship to properties. In Art Rowcliffe's group, the main efforts are irradiating, characterizing, and testing developmental alloys for fusion reactor applications and feeding this information back to guide the development of improved alloys. In my group the emphasis is on understanding the mechanisms of radiation effects by means of combined theoretical and experimental research. The aims are to predict behavior during irradiation, to develop principles for altering microstructure and composition to improve alloys' resistance to radiation effects, and to explore the unique research opportunities made possible by the ability to displace atoms.

Research Capabilities

At ORNL we have extensive capabilities for research in these areas. The first low-temperature neutron irradiation device in the world operated at the Graphite Reactor. Its modern counterpart at ORNL, the sophisticated Low-Temperature Neutron Irradiation Facility (LTNIF) spearheaded by Ralph Coltman and Rich Kerchner, has recently begun operating at the Bulk Shielding Reactor (see sidebar on page 102).

The ORR and the High Flux Isotope Reactor (HFIR) are used extensively for high-dose, elevated-temperature irradiations both for basic research and for alloy development activities. For microstructural characterization, the Laboratory has a first-class center for state-of-the-art electron microscopy. The capability was built up initially under Stiegler's leadership in response to the demands for microcharacterization of irradiated materials. Under Jim Bentley's supervision, the facilities continue to evolve and the extensive capabilities are now being applied to a wide range of materials science research.

We have also developed unique capabilities for ion irradiations. Energetic ions from accelerators can produce atomic displacements that are qualitatively similar to those produced by neutrons from reactors. However, ion irradiations offer many advantages for research. Damage can be produced at rates 10^3 to 10^4 higher than in reactors, more flexibility exists in controlling variables, and accelerator experiments are much less expensive and difficult.

ORNL is one of the pioneering laboratories in applying ion beams in radiation effects research. We have developed a dual-beam facility consisting of 5-MV and 400-kV Van de Graaff accelerators. The higher-energy machine is used for heavy ions such as nickel or iron to produce radiation damage, and the smaller machine simultaneously injects helium or hydrogen (or both) to introduce artificially the important transmutation products that would be produced during neutron irradiations. Monty Lewis, assisted by Roy Buhl and Sy Cook, is largely responsible for the extensive application of ion-beam research in our experimental program (see sidebar on page 103).

In the 1970s, we began work on the kinetic theory of radiation effects. This work guides the experimental program and builds on its results. Much of my research effort has been concentrated in this area. The theory is based on the mechanisms and kinetics of defect reactions. An extensive mathematical framework has been developed in the form of a theory of reaction rates. It describes defect diffusion and agglomeration, the evolution of microstructural features, and the ultimate changes in macroscopic properties. Our combining of theory and experiments has rapidly increased our understanding of a variety of phenomena.

The Low-Temperature Neutron Irradiation Facility

From the earliest experiments, researchers studying radiation-induced damage to materials speculated that the defects produced by radiation in materials at room temperature might be mobile. If true, the interpretation of property-change measurements on an atomic scale would be difficult because defect self-interactions and interactions with intrinsic material defects would be occurring while specimens were being irradiated. To simplify the experimenter's task, a "stop action" approach was needed. Because defect migration is believed to be thermally activated, low-temperature irradiation experiments were performed in the hope that defects could be "frozen in."

In 1951 experimenters at ORNL's Solid State Division made the first low-temperature neutron irradiations at 80 K, using a liquid nitrogen cryostat located in the ORNL Graphite Reactor. The results of the first 80-K experiments confirmed earlier speculations about defect mobility and showed that even lower temperatures were needed to immobilize defects. Through the use of surplus refrigeration equipment from H-bomb tests at Eniwetok, ORNL workers achieved temperatures as low as 15 K in 1955. Although the new results were dramatic in exposing the complexity of defect interactions, immobilization still was not achieved. In 1958 the downward temperature push at ORNL reached 3.5 K, which proved to be cold enough to freeze in all radiation-produced defects except for those in a few die-hard elements such as cadmium, gold, silicon, and lead. Through the use of low-temperature irradiation facilities, researchers could retain all the defects produced during irradiation and then study their interactions under controlled postirradiation warm-up conditions.

During the 1960s low-temperature neutron irradiation facilities were built in France, Germany, Belgium, and Japan, and the field flourished for many years. During this time many of the properties of defects and their interactions were established, but not without controversy. One particular controversy had to do with the configuration of an atom displaced from its lattice site by irradiation.

Because the existing neutron irradiation facilities had become inadequate for the kinds of low-temperature irradiation studies needed, the Department of Energy (DOE) conducted a series of workshops beginning in 1982 to determine the needs of basic research and nuclear energy technology that could be met by an upgraded facility. In May 1983 DOE decided to construct a new Low-Temperature Neutron Irradiation Facility (LTNIF) at ORNL's Bulk Shielding Reactor (BSR). The LTNIF, which is a user facility, is available to qualified experimenters at no cost. The facility, which began operating in 1986, provides a combination of high radiation intensity and special environmental and testing conditions that were not previously available in the United States.

Main features of the LTNIF are:

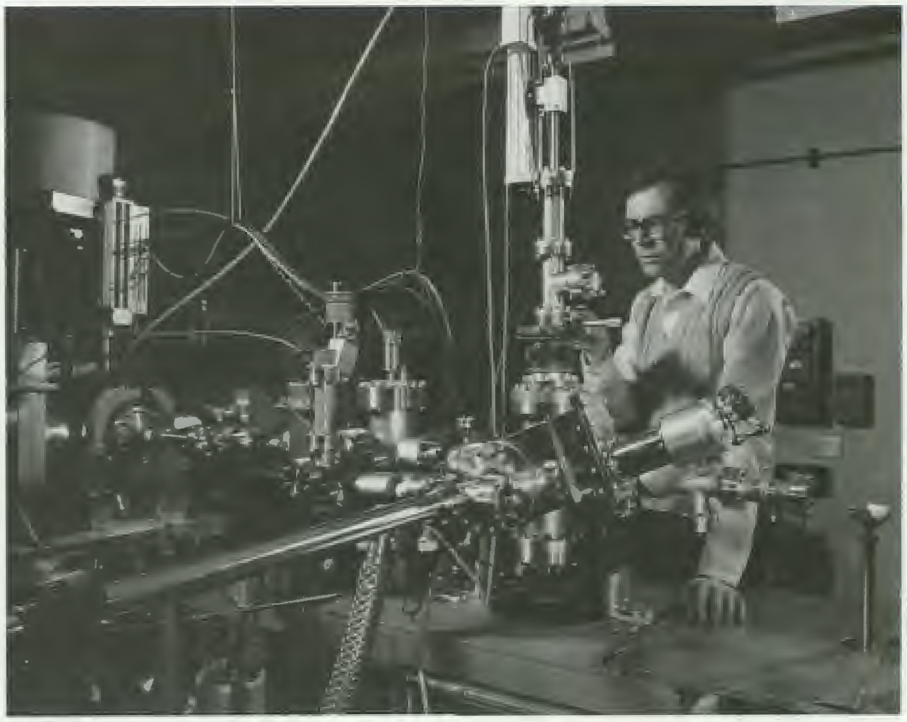
- Radiation characteristics at full BSR power (2 MW): fast neutron intensity $= 2 \times 10^{17}\ \mathrm{n/m^2 \cdot s}$ ($E > 0.1$ MeV), thermal neutron intensity $= 1.5 \times 10^{17}\ \mathrm{n/m^2 \cdot s}$, and gamma-ray intensity (in Al) $= 0.32$ W/g
- An active irradiation zone of 38 mm diameter × 250 mm long
- A 200-mm-diameter x 300-mm-long test chamber into which specimens can be moved without warm-up, located 1.5 m above the irradiation zone
- Irradiation temperatures from 3.5 to 350 K in the primary cryostat and up to 800 K in an auxiliary facility
- Transfer of specimens at 4.2 K into test devices or into vessels for shipment to other laboratories
- On-line data acquisition and computer capability
- A 12-T superconducting magnet test assembly for use at poolside and in the test chamber of the cryostat
- Irradiations with modified fast neutron spectra or highly isolated thermal neutrons or gamma rays
- An electron microscope facility for low-temperature studies of solids irradiated by neutrons at low temperatures, without subsequent warming

Our in-house research program on radiation effects in solids will be concerned with the production of defects in solids by reactor irradiation; the understanding of the configuration of defects in displacement cascades; the interactions between defects at high concentrations; the transformation of solids from crystalline to amorphous states by neutron irradiation; and the effects of reactor irradiation on the electrical, magnetic, and mechanical properties of solids. Outside experimenters make arrangements to use the facility by contacting the LTNIF Director, Rich Kerchner of the Solid State Division.—*Ralph R. Coltman, Jr., Solid State Division.*

Damage Production

The initial events leading to radiation effects involve the production of point defects by displacement. The earliest theoretical work in this area at ORNL was done by W. S. Snyder and J. Neufeld in the mid 1950s. They developed a method for calculating the number of vacancies and interstitials produced by neutron irradiations. Damage production is now a specialty in which many contributions have been made by Mark Robinson and Dean Oen on the theory and by the late Tom Noggle, Ralph Coltman, Jim

Dual Accelerators for Materials Research



Monty Lewis is responsible for the dual accelerator laboratory in the Metals and Ceramics Division materials research program.

ORNL's Metals and Ceramics Division currently operates two positive-ion accelerators for materials research. The first of these is a CN-type Van de Graaff built by High Voltage Engineering Company (HVEC) in the early 1950s. The accelerator name comes from the name of Robert van de Graaff, the American physicist who pioneered the method of positively charging a terminal to millions of volts by a rotating charging belt. When positive ions generated by an ion source in the terminal are subjected to an electric field outside the terminal, they are accelerated. Originally the ORNL accelerator was designed to produce ion beams of hydrogen (protons or deuterons) and helium (alpha particles) having energies up to 5 MeV. Since that time, it has been upgraded to produce beams of heavy ions (up to zirconium and molybdenum). Even the physical size of this machine has been increased to allow more space in the terminal for additional electronic devices.

The second accelerator is an AN type Van de Graaff, also built by HVEC in the early 1970s. This machine is much smaller and more compact than the CN and is designed to produce singly charged ions of hydrogen and helium up to an energy of 450 keV. Beams of nitrogen, oxygen, and other species can also be accelerated by the AN.

Both accelerators are aligned toward a single target chamber so that target samples can be bombarded simultaneously with two ion beams (dual-ion irradiations). For example, the CN can be set up to produce 4-MeV ions of iron (Fe^+), while the AN produces 300-keV ions of helium (He^+). The range of 4-MeV Fe^+ ions is similar to the range of 300-keV He^+ ions. In this way, the dual-ion irradiation produces a high density of radiation damage in the target from the Fe^+ ions and an accumulation of helium gas from the He ions. In practice, the energy of the He^+ is made to sweep automatically from 200 to 400 keV, so that the helium is deposited over a broad depth range, reducing the effects of depth uncertainties in the final microstructural analysis of the target sample. These conditions can simulate a situation similar to that of a neutron flux in a reactor. In a reactor, the neutrons produce the radiation damage and generate helium from the (n, α) transmutation reaction with the nuclei of various reactor structural materials. Helium turns out to be one of the most important transmutation products affecting the development of microstructure during irradiation.

The dual-ion facility can also be used to study the diffusion of gases in solids. In a typical case, the AN can implant deuterium into a target, and the CN can be used to measure the concentration vs depth profile of the implanted deuterium as a function of time and target temperature. To measure deuterium profiles the CN is used to irradiate the target surface with 1- to 2-MeV helium-3. These helium ions cause a nuclear reaction with the implanted deuterium, and the reaction products can be energetically analyzed by a surface barrier detector. An analysis of the energy spectrum of the reaction products yields helium depth and density information.

In some applications, the CN alone is used, for example, to irradiate layered targets causing the interface between two layers to "dissolve" even at low temperatures. This dissolution is the result of atomic collisions (initiated by the beam), which eject atoms from the lattice site in one layer across the interface into the lattice of the other layer. This is called "ion-beam mixing" and has many applications in science and industry that are not necessarily related to radiation-damage studies. In another example, a simple application of the CN is to implant metal ions into various metals or ceramics and produce a new alloy within a microscopic region of the host material. Because this can be carried out at relatively low temperatures, it is possible to produce metallurgical phases hitherto unknown.

Thus, ion accelerators offer a mechanism both to add or to rearrange atoms in the crystal lattice of a solid and to measure microscopically the resulting effect of such additions or rearrangements. These techniques have many applications in a large variety of energy-technology problems.—*Monty B. Lewis, M&C Division.*

Roberto, Jagdish Narayan, and others on damage-production experiments.

Two contributions of ORNL's theoretical work are especially relevant: the damage-production code MARLOWE and the Norgett-Robinson-Torrens (NRT) standard method of calculating damage production. The MARLOWE code currently is widely applied for calculating point-defect production. It gives, for example, the number of defects produced for a projectile of a given energy, the spatial dispersion of defects after most of the energy is dissipated, and the history of defect positioning. It works for any specified crystal system and is also used in sputtering and channeling calculations. Figure 2 shows a typical configuration of vacancies and interstitials in copper that was produced by the code.

The NRT method is generally used to estimate the effects of exposing materials to damaging radiation. The end result is a calculated number of displacements per atom for a given material and a particular kind of displacive particle irradiation. In a material that has received one displacement per atom, each atom has been knocked out of its lattice site once on the average. First, the incident particle interacts with an atom of the solid—the "primary knock-on atom" (pka). Each type of projectile of a given energy (e.g., proton, neutron, heavy ion) produces its own characteristic probability distribution of pka energy; this "pka spectrum" describes the likelihood that the displaced atom will emerge with a given energy from the collision. The displaced atom slows down both by losing energy to the electrons distributed throughout the solid and by displacing other atoms of the solid, which in turn may lose energy in similar fashion. This sequence is called a collision cascade. An important part of the method is a prescription for the partitioning of the pka energy into electronic and "damage energy." The damage energy represents energy transfer to nuclei. In a metallic alloy, only this energy causes atom displacements. A displaced atom must absorb a minimum level of energy (usually in the range of 10 to 100 eV), the "displacement threshold energy," to create a stable vacancy-interstitial pair; otherwise, it will not become sufficiently separated from its lattice site.

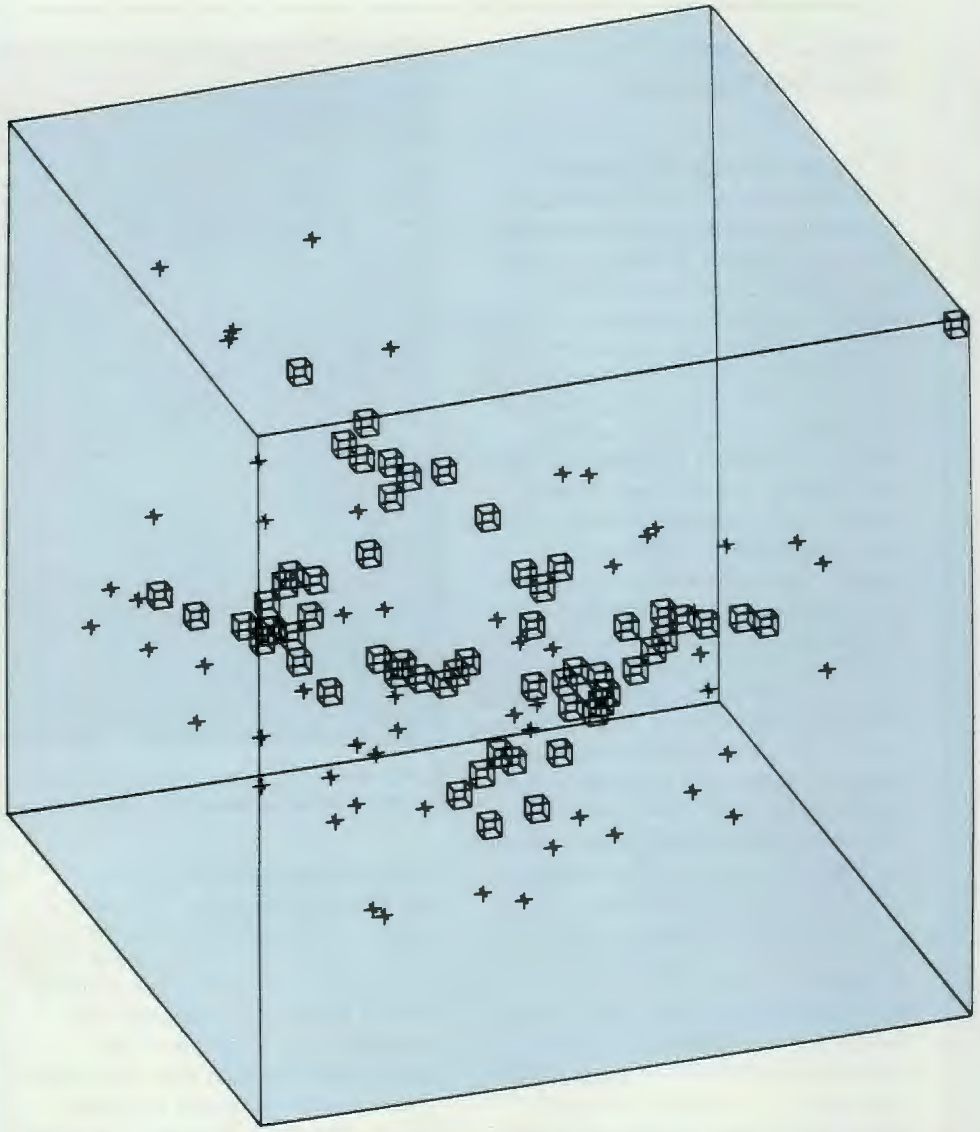


Fig. 2. Three-dimensional representation of a cascade. The energy of the initiating pka is 5 keV and the material is copper. Vacancies are shown as small cubes and interstitials are shown as three-dimensional crosses. Undisplaced atoms are not shown. The edge of the large cube is 20 lattice parameters, and the primary knock-on atom entered from the top. From the work of H. L. Heinisch of the Hanford Engineering Development Laboratory using the computer code MARLOWE developed by Mark Robinson of ORNL.

Using these concepts, the number of displacements can be calculated. First, the energy of a given pka is partitioned. The ratio of the damage energy to the average displacement threshold energy, when multiplied by a numerical factor, then gives the number of displaced atoms directly. When the number of displaced atoms for a given pka type and a given energy is averaged over the pka spectrum and over the incident projectile energy spectrum, the number of displaced atoms per unit incident particle flux is obtained.

A prediction of this model is that the damage produced by various kinds of radiation should scale with damage energy. An important technological question is whether the damage that would be produced in a fusion reactor, whose neutron spectrum will be rich in 14-MeV neutrons, can be related to the damage in fission reactors, where the mean neutron energy is about 1 MeV or less. Because fusion is in the research and development stage and no operating fusion reactors exist, no data are available on long-term damage effects; on the other hand, many measurements have been made of fission-reactor neutron damage. If it could be shown that the scaling with damage energy holds up, the number of displacements to be expected in a fusion reactor spectrum would be clear. The fusion irradiation could then be compared (at least with respect to overall displacements) with irradiations in a fission reactor.

Experiments were undertaken to demonstrate this comparison by a group including Jim Roberto, Charlie Klabunde, Jim Williams, Ralph Coltman, and Mike Saltmarsh. The experiments compared the retained point-defect concentration produced by high-energy neutrons centered about 15 MeV with that produced by fission-spectrum neutrons (centered about 1 MeV). The high-energy neutrons were obtained using the Oak Ridge Isochronous Cyclotron, which bombarded a beryllium target with 40-MeV deuterons, producing a broad neutron spectrum centered about 15 MeV. Based on damage-energy calculations, Robinson had predicted that the point-defect production in copper, niobium, and platinum would be about three times as high per unit fluence for the high-energy neutrons as for the low-energy neutrons. The results of the experiments agreed with his predictions within about 10%.

Kinetics and Microstructure

Defect transport and the evolution of microstructure, initiated by point-defect production, are responsible for wholesale changes in properties that can be produced by irradiation. To attack this complex area we have built up an understanding based on theory and experimentation. The theory of microstructural evolution encompasses aspects of diffusion theory, thermodynamics, kinetic theory, phase transformations, and mechanics. My co-workers in these theoretical developments have been Alan Brailsford of Ford Research Staff and Bill Coghlan (formerly of ORNL) of Arizona State University, recently joined by Dora Pedraza and Roger Stoller at ORNL.

Part of our research has focused on developing a fundamental understanding of cavity swelling initiation and determining what can be done about it. Helium generated by transmutation reactions or injected by accelerator is crucial in this picture. The theory shows that of the equal numbers of point defects generated, excess interstitials are absorbed on dislocations because of elastic interactions. This preference is termed the point-defect "bias." Excess vacancies are, thus, freed to agglomerate into cavities. This excess vacancy flux is countered by thermally driven vacancy evaporation from cavities; the evaporation is exponential in the ratio of the surface free energy to the cavity radius. If the cavity is pressurized, however, this thermal emission effect is partially counteracted. In general, a gas-pressure-dependent critical radius exists at which the net excess vacancy influx is precisely countered by thermal vacancy emission. For a critical number of gas atoms n^*_g the critical radius reaches a minimum r^*_c. If any more gas is added, the critical radius abruptly disappears and a cavity of any size containing more than this number of gas atoms will grow inexorably by excess vacancy absorption.

The theoretical result is extremely important because of several consequences. At high temperatures, where the critical radius and critical number of gas atoms are large, it is predicted that the critical number of gas atoms must be accumulated prior to the onset of swelling. Thus, because helium is related to the irradiation dose, the dose to swelling onset should be predictable. This concept is the basis of powerful tools for alloy design for swelling resistance. Another consequence expected is that the size distribution of cavities will be bimodal. Cavities having less than n^*_g should tend to be stable at sizes below r^*_c, whereas cavities having exceeded these critical quantities should grow. Thus, two distinct groups of cavities should be observed, separated by a gap that increases with increasing dose. Measuring the critical size directly in this way enables us to uncover some intrinsic material properties that are crucial to understanding and predicting radiation effects.

As an example of work in the first area, Eal Lee and I working under the basic material sciences program, together with Phil Maziasz and Art Rowcliffe of the fusion materials alloy development program, have been able to tailor alloys that are highly resistant to swelling. The idea is to delay the accrual of a critical number of gas atoms in a cavity and, thus, delay the onset of swelling. We developed a swelling-resistant material by adding phosphorus to an iron-chromium-nickel (Fe-Cr-Ni) alloy, thus producing needle-shaped particles of iron phosphides that were very finely dispersed throughout the material. These precipitates effectively "spread" the helium around as fine bubbles so it cannot collect in large enough amounts to provide n^*_g to any cavity.

Significantly, the phosphide precipitates were produced by irradiation, not by thermomechanical treatments, thus illustrating a peculiarity of tailoring alloys for irradiation applications. Often microstructures produced before irradiation are erased during irradiation. What must be built into an alloy, therefore, is the potential to produce desired features during irradiation. The enormous amount of precipitate-matrix interfacial area so introduced traps helium in a very fine distribution of bubbles. Using this technique, we found that the number of cavities can be increased by more than three orders of magnitude. For a given critical number of gas atoms per cavity (actually the required critical number is also increased by this alloying procedure—an added benefit), the time until the onset of swelling can be increased by a similar factor. Enormous delays in the onset of swelling and great increases in the amount of helium that can be accommodated have been demonstrated by this helium-dilution procedure. It is now possible to achieve doses that are >100 dpa (displacements per atom) and have gas contents greater than several thousand appm without causing swelling. In principle, even greater increases are possible. These numbers represent radical improvements over those alloys not designed to be swelling resistant (see Fig. 3), and the new phosphorus-doped alloys represent some of the most swelling resistant materials available.

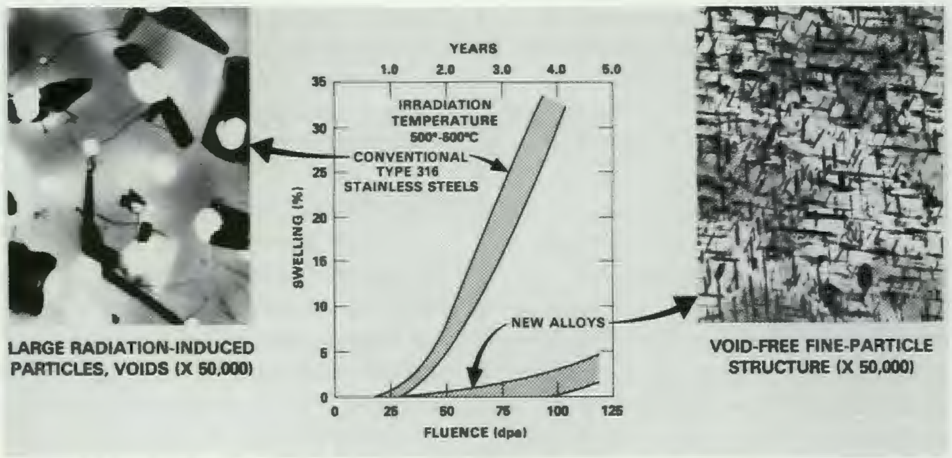


Fig. 3. During neutron irradiation, conventional stainless steels swell because of the formation of voids. The association of voids with large precipitates that develop during irradiation increases swelling. In the new phosphorus-modified alloys, swelling resistance is imparted by a very fine dispersion of phosphide precipitates and the elimination of the coarse precipitates. The fluence is given in displacements per atom, and the scale at the top is time of irradiation in a reactor such as HFIR.

Experiments to deliberately induce bimodal cavity size distributions have led to important insights. Eal Lee, Ken Farrell, Linda Horton, and Nick Packan have been involved in a number of experiments of this type. For example, physical reasons for the well known but unexplained variation in swelling in austenitic (face-centered cubic structure) Fe-Ni-Cr alloys having differing nickel contents have been uncovered by this work. Similarly, we have used this approach to understand the inherent swelling resistance of ferritic (body-centered cubic structure) Fe-Cr alloys. These alloys are respectively prototypes for the austenitic stainless and the ferritic steels that are of great technological interest.

In the early 1970s, Bill Johnston of the General Electric Research Laboratory discovered that swelling in Fe-Ni-Cr alloys during ion bombardment varied strongly with nickel content. The result was later confirmed in neutron irradiations. Many hypotheses have been formulated worldwide to identify the mechanism(s) for this effect, but none has been clearly successful. Recently, we devised experiments, based on theoretical considerations, that uncovered the cause. The critical experiment, which proceeded in two stages, involved two alloys, Fe-15Cr-15Ni and Fe-15Cr-35Ni. The first stage was to produce bubbles that span the critical radius and critical number of gas atoms in both alloys by injecting the alloys with helium and then annealing them to produce stable helium bubbles. Our hypothesis was that if the critical radius is larger in the high-nickel alloy than in the low-nickel alloy, that difference could explain its greater resistance to swelling. So, after the anneal we carried out an irradiation of the two alloys with nickel ions. If our hunch was correct, the distributions in both alloys would be bimodal. The point of separation should be different in each alloy, however, with the high-nickel alloy separating at a larger r^*_c and the low-nickel alloy at a small r^*_c. The larger critical number n^*_g associated with the larger r^*_c in the high-nickel alloy would, of course, take longer to accumulate in a normal experiment in which helium and dose accumulate simultaneously. This delay might explain the high-nickel alloy's swelling resistance even when exposed to high radiation doses.

A rare event in science, the experiment turned out almost as we had predicted. As shown in Fig. 4, the high-nickel alloy indeed

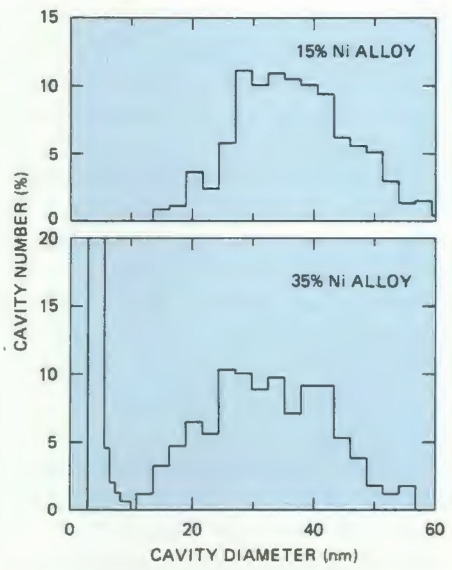


Fig. 4. Histograms of the unimodal (above) cavity size distribution for the 15% nickel (Ni) alloy and of the bimodal (below) cavity size distribution for the 35% Ni alloy observed after sequenced helium injection, annealing, and irradiation with Ni^+ ions to 40 dpa. This experiment showed for the first time that the critical cavity radius for swelling is different in the two alloys.

exhibited a bimodal distribution: r^*_c at the rather large size of 5 nm. However, the low-nickel alloy exhibited only a unimodal distribution. Our interpretation is that this distribution also actually did break up into a bimodal distribution (as required by the theory), but that we could not detect it because r^*_c in the low-nickel alloy was below the electron-microscope resolution limit (1 nm under these conditions). This insight suggests that the critical radii in the two alloys differ by a large factor. Theory shows that the corresponding difference in the required critical number of gas atoms would be greater than a factor of 20. Thus, there should be a corresponding difference in the radiation dose required to effect the onset of swelling. This prediction is consistent with observed results in experiments in which helium is introduced while ion or neutron damage is being inflicted; high-nickel alloys begin swelling at doses up to two orders of magnitude higher than the corresponding doses for low-nickel alloys.

However, as in all basic research, by answering this question, we have raised others that we suddenly became knowledgeable enough to ask. For example, why does the critical radius depend on nickel content? The answer appears to lie in the different kinds of dislocation structures that we discovered were produced in the two alloys. The dislocations determine the partitioning of excess interstitials to dislocations and the resulting flow of vacancies to cavities (the bias). We are now carrying out detailed analyses of microstructures in a variety of alloys of differing nickel contents to assess the origins of the dislocation differences.

Mechanical Properties

Another very important area of study for us is the connection between damage production and changes in mechanical properties. One of our recent major efforts applies a new theoretical approach—cascade diffusion theory—to understanding irradiation creep. To describe this, the theoretical approach must be outlined briefly. Conventional reaction rate theory views a material as an effective continuum wherein point-defect production and loss occur continuously in time and uniformly throughout. This continuum is an approximation to a real material in which point defects are produced in discrete bursts (cascades) and lost at discrete sinks (cavities, dislocations, grain boundaries, etc.). In the continuum theory, however, each point has an infinitesimal increment of point-defect sink and source character. Each point defect, in effect, is generated by an infinite number of infinitesimal contributions. This description is constructed to give the correct average production and loss rates over finite volumes and times.

The picture is simple and easy to use. We have shown it to be adequate for many purposes such as calculating the growth of large cavities or the irradiation creep rates that depend on long-term cumulative differences in point-defect absorption. However, by definition, it cannot recognize local fluctuations in defect concentrations or processes that depend upon them.

The picture revealed by the cascade diffusion theory has more fidelity to the actual situation. Fluctuations in local point-defect concentrations are extreme (see Fig. 5, which shows calculated point-defect profiles). Armed with this information, we could visualize a new mechanism of irradiation creep. A dislocation can be pinned on an obstacle (e.g., a precipitate) like a rubber band snagged on a peg. For the band to slip off the peg, it must climb over the peg. This climb is accomplished by the net absorption of one type of defect. When the dislocation climbs to the point where it slips off the obstacle, the slip leads to an increment of creep. Current models of irradiation creep generally invoke some cumulative partitioning of point defects resulting from a bias, so that the dislocation climbs inexorably in one direction. The cascade diffusion theory, however, shows that even in the absence of long-term net climb in one direction, the dislocation will execute up-and-down climb excursions in response to the unbalanced local fluctuations in point-defect concentrations shown in Fig. 5. There is a calculable probability that during one of these excursions, the dislocation will slip off the obstacle and undergo irreversible slip before it is pinned by the next obstacle. Our recent calculations quantify this effect and show that this creep mechanism may be responsible for a major component of irradiation creep.

Embrittlement, or loss of ductility, is another result of irradiation that can lead to serious technological consequences. Much engineering support work at ORNL has characterized the effect as a function of irradiation conditions and materials. Recently, we have been trying to obtain a more basic understanding of how embrittlement depends on radiation-induced changes in microstructure and microcomposition. Probing this dependence for embrittlement is more complicated than it is for swelling and creep; in the latter cases, point-defect absorption at microstructural features translates directly into volume and shape changes—the properties of interest. In embrittlement, however, changes in microstructure and microcomposition create essentially a new material. So we must go further to understand how this radiation-modified microstructure and microcomposition lead to loss of ductility through hardening of the matrix, weakening of the grain boundaries, and changes in crack-propagation behavior when the material is subjected to stresses.

Recent work by Ken Farrell, Bob Clausing, Lee Heatherly, and Nick Packan, is helping to clarify the situation. Part of their work is aimed at assessing the relative importance of three underlying mechanisms known to be involved: (1) helium accumulation, (2) solute segregation at grain boundaries and other microstructure features, and (3) hardening of the matrix (by cavities, dislocation loops, clusters, and precipitates). Figure 6 shows profiles of solute segregation near a grain boundary in a high-nickel alloy that becomes severely embrittled after high-dose neutron irradiation. The results of Auger electron spectroscopy at a fractured grain boundary have been obtained, together with the results on a similar boundary sampled from the bulk by analytical electron microscopy. The results are in qualitative agreement. During the fracture, helium was monitored and found to be present at the grain boundary. The combined application of these independent techniques to the problem of radiation-induced solute segregation at a grain boundary is a unique approach. The vicinity of the grain boundary is either enriched or depleted in the alloying elements. This demixing occurs by the persistent annihilation of point defects at the grain boundary throughout the irradiation. The material near the boundary as a result has much different physical and mechanical properties than does the bulk material. Work is now under way to show how solute segregation and helium at grain boundaries are linked to embrittlement.

Trends and Outlook

As a result of sustained efforts at ORNL and elsewhere, our understanding of swelling and irradiation creep is well advanced. Less effort is now required in these areas, and even more challenging areas can be tackled. Radiation-induced phase instability and radiation-induced embrittlement are two we have targeted. While we have been using ion beams mainly to study the effects of displacement damage, others like Bill Appleton, Woody White, Carl McHargue, and co-workers have been leaders in using ion beams in the burgeoning field of surface modification. Dividing lines between the disciplines are now disappearing. Ion-beam researchers are focusing more attention on questions of displacement damage, microstructural changes, and phase stability, while scientists who have developed ion-bombardment techniques for nuclear materials research are exploiting them for other materials science applications. Research plans in each of these areas are mentioned below.

In the area of phase instability, Eal Lee and Phil Maziasz have characterized extensively the

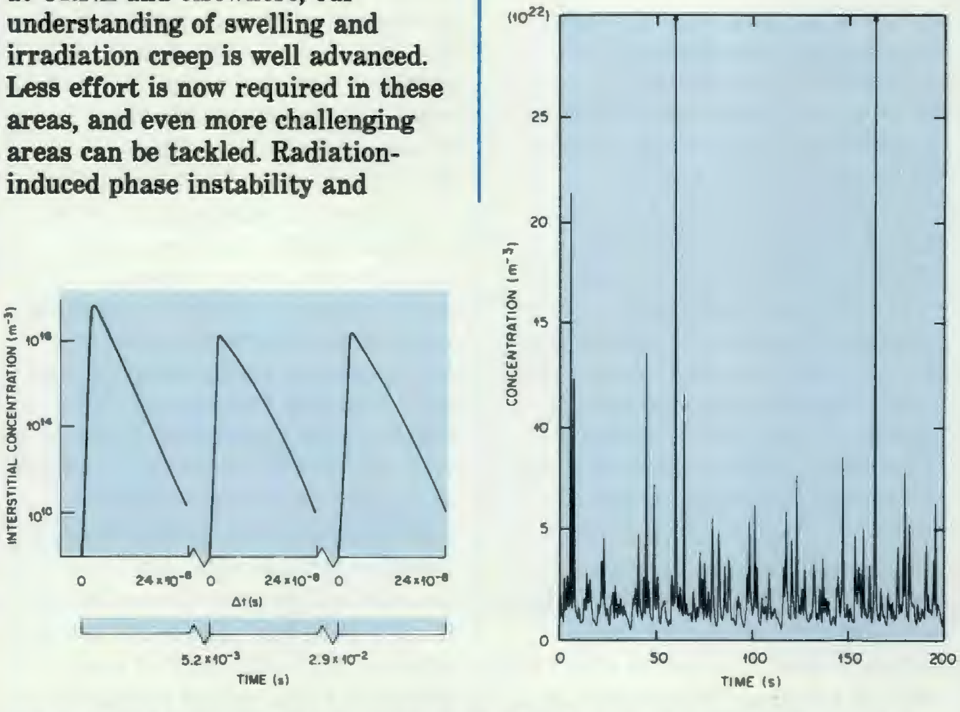


Fig. 5. Point-defect concentrations calculated using the cascade diffusion theory at an arbitrary reference point for a neutron irradiation of nickel at 500°C and 10^{-6} dpa/s (interstitial concentration on the left, vacancy concentration on the right). On the interstitial plot, two time scales are shown for this arbitrary selection of three cascades. The upper scale measures the duration of the concentration wave, and the lower scale measures the separation of waves from consecutive cascades.

radiation-affected phase changes in Fe-Ni-Cr base alloys. More basic work to understand the physical mechanisms has sprung from this effort. Recently, we began work in an area of extreme phase instability, where rather the crystal structure itself is eradicated—that is, the crystal is transformed to an amorphous state. Dora Pedraza is developing a theoretical model of radiation-induced amorphization. Ongoing experiments will shed light on the mechanisms involved in this fascinating and technologically important phenomenon.

Our work in embrittlement applies a threefold experimental approach using reactor irradiations, accelerator irradiations, and the "tritium trick." For the accelerator work, we are developing a special chamber to apply a stress during proton irradiation. Accelerator irradiation conditions can be more carefully controlled than corresponding reactor irradiations, and the accelerator approach is faster, less expensive, and more convenient. The tritium trick is another device to help with basic questions. Through it, helium can be introduced in the absence of atomic displacement by energetic particles. Here, tritium is allowed to diffuse into the specimen at the rapid rates characteristic of hydrogen. It then undergoes a β^- decay deep in the material to yield an atom of helium-3. Helium is, thus, readily "implanted" even into materials where its diffusion is essentially nil at temperatures of interest in many structural materials. Dave Braski and Ken Farrell are using this technique with good success to separate helium embrittlement from the other factors leading to embrittlement. Figure 7 shows results from Braski's work on vanadium alloys; initially, the material was ductile but after application of the tritium trick and the resultant implantation of helium, it fractured entirely intergranularly.

Work is also beginning in the relatively new area of ceramics irradiation. Comparatively little is known about the characteristics of irradiation response and even less about mechanisms. The materials are complex and offer high challenges for basic scientific understanding. They are also of technological interest in fusion reactor technology. The initial work of Linda Horton and Steve Zinkle in this area has examined the effects of helium on microstructural development because, in fusion applications, transmutation reactions are expected to produce high helium contents.

Part of our group's efforts will now be directed toward ion-beam modifications of surfaces. For example, we are conducting ion bombardments to produce very fine dispersions of phosphide and carbide precipitates because these microstructures have proven to be highly resistant to swelling. However, the fine dispersion also suggests a highly deformation-resistant microstructure by providing obstacles to dislocations. Thus, we are ion-beam treating surfaces to improve their mechanical properties through these precipitate reactions. We are also conducting experiments to amorphize or cause other phase changes in the surface regions of several alloys. By means of these treatments, we hope to radically improve the surface-sensitive mechanical properties by, for example, inhibiting surface crack initiation.

Another part of this ion-beam research, which is unrelated to surface modification, is directed toward deriving information on unique nonequilibrium materials or materials that are difficult to fabricate by conventional methods but can be obtained through ion-beam techniques. We expect to find unique microstructures and phase relationships and possibly superior mechanical and physical properties.

New facilities are being developed. The LTNF (see sidebar on page 102) is expected to become a world center for low-temperature radiation effects research. The HFIR is being modified to provide greater capability for high-temperature neutron irradiation. The CNR, now in the planning stages, promises greatly expanded capabilities for neutron irradiations. We are planning an important upgrade of our current dual ion-bombardment system consisting of 5-MV and 400-kV Van de Graaff accelerators. A new 2.5-MV accelerator will be added to permit simultaneous triple-beam ion bombardments.

We believe that the new accelerator is essential for the best research in ceramics. By bombarding with the present two accelerators, only one type of high-energy ion can be directed to the target. Thus, buildup of excess cations or anions cannot be avoided when using self-ions. However, it is well known that defect structure and behavior is sensitive to deviations from stoichiometry in ceramics. Thus, one application for the new system will be to inject cations and anions simultaneously in the correct stoichiometric ratio, so that displacement damage can be separated. With this capability, more general investigations will also be carried out by varying the ratio of beam currents to establish definitively the range of compositional effects on ceramics of interest. The small existing accelerator will be used to inject helium or hydrogen for investigations of interest to fusion-reactor applications (actually, four simultaneous beams are possible with these three accelerators). More generally, the triple-accelerator system will give us unique capabilities for research in the materials science of ion-beam modification.

In this article I have tried to show how the displacement of

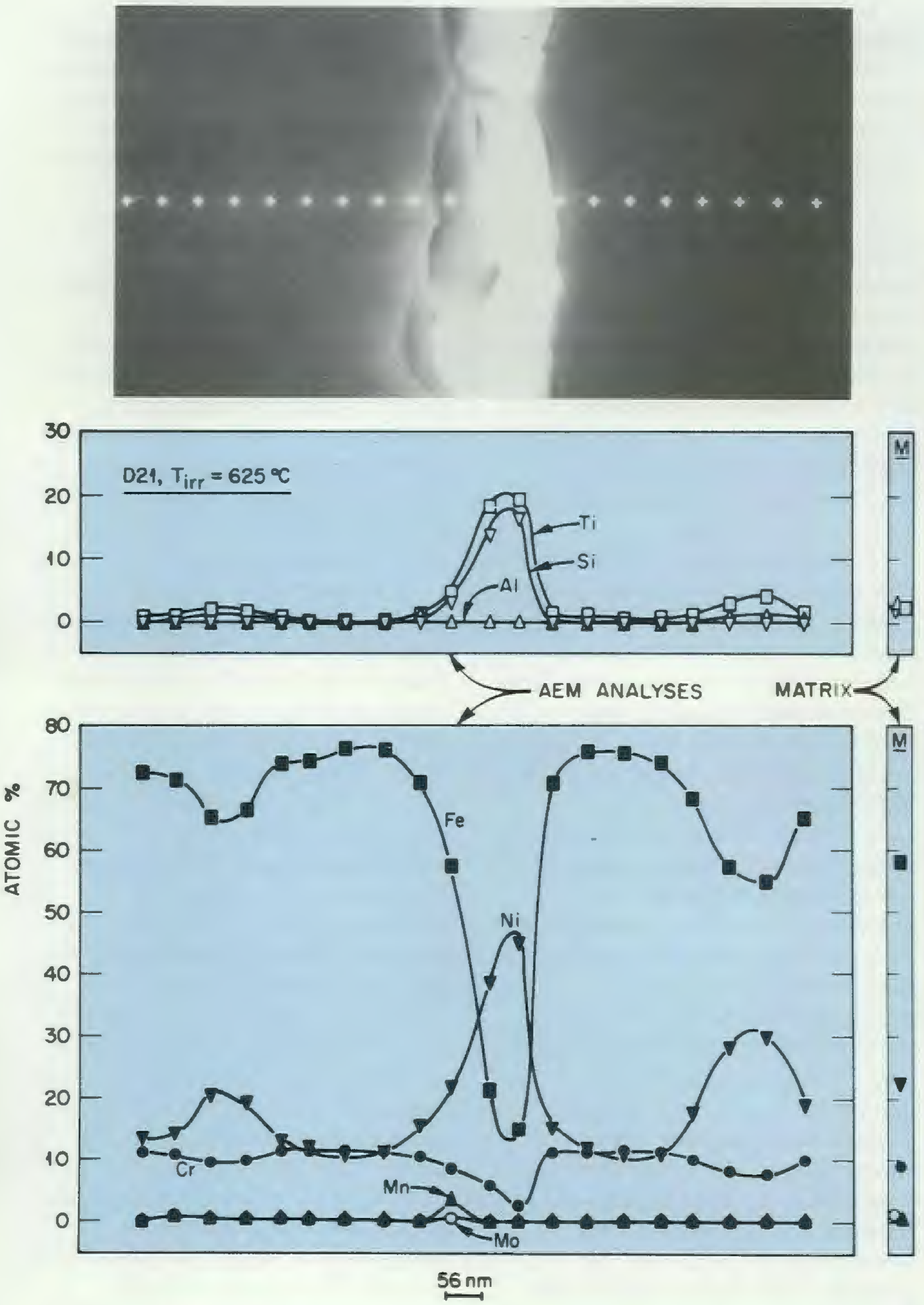


Fig. 6. Compositions obtained by analytical electron microscopy during a traverse across a grain boundary containing precipitates in a neutron-irradiated Fe-25Ni-8Cr base alloy. Significant enrichments and depletions of alloying elements are observed. The scale on the right marks the composition of the bulk material. The specimens were irradiated to 12 dpa at 625°C. The material was severely embrittled by this irradiation, showing very little ductility and exhibiting mainly intergranular fracture.

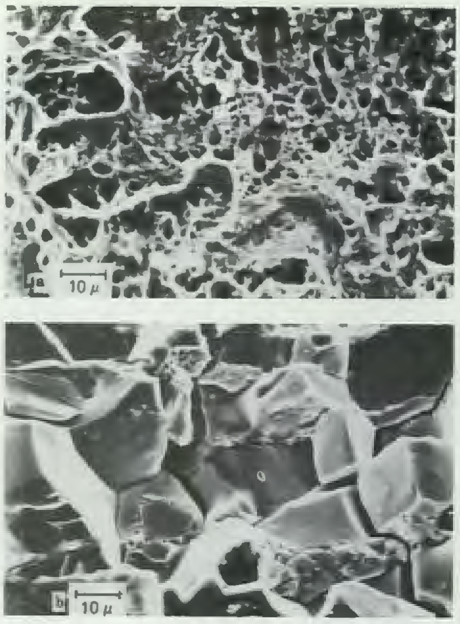


Fig. 7. Scanning electron micrographs of fracture surfaces of specimens of an alloy of vanadium-chromium-titanium (V-15Cr-5Ti) irradiated in the Fast Flux Test Facility in Washington to 40 dpa and tested at 600°C. (a) Specimen contains no pre-implanted helium and fractures in a ductile manner after a total elongation of 12%. (b) Specimen contains 74 appm of helium-3, pre-implanted using the "tritium trick." The helium forms relatively large bubbles on the grain boundaries and causes the specimen to fracture in a brittle manner along those boundaries after a negligible total elongation.

atoms by energetic-particle irradiation is at once the source of technological problems in the structural materials of fission and fusion reactors and the basis of unique capabilities in the hands of scientists who probe and manipulate the structure and properties of solids. Production of point defects by displacement as well as the phenomena of irradiation-induced swelling and creep in metals and alloys are now reasonably well understood as a result of sustained theoretical and experimental research.

I have already indicated the near-term directions of some of the research. For the long term it is perhaps best to view the research from a more general perspective: particle irradiation offers the possibility of disassembling and reassembling materials on an atomic level with respect to composition, structure, and defect microstructure in a manner that is otherwise generally inaccessible. All materials processes and properties are therefore potentially affected by particle irradiation. Exploring the underlying physics and discovering beneficial manipulations will remain among the most exciting and fruitful areas of physical research.

New Electron Microscope Advances Materials Research

Research into the relationship between structure and properties of materials is a never ending quest. Knowledge of structure-property correlations leads to deeper understanding of materials and often to the discovery of principles for the design of new materials having especially desirable properties. An important technique for reaching this goal is the rapidly evolving technology of analytical electron microscopy (AEM). Thus, members of the Electron Microscopy Group in ORNL's Metals and Ceramics Division are using AEM to characterize, at nanometer resolution, the microstructure and composition of materials having known properties so that structure-property correlations can be developed.

One contribution of AEM, in conjunction with atom-probe, field-ion microscopy, has been to reveal and characterize the fine-scale phase transformations that occur in stainless steel primary coolant pipes of nuclear reactors during low-temperature aging over many years. These phase changes have been linked to the degradation of the steel's mechanical properties.

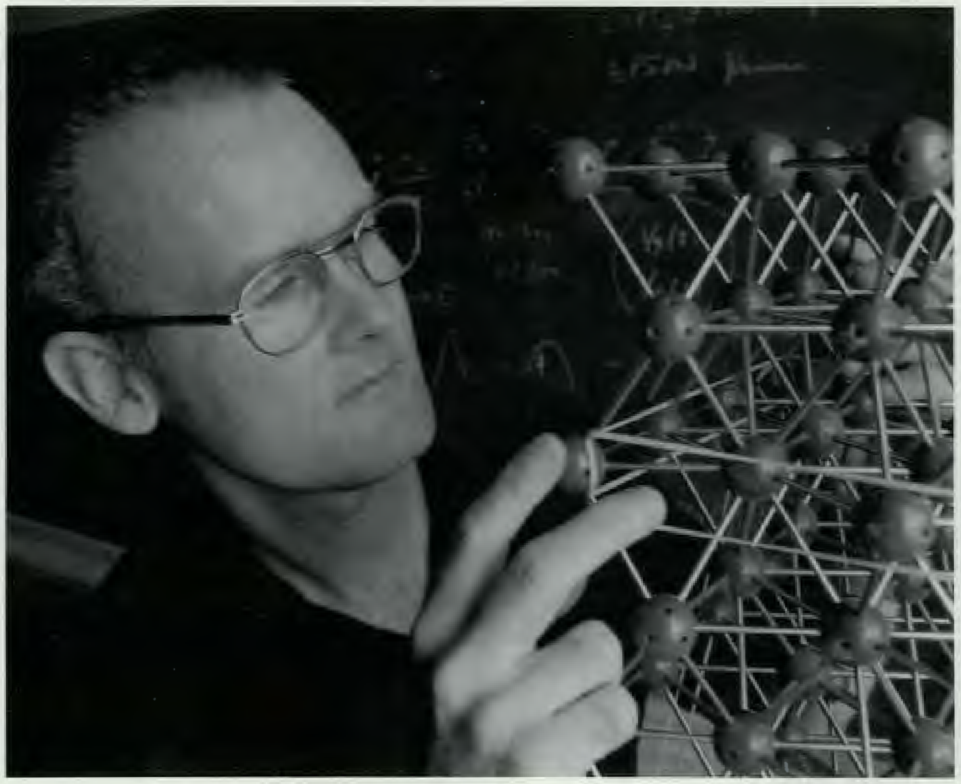
A new 300-kV Philips EM430T analytical electron microscope has been added to the battery of AEM instruments available to ORNL scientists in this field. This electron microscope is designed to outperform conventional 100-kV instruments. For example, the higher-energy electrons of this instrument penetrate the material more easily, allowing thicker specimens to be imaged. For electron-energy-loss spectroscopy, the allowable specimen thickness is increased by more than a factor of 2.

The resolution for the Philips AEM is ~0.23 nm compared with ~0.4 nm for 100-kV instruments. This improved resolution allows a direct interpretation of atomic resolution "lattice images" of the crystal planes of many materials. In addition, in the 300-kV Philips instrument, the sensitivity and spatial resolution of X-ray microanalysis are improved. A scanning transmission electron microscopy (STEM) attachment was added recently to satisfy additional analysis needs. Many ORNL experiments previously performed in the 1-MV high-voltage electron microscope (HVEM) can be carried out more productively in the 300-kV instrument because the latter has AEM capabilities, which the HVEM lacks.

The capabilities of the new instrument are already allowing the study of a wider range of materials behavior. New information should contribute to the development of superior structural materials needed by modern technologies.—*Jim Bentley, Metals and Ceramics Division.*

Jim Bentley studies the microstructure of materials using the 300-kV Philips analytical electron microscope.

John F. Cooke has been head of the Solid State Theory Section of ORNL's Solid State Division since 1981. Prior to coming to ORNL in 1966, he worked at the Atomic Energy Research Establishment in Harwell, England. A native of Florida, he received a Ph.D. degree in physics in 1965 from Georgia Institute of Technology. He has been a visiting scientist at laboratories in Denmark, the Federal Republic of Germany, and England. In 1986 he received a publications award from Martin Marietta Energy Systems, Inc. His research interests include magnetism, electronic structure, and many-body theory.



Theoretical Research on Solids

By JOHN F. COOKE

Theoretical research in the Solid State Division of Oak Ridge National Laboratory covers a wide range of disciplines and interests. This diversity results largely from close interaction with various experimental programs within the Division. Another contributing factor is the tradition of collaboration with other theoretical and experimental programs both within the United States and abroad. Such diversity enables the theory program to fulfill an important role—to provide backup and support as well as direction for the Division's research activities. Today the theory program addresses four solid-state areas: surfaces and interfaces, particle-solid interactions, electronic and magnetic properties, and laser annealing and rapid solidification. Because of the number and scope of current research topics, it is impossible to describe the overall program comprehensively here. Consequently, I have chosen a relatively few topics from each category to provide a representative account of the types of problems under investigation.

Ion-Solid Interactions

The detailed study of the scattering of atoms from solids forms the basis of a number of important areas of theoretical research, including the broad areas of ion damage and channeling. Originally, ion-damage research was synonymous with the study of radiation damage in fission reactor materials. Later, the field was expanded to include research in support of the fusion energy program. One important phenomenon in fusion reactors that must be understood is the unavoidable exchange of hydrogen isotopes (deuterium and tritium atoms) between the magnetically confined plasma and the walls of the confinement vessel. Unfortunately, direct measurement of the number and types of reflected particles is difficult because most of these particles, which strike the walls as ions (charged atoms), lose their charge as they rebound from the walls. The traditional approach to obtaining information about reflected neutral particles is to rely on computational models that have been fitted to experimental data taken at particle energies higher than those usually found in the containment vessel.

Ion damage studies are also of fundamental interest in a relatively new area of research, ion implantation. In this technique various ions are accelerated and then driven into a solid. A number of important consequences result

Theoretical research in ORNL's Solid State Division addresses surfaces and interfaces, particle-solid interactions, electronic and magnetic properties, and laser annealing and rapid solidification. Indications of the excellence of the work in the Solid State Theory Section are the many experimental verifications of the theories, publication of many papers from the group in prestigious physics journals, and the awards given to four section members in 1986 by Martin Marietta Energy Systems, Inc.

from this treatment. For example, it has been found that relatively small amounts of certain ions can drastically alter the properties of the original solid and, in some cases, create new alloys having useful properties. This method also creates considerable damage in the host material. In many cases this damage is unwanted, so a detailed understanding of the nature of the damage is needed to develop ways of minimizing or removing it efficiently.

To understand these and other problems, a theoretical analysis of the damage process is clearly needed. Usually the first and simplest approach is to develop phenomenological models to describe the process. Such models have been developed, but they oversimplify the physics to the extent that they do not contribute to an understanding of the details of damage production. For example, all collisions between particles were assumed to be elastic (i.e., billiard-ball scattering) and the crystal structure was ignored completely. To deal with this problem, Mark Robinson of the Solid State Division developed an elaborate computer code called MARLOWE in the late 1960s and early 1970s.

This program follows each ion striking a crystalline solid, collision by collision, until it either leaves the solid or comes to rest somewhere inside. The structure of the target solid is also correctly modeled. In addition, the program keeps track of all particles in the solid that are displaced by the incident ion and those that the displaced particles displace. In this way a detailed picture of all of the damage produced by the incident ion can be determined. The results predicted by this computer simulation are not exact because the interactions between all the particles involved in the damage cascade are only approximated. However, MARLOWE represents a giant step beyond the phenomenological models that are conventionally used to study damage in both crystalline and amorphous materials.

Over the years MARLOWE has been used to study a variety of problems too numerous to mention here. Some of the more recent work, in addition to the fusion and ion-implantation studies, has led to important insights into such problems as radiation-induced damage produced by high-level radioactive waste encapsulated in monazite (a mineral), self-sputtering yields of polycrystalline uranium, and the backscattering of ions from layered targets. One important and surprising result that has come from recent studies using MARLOWE is that the amount of energy lost in the near-surface region of a crystalline material is much smaller and that the amount of energy deposited deeper in the solid is larger than that predicted by model calculations. This result demonstrates clearly that model calculations are simply not reliable enough for studies of ion damage in solids.

One of the most significant discoveries that came out of research on ion damage was, however, an effect that ironically produces very little damage in solids. The discovery was made by Ordean Oen and Mark Robinson in 1962, using a computer program ancestral to MARLOWE. Because of the regular arrangement of atoms in a solid, open regions, or channels, extend along certain directions throughout the solid. If the incident ion beam is aligned with one of these channels, the ions can move through the solid without hitting much of anything, thereby creating very little damage. This effect is called channeling. If something happens to the solid to alter the normal order, then atoms may move into the channels, and dechanneling (scattering of channeled ions out of the channel) will result. This effect has been used to provide information about the extent to which the state of a solid is altered by the introduction of impurities. Interpretation of the experimental results, however, relies on a corresponding theoretical analysis. As in the case of ion damage, this effect requires detailed numerical simulation of the channeling process. An elaborate computer simulation code has been developed and used extensively by John Barrett at ORNL. One of the recent successes of his progam has been the demonstration that dechanneling could be used to measure the amount of misalignment that occurs when two different semiconductor crystals are grown together. Such studies of these so-called semiconductor superlattices are of great interest because of their potential use in optical and electronic devices.

Surfaces and Interfaces

The investigation of surfaces and interfaces has also been an area of intense theoretical activity. Surfaces and interfaces not only pose a wide variety of new and exciting problems to work on but also have great technological importance. To make any progress in understanding the complicated nature of surfaces, scientists must know the location of the near-surface atoms (i.e., the surface crystallography). During the past few years a combined theoretical and experimental effort carried out by Harold Davis and John Noonan has demonstrated conclusively that proper analysis of the measured scattering intensity of low-energy electrons incident on the surface can lead to a very accurate description of the surface structure. Low-energy electron diffraction (LEED), however, is difficult to treat theoretically because the incident electrons are scattered many times in the near-surface region before they emerge from the surface to be counted. Again, sophisticated computer programs are required to obtain accurate results for real materials. Calculations for various configurations of atoms are carried out, and results are then compared with experimental data to determine the atomic configuration of the surface.

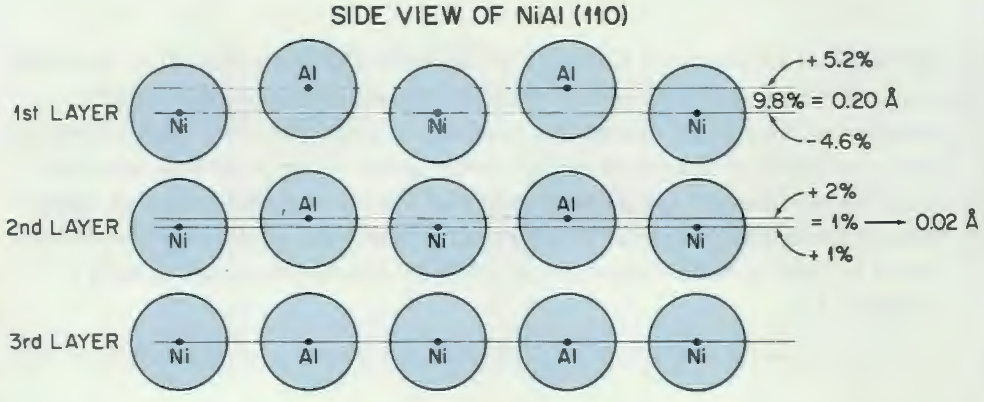


Fig. 1. Example of rippled relaxation at the (110) surface of nickel aluminide. Percentages refer to changes from bulk values.

LEED has been used with great success to determine the structure of many semiconductor and metal surfaces. Many different effects have been found. For example, the spacing between various layers of atoms in the near-surface region has been shown to vary with depth into the solid and to be different from the layer spacing deep in the solid, an effect discovered at ORNL and known as multilayer relaxation. In addition to this type of relaxation perpendicular to the surface, relaxation of the entire first plane of atoms parallel to the surface has also been documented. The most exotic case found to date, and another first for ORNL, is called rippled relaxation. Davis and Noonan of the Solid State Division discovered this phenomenon in a nickel-aluminide alloy. Deep in the NiAl solid, layers contain half nickel and half aluminum sites. Near the surface, however, the bulk layer consists of aluminum and nickel sites that actually split to form two separate layers in which the aluminum layer is displaced above the nickel layer. This effect is shown in Fig. 1, which also illustrates that layer splitting can occur deeper into the solids. Thus, many different types of relaxation are possible at surfaces, and great care must be taken to determine the correct type(s).

The study of realistic interfaces poses some problems different from those encountered in the surface interface case. For a start a real interface cannot be considered as a simple plane; most are rough at best. Such is the case for electrochemical devices. All such devices consist of a pair of electrodes immersed in an electrolyte. The process of transferring electrical charge from the electrode to the electrolyte is important to the operation of the device. It has been known for decades that such metal-electrolyte interfaces have unusual electrical properties that cannot be explained by theories that have been used in the past to study interfacial phenomena.

In an altogether different approach, Sam Liu and Ted Kaplan of the Solid State Division have successfully modeled rough interfaces by a fractal (see Liu's article on fractals in the ORNL *Review*, No. 3, 1985). A fractal is a geometrical object that looks the same regardless of the length scale used to examine it. The particular fractal used to model the rough interface is called the Cantor bar. By extending only the mathematics already developed for treating fractals, it has been shown that this model accurately describes the unusual electrical properties found experimentally, such as the universal power-law relationship between the impedance and the angular frequency with an exponent that varies only between zero and one. This novel approach of using fractals to model rough interfaces has helped our basic understanding of the electrochemical interface and may be an important step in understanding the characteristics of general interfaces that are technologically important to many other electrical devices.

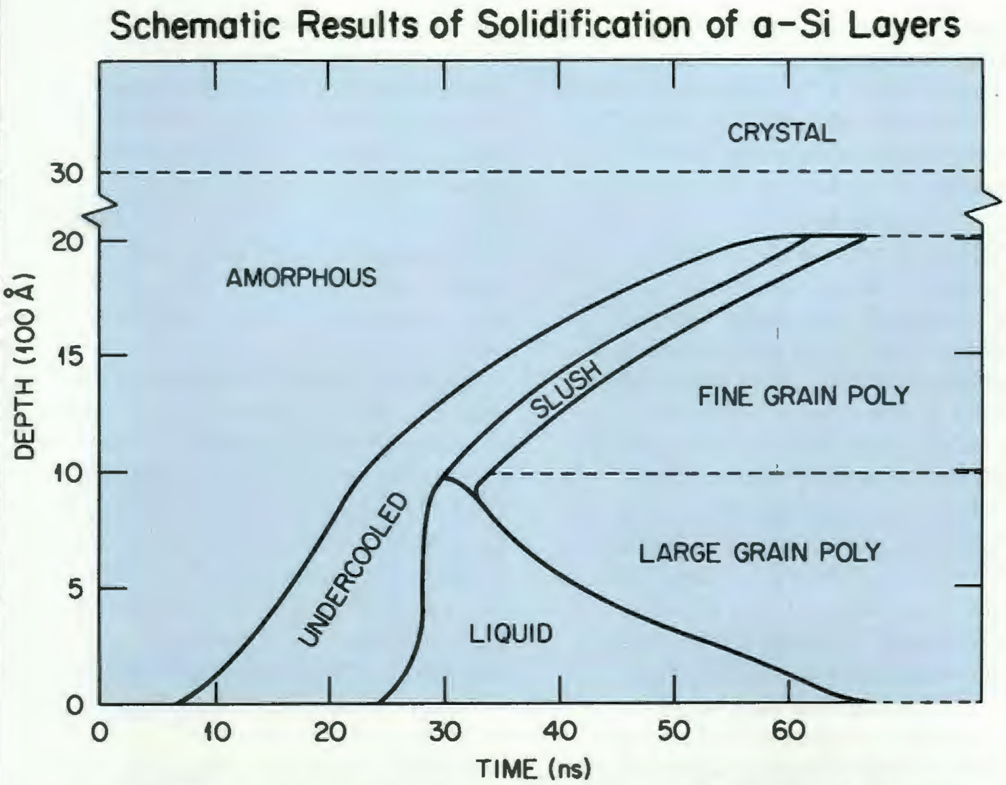


Fig. 2. Illustration of the calculated complex melting and solidification behavior of an amorphous (glassy) silicon layer irradiated with an intense nanosecond laser pulse. The "undercooled" region contains liquid silicon as much as 200° below the normal solidification temperature. The undercooled silicon solidifies as fine-grained polycrystalline material, while the normal liquid solidifies as much larger-grained material.

A different kind of theoretical problem occurs when an interface is set in motion. Phenomena associated with the rapid movement of liquid-solid interfaces have recently received widespread attention in connection with the irradiation of semiconductors with intense laser pulses. Pioneering work in the Soviet Union on laser annealing of ion-implanted semiconductors stimulated Rosa Young and other scientists at ORNL to study the use of lasers for making solar cells from silicon. A theoretical problem that arose concerned the specific mechanism for the annealing, or repair, of the damage to the crystal lattice caused by the ion implantation. Calculations first carried out by Jim Wang and Dick Wood at ORNL established that the annealing process almost certainly involved very rapid melting and resolidification. According to their theory, this process both removed lattice damage and incorporated the implanted dopant ions into the silicon lattice at concentrations that far exceed their normal equilibrium concentrations. Although the melting model was not universally accepted at the time, subsequent developments have shown it to be correct.

Because of the rapid motion of the melt front, the entire process is never in equilibrium, thus making reliable calculations extremely difficult. Nevertheless, ORNL mathematicians Gary Giles and Al Geist, working with Wood, have combined classical heat flow theory, phenomenological phase-change models, and the latest computational techniques with good success. Results from calculations of the distribution of dopants in the melted region were found to be in agreement with experimental data. These models have also been used to investigate the solidification process in highly undercooled silicon and germanium—that is, at temperatures below their normal melting temperature. Numerical results obtained from these models predict a remarkable variety of solidification phenomena, such as the existence of liquid and "slush" layers in the interior of a sample after the near-surface region has already solidified (see Fig. 2). Although these models have been useful in unraveling the complicated nature of the processes that occur, a more fundamental microscopic theory based on nonequilibrium thermodynamics is needed and is now being developed at ORNL.

Neutron Scattering and Theory

Because neutron-scattering experiments over the years have provided a wide variety of direct and useful information about solids, a close relationship has existed between the neutron-scattering and theory programs. Two important areas of collaboration have been lattice structure and magnetism.

Neutron-scattering experiments have helped determine crystal structure and obtain information about the types of vibration that can be excited in the lattice. Theory has shown that knowing the forces that hold a solid together is sufficient to determine the position of the atoms (the lattice structure) and the vibrations that the lattice can sustain. Much work has been done at ORNL to develop a general theory of forces accurate enough to predict the measured lattice structure and the lattice vibrational energies. Comparison of these predictions with the neutron-scattering results then provides a detailed test of the theory.

The problem with this approach has been that either the lattice structure or the vibrational information can be predicted accurately, but not both at the same time. In fact, recent studies of a highly publicized method for determining the lattice structures of arbitrary materials have been shown to yield complete nonsense for the vibrational spectra of materials having the so-called rutile structure. At ORNL a new approach to this problem has been developed by Mark Mostoller and Wang; this approach leads to reasonable agreement with the neutron-scattering data on both a material's lattice structure and its vibrations. Although further refinement of this approach is needed to improve the agreement, this work represents a major step in making use of neutron-scattering data to infer fundamental information about the forces that hold solids together and account for their mechanical and electrical properties.

From this research it became evident that the use of pairwise central potential models was inadequate for describing the lattice dynamics of solids having low symmetry. Pairwise central models assume that the forces between the atoms which hold the solid together act only between pairs of atoms at a time and are the same in all directions. Many of the models used in the past to describe the lattice dynamics of solids incorporate corrections to the pairwise central force model, but only in an approximate way. Jerry Mahan (University of Tennessee–ORNL Distinguished Scientist) and Mostoller have recently developed a theory that incorporates the most important correction terms exactly.

These correction terms correspond to an indirect force between the atoms. This indirect force can be visualized by considering a group of atoms consisting of a "central atom" and all adjacent atoms in the solid. If one of these nearest neighbors is moved, it causes the central atom to move and distort, thus exerting altered forces on the nearest neighbor atoms, and so on. Fortunately, the forces derived from this process were found to be short-ranged—that is, they apply only to the nearest neighbors of the central atom. Mahan and Mostoller showed that this indirect force contributes significantly to the lattice dynamics of alkali halides. Work is continuing to investigate the importance of this effect in other ionic crystals, particularly those having lower symmetry.

Since the development of quantum mechanics in the early part of this century, magnetism has been a subject of intense activity. As with many other material properties, any reasonable explanation of magnetism must begin with an accurate description of the electronic system—that is, the relative locations and energies of the electrons. Electrons in magnetic systems include those that are rigidly fixed to particular sites (localized) and those that are free to move throughout the solid (itinerant). The type of behavior that electrons exhibit is, of course, reflected in the nature of the electronic wave functions and energies. From this starting point, the wide variety of magnetic properties that have been observed in solids can be described. Neutron scattering is ideally suited for providing such information about magnetic systems because the scattering of the neutrons by a solid results from the interaction of the neutron spin with the spin of electrons and nuclei in the solid. (The spin of these particles produces the magnetism.) This information is vitally important for testing proposed theories.

One example is the measurement of a quantity called the magnetic form factor, which depends directly on the electronic wave functions. Comparison of results from theoretical calculations of this quantity with measured values provides a sensitive test for wave functions. This test can be carried out for essentially all intrinsically magnetic materials as well as a large number of materials that can be magnetized by application of an external magnetic field. Calculations of the magnetic form factors for localized electron systems have been made for many years at ORNL. Only during the past two years have realistic calculations been undertaken for itinerant electron systems. This delay in performing these calculations stemmed from the complicated nature of the theoretical expression and the need to develop accurate numerical techniques for evaluating it. Numerical results for the magnetic form factor have been obtained by Liu and me at ORNL for all of the itinerant electron materials that have been studied experimentally.

The general conclusion of this large body of work is that the electronic wave functions generated by the itinerant theory of magnetism are, for the most part, in good agreement with experimental results. In some cases, however, the agreement is poor. Now that reliable methods have been developed to generate the form factors, work can begin on refining the theory to provide a more accurate description of the electronic system.

The study of magnetic excitations called spin waves in the itinerant magnets nickel and iron provides an excellent example of how theory and experiment working together can lead to new and quite unexpected results. For

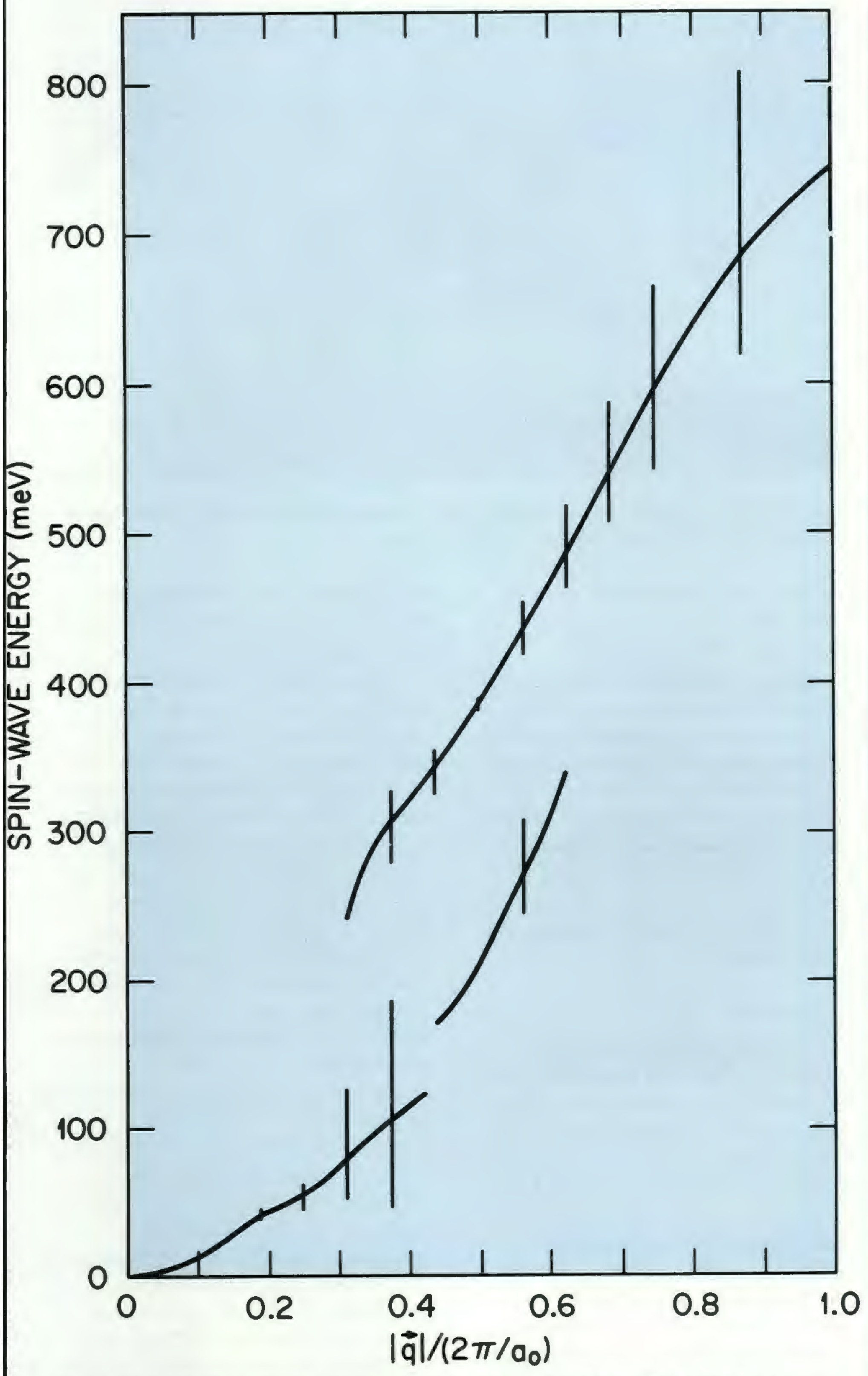


Fig. 3. Theoretical prediction of spin-wave energies along the <100> direction for ferromagnetic iron. The vertical lines indicate the half widths of spin-wave peaks in a neutron-scattering experiment. The measurement of energies above about 150 MeV is not possible using conventional steady-state reactor sources but would be possible in the Center for Neutron Research reactor proposed by ORNL.

over 50 years scientists have argued about the origin of magnetism in materials like nickel and iron. Much of the controversy centered around whether the electrons responsible for the magnetism were localized or itinerant. Itinerant electron theory predicted spin-wave behavior, which in certain respects was quite different from that expected from a localized picture. Spin-wave behavior, therefore, represented an important test for the proposed theoretical models.

Fortunately, neutron-scattering experiments provide the precise type of information about spin waves that enables scientists to differentiate between the localized and itinerant models. Experiments carried out at ORNL's High Flux Isotope Reactor (HFIR) in combination with theoretical work by Davis and me established the validity of the itinerant theory in nickel and iron. The theoretical calculations based on the itinerant theory also predicted that spin waves in nickel might exist at energies higher than could be reached in HFIR.

Recent theoretical calculations that I have done with others have indeed revealed, quite unexpectedly, a rich picture of spin-wave behavior in nickel and iron at energies well above the range of energies that can be studied at HFIR. Some theoretical results for iron are shown in Fig. 3. The bottom segment of the spin-wave spectrum was measured at HFIR and agrees with the theoretical prediction. Unfortunately, the higher-energy part of the spin-wave spectrum cannot be measured at HFIR because of the relatively small flux of high-energy neutrons. The recent upgrade of the hot source at the Institut Laue-Langevin (ILL) reactor at Grenoble, France, combined with the availability of large crystals of nickel and iron grown at ORNL, have made it possible to investigate experimentally at least part of this higher-energy range. Experimental results obtained thus far have confirmed the theoretical predictions for both nickel and iron. The search for even higher-energy spin waves in these materials poses an exciting challenge for experimentalists working at the limits of capability of steady-state reactor sources, and provide a novel experiment for newly developed spallation neutron sources. Research on these materials could also continue in the mid 1990s at ORNL's proposed Center for Neutron Research, which will have the world's highest neutron flux; like the ILL, the CNR should yield important information for future theoretical research.

Quantum Hall Effect

The application of external magnetic fields to materials sometimes produces effects that lead to the discovery of new phenomena. Such is the case of the quantum Hall effect. In 1980 K. von Klitzing discovered that when a large magnetic field was applied to the semiconducting material gallium arsenide, a quantity called the Hall conductance was found to change in abrupt steps as the magnetic field was continuously changed. The amount of the change was always found to be in integer multiples of a certain basic number. Later, systems were found for which the Hall conductance changes by certain fractions of the same number—the fractional quantum Hall effect.

In some recent work at ORNL Mark Rasolt proposed yet another interesting effect for systems displaying the fractional quantum Hall effect. He predicted a new type of excitation for silicon placed in a large magnetic field; as a result of this excitation, silicon behaves much differently than do other semiconductor materials under similar conditions. In particular, he predicts that some of the abrupt changes found in the Hall conductance of other materials will not occur in silicon unless the crystal is strained. This new prediction will significantly expand the original scope of theoretical and experimental work in an area of solid-state physics that has recently attracted the Oliver E. Buckley and Nobel prizes.

Sam Liu, Jerry Mahan, John Cooke, and Harold Davis (from left to right), theorists in the Solid State Division, discuss many-body theory.

Conclusion

The long-range impact of this research is difficult to predict, but the ORNL work already has had some gratifying consequences. The results of the research described in this article has been published in 13 articles in *Physical Review Letters* (as well as numerous articles in other journals) during the past two years. In 1986 four Martin Marietta Energy Systems awards were presented to members of the Solid State Theory Section: Davis for work on the theory of low-energy electron diffraction, Liu for work on fractals, Rasolt for work on dilute Bose systems and the quantum Hall effect, and me for work on high-energy excitations in itinerant magnets.

Many of the article's examples rely heavily on the use of large-core, high-speed computers. The development of this tool together with relevant numerical techniques have helped to remove theoretical research's past stigma of being "ivory tower" in nature. Relatively accurate numerical predictions based on complicated theory can now be obtained in many cases for realistic systems. This capability provides not only better tests for theory but an indispensible tool for the analysis of data from experiments that are not sufficient by themselves to lead to an adequate understanding of complex solid-state phenomena. Important advances in solid-state research tend to come from completely unexpected sources (e.g., quantum Hall effect, superconductivity, Josephson junctions, channeling, etc.). It is, therefore, difficult to predict the future course of theoretical research; this unpredictability, however, keeps the field exciting.

Mathematical Sciences Research at ORNL

By ROBERT C. WARD

The name mathematical sciences is increasingly being used to denote collectively the intertwining disciplines of pure mathematics, applied mathematics, statistics, computer science, optimization, and operations research. Oak Ridge National Laboratory is currently engaged in active research in three of these disciplines: applied mathematics, computer science, and statistics. This article provides a brief historical setting for mathematical sciences research at the Laboratory and presents some recent accomplishments in this growing field.

Mathematical sciences research at Oak Ridge National Laboratory began with the formation of the Mathematics Panel by Alston S. Householder in 1948. In the 1950s Householder attracted a number of

Bob Ward is head of the Mathematical Sciences Section in ORNL's Engineering Physics and Mathematics Division. He received a B.S. degree in mathematics from Tennessee Technological University, an M.S. degree in mathematics from the College of William and Mary, and a Ph.D. degree in applied mathematics from the University of Virginia. After working at NASA Langley Research Center for eight years, Ward came to ORNL in 1974 as a numerical analyst with research interests in matrix computations and error analysis. He currently serves on the Society for Industrial and Applied Mathematics (SIAM) Council and is chairman of the SIAM Activity Group in Linear Algebra. He has also been elected Fellow of the American Association for the Advancement of Science. Here, Ward (seated) reviews one of the Mathematical Sciences Section's reports with (from left) Michael Heath, Alan Solomon, and David Gosslee.

excellent mathematical and computational scientists to his staff and spearheaded the effort to acquire and operate one of the nation's early vacuum-tube computers—the Oak Ridge Automatic Computer and Logical Engine (ORACLE). By 1962 the panel, together with the personnel associated with computer operations, had become the Mathematics Division at the Laboratory. Distinguished mathematicians, statisticians, and computer scientists at the forefront of research in their disciplines (e.g., Walter Gautschi, Wallace Givens, David Hoel, Alan Kimball, and G. W. Stewart) spent many fruitful years of study and research at the Oak Ridge federal facilities during the 1950s and 1960s.

In addition, Oak Ridge was a regular stop for visiting researchers in the mathematical sciences from across the nation, as well as from foreign countries. Many organizational changes made in the 1970s and early 1980s reflect the effect of computers and mathematics on scientific research. Currently, research in the mathematical sciences is carried out within ORNL's Mathematical Sciences Section, which became part of the Engineering Physics and Mathematics Division in 1984.

The Mathematical Sciences Section has two main objectives: to perform research in the mathematical sciences germane to the solution of national energy problems and to consult and collaborate with other scientists working on these problems. Funding support for our basic research has primarily come from the Applied Mathematical Sciences Program and the Office of Health and Environmental Research, both in the Department of Energy Office of Energy Research. Our consulting expertise has been used and supported by projects spanning almost all scientific disciplines and ORNL divisions.

Research performed at ORNL in each of three disciplines—computer science, mathematics, and statistics— is described in detail below. Much of the technical content for these sections was provided by several members of our research staff: Michael Heath (Computer Science); Len Gray, Alan Solomon, and George Wilson (Mathematics); and John Beauchamp, David Gosslee, and Toby Mitchell (Statistics).

Mathematical sciences research at ORNL has a long and rich tradition extending back to 1948. Today ORNL's Mathematical Sciences Section performs research in computer science, mathematics, and statistics relevant to national energy problems and consults and collaborates with other scientists working on these problems.

Computer Science

Because of the central importance of linear algebra in the formulation and solution of many problems in science and engineering, matrix computations have traditionally been the area of greatest emphasis for research in computational mathematics at ORNL. Both "Householder reflections" and "Givens rotations", two of the most fundamental tools of numerical linear algebra, were pioneered at the Laboratory in the 1950s. They have been applied to such important problems as the solution of linear systems, least-squares problems, and eigenvalue problems. In the years since, algorithms and software developed at ORNL for such matrix computations as generalized eigenvalue problems and the matrix exponential have become standards. Recent efforts in this area have included algorithms for linear dependency analysis, the singular value decomposition of a matrix product, and the solution of M-matrix problems arising in queuing networks and Markov chains.

The association of ORNL with research in matrix computations began with a series of International Symposia in Numerical Algebra organized by Householder. The first symposium was held in Gatlinburg in the late 1950s. Even though subsequent symposia have been held at 3-year intervals in such diverse locations as Chicago, Albuquerque, Munich, Asilomar, Oxford, and Waterloo, they have retained the informal name "Gatlinburg." The series will return to Tennessee in 1987, when *Gatlinburg X* will be held at Fairfield Glade.

By the late 1970s, the research emphasis at ORNL turned to the development of algorithms for large sparse-matrix computations, that is, computations on matrices with a large number of rows or columns but containing only a few nonzeros. Such matrices are abundant in scientific computing, e.g., in numerically solving partial differential equations and network and optimization problems. ORNL-produced algorithms and software have become standards for large sparse problems in the areas of linear least squares and eigenvalues of symmetric matrices. ORNL also sponsored international symposia on sparse-matrix technology at Knoxville in 1978 and at Fairfield Glade in 1982. Work in sparse-matrix computations is expected to remain a cornerstone of computational mathematics research at ORNL; the primary emphasis will be the development and implementation of algorithms for solving sparse-matrix problems on advanced computer architectures.

In the past two years we have begun a vigorous new research program in parallel computing. Our objective is to develop general methodology and specific algorithms for effectively using multiprocessor computer architectures for solving scientific problems. This emerging new generation of computers potentially enables significantly higher performance than conventional single-processor machines but places much greater demands on the algorithm designer and programmer.

The initial emphasis of our research in parallel computing has been focused on matrix computations. We have developed parallel algorithms for several matrix factorizations, including Cholesky factorization of symmetric positive definite matrices, LU factorization by Gaussian elimination with partial pivoting, and QR factorization by Givens rotations. Using these factorizations as direct methods for solving linear systems, we have attained very high speedup and processor utilization by pipelining operations on successive columns or rows of the matrix. Figure 1 shows the number of processors that are active at any point in time during the computation of the Cholesky factorization of a sparse matrix on a hypercube parallel computer having eight processors plus the host. We have also developed parallel algorithms for eigenvalue problems, including a parallel version of the QR iteration and a parallel-block Jacobi algorithm that uses systolic arrays (special-purpose numeric processors) for solving subproblems. The problem domains we have considered include both dense and sparse matrices, and the computer architectures include both shared-memory and distributed-memory systems.

In addition to extending our matrix computation research into this new domain, our research now includes other areas of computer science: operating systems, networks, languages for parallel computation, software tools for debugging parallel algorithms and analyzing their performance, interprocessor communications, and computer security.

In July 1985, we acquired an Intel iPSC/d6 hypercube multiprocessor having 64 processors (nodes) and 32 megabytes of random access memory. This parallel computer was the first commercially built hypercube of dimension 6 and has been used as an experimental machine for our parallel computing research on distributed-memory systems. The availability of this computer has naturally focused much of our recent attention on developing algorithms specifically for the hypercube. In addition, a Sequent Balance 8000 multiprocessor having 8 asynchronous processors was acquired in February, 1986, providing a shared-memory machine for experimentation. We have also developed several hypercube simulators, including one that uses the Sequent's parallel capabilities, which aid greatly in debugging and performance analysis of parallel algorithms.

Our work on the Intel hypercube, the Sequent computer, and the simulators has produced some interesting conclusions:

- To attain high performance, the size of the problem must be significantly larger than the number of processors assigned to compute its solution. For example, for dense systems of linear equations, the order of the matrix should be at least an order of magnitude larger than the number of processors. This difference is expected to be significantly greater for sparse matrix calculations.
- The original design of algorithms and data structures may be more difficult for distributed-memory systems, but such algorithms seem less prone to subtle synchronization errors than shared-memory algorithms.
- Maximizing concurrency and minimizing communications for hypercube algorithms are often conflicting objectives. Which is more important depends partly on the relative speeds of computation and communication and on the algorithm. Again using the linear system example, "wrap" mapping (assigning columns to processors like dealing cards) requires more communication but has much better concurrency than "block" mapping (assigning contiguous columns to the same processor); thus, wrap mapping is uniformly superior.

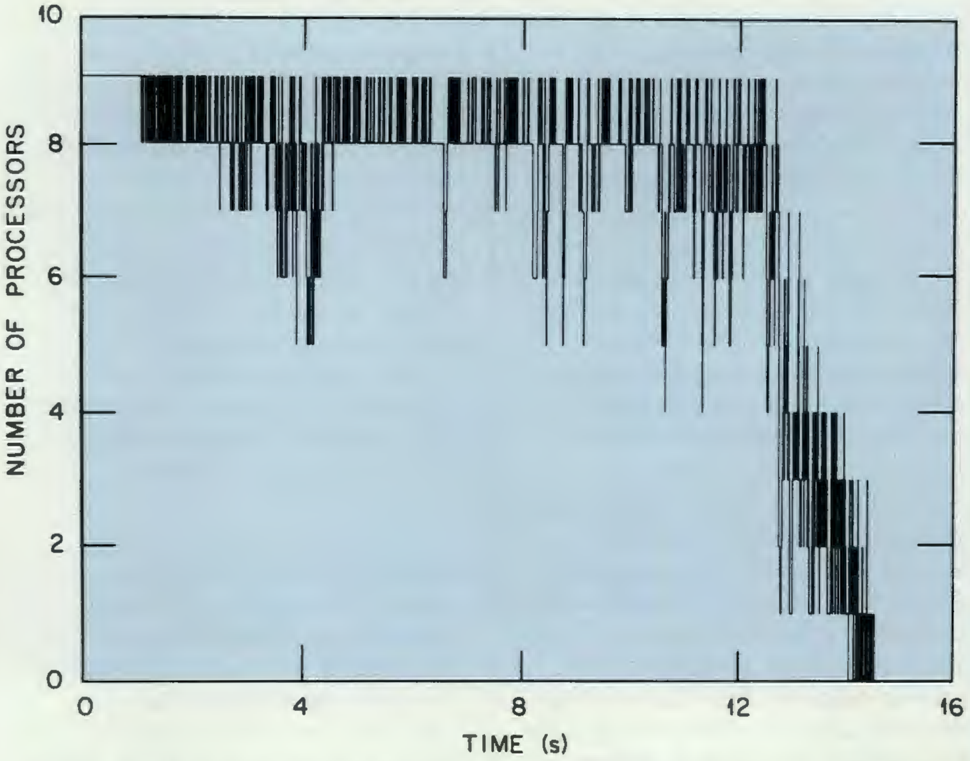


Fig. 1. Number of processors active every 25 microseconds during Cholesky Factorization of a sparse matrix. The matrix is of order 406 and contains 2310 nonzero elements. The combined average utilization of all the processors is 86%.

- A straightforward implementation on the Intel hypercube of a parallel algorithm for a general message-passing environment will produce speedups in the range of 50 to 60% of the theoretical maximum for sufficiently large problems. After fine tuning the code, speedups in the range of 70 to 90% can be attained.
- Some hardware and software changes should be made in today's commercially available hypercubes. Each node should have a separate communications processor and at least four megabytes of memory, and the operating system should allow for optimal broadcasting of messages using the full richness of the hypercube connectivity.

Mathematics

The process of materials passing through a change of phase (e.g., melting, solidification, crystallization) occurs in many scientific and engineering applications, and the mathematics for describing these problems has long posed a challenge to applied mathematicians. The pioneering work of the 19th-century German mathematical physicist, J. Stefan, leading to the formulation of the problem of predicting the freezing rate of a material, arose from his fascination with the depth and formation of polar ice caps. Whether in the prediction of the strength of welds, the time needed to destroy unwanted tissue by cryosurgery, the amount of thermal energy stored by solidifying wax, or the methods used in optimally performing continuous metal castings, mathematical modeling and analysis of phase-change processes are essential.

ORNL began research into phase changes in the mid 1970s by investigating mathematical problems in the slightly broader field of moving boundaries. These problems are concerned with diffusion-controlled processes in an evolving region whose boundaries must be determined along with the other model variables. An international symposium was co-sponsored by ORNL on this topic in 1977 in Gatlinburg. The proceedings, which were published by Academic Press, are frequently cited in the literature.

By around 1980 ORNL mathematicians were focusing on heat and mass transfer problems involving phase changes. Our interest has been on analytical and numerical methods that provide information on the progress and key factors in the processes of melting and solidification. We have dealt with these problems in a number of contexts, from the development and analysis of simple models for idealized processes to complicated models for including both heat and mass transfer with nucleation. These models are analyzed for the usual concerns of existence of, uniqueness of, and continuous dependence of the solution on the data and for the ability of the data to accurately represent the actual physical process. Other qualitative measures, such as parameter sensitivities and initial and steady-state behavior, are evaluated. Quantitative analysis of the models has ranged from the use of sophisticated numerical methods on advanced supercomputers for highly accurate solutions to the use of old-fashioned methods of mathematical approximations for estimates of the parameters of interest.

In addition to studying the solidification of a pure material, we have devoted considerable attention to the solidification of alloys. Alloy solidification involves heat and mass transfer in both liquid and solid phases. The problems associated with accurately modeling and analyzing such a complicated process are typical of a wide class of phase-change problems. The models must incorporate the basic laws of physics and the specific properties of the materials involved. Our knowledge has gone far beyond the idealized models found in most mathematical and engineering texts to incorporate many of the subtleties in the process. For example, we have simulated the solidification of an alloy consisting of copper and nickel (see Fig. 2). Our model is the first to allow the existence of "mushy" regions and to track their progress during the solidification process.

Some of our recent significant achievements for pure materials and alloys are given below.

- A standard assumption of mathematical and computational models of phase-change processes has been that the transition occurs at the so-called equilibrium melting temperature. However, most materials freeze at temperatures slightly below their equilibrium melting temperatures, and some materials may appreciably undercool before freezing. Heretofore, the enthalpy method has been incapable of treating any degree of supercooling—a serious shortcoming. An enthalpy model has been developed that includes supercooling before solidification, and the numerical methodology for its solution has been implemented and verified.
- A mathematical model for the evolution to steady state of a solid sphere growing inside its supercooled liquid phase has been developed. The model includes equations representing chemical, mechanical, and thermal equilibrium as well as conservation of energy and mass. One result of our analysis has been a change, by a factor of about two, in the so-called Gibbs-Thomson relation that relates the local radius of curvature of a growing solid to the corresponding local depressed-equilibrium solidification temperature. As a consequence we have obtained a correction to the classical relations for the critical radius of a nucleated sphere. Our results will enable researchers to take into account for the first time the effects of heat transfer, latent heat liberation, and pressure drops, as well as surface tension, when modeling the growth of a solid in its supercooled liquid phase.
- We have developed a model for the growth and upward movement of a buoyant solid formed in its supercooled liquid phase. Many materials can be significantly supercooled without solidifying. Some of these form solids that are less dense than their liquid phase. Examples of considerable practical interest are the cadmium-rich alloys from the ternary system of mercury-cadmium-telluride. These solids

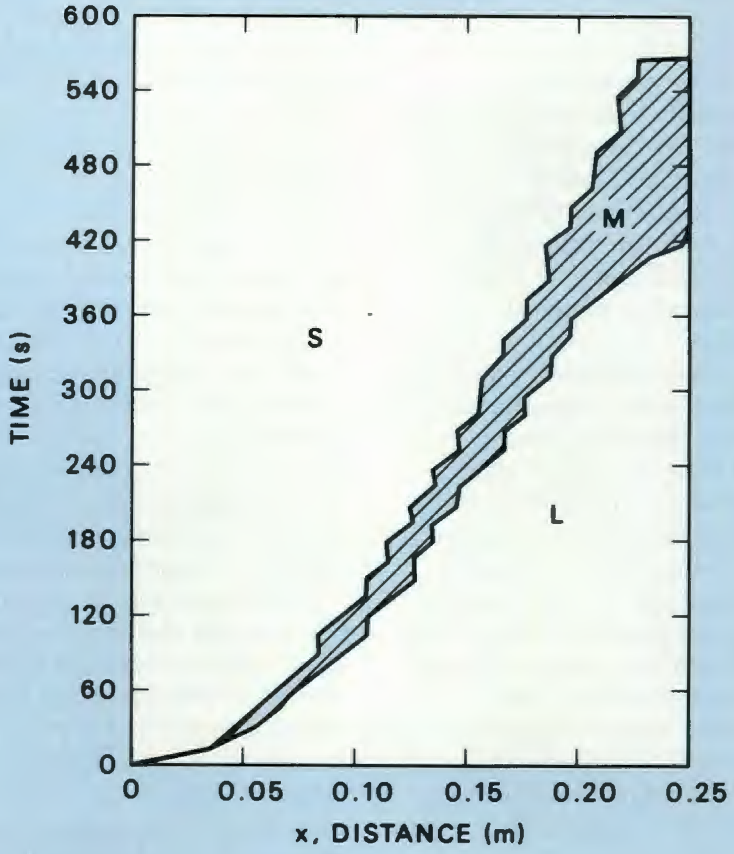


Fig. 2. Results from the simulation of the solidification of copper/nickel alloy. The alloy was liquid at $t=0$ and subjected to its solidification temperature at $x=0$. S, M, and L denote solid, mushy, and liquid regions, respectively.

may be formed by homogeneous nucleation from the melt or by the breaking off of a dendrite. It is of great interest to determine the effect of the buoyancy of the solid on the variation in composition of the final solidified material. Our new model provides a tool for investigating the rates of the simultaneous growth and rise through the melt of the buoyant solid and how these rates depend on material properties.

- Many numerical codes have been written to solve phase-change problems. Recently, codes have been written to implement (a) our alloy-solidification model in cylindrical polar coordinates for both sequential and vector computers and (b) our thermal energy storage models for a space station and for a passive, direct-gain solar structure. The numerical methods employed include both standard techniques and novel approaches such as an adaptation of Keller's "box scheme."

We are beginning to investigate ultrarapid phase-change processes in which heat transfer is governed by a hyperbolic partial differential equation. These processes present new challenges for our researchers.

In addition to the above basic research, our mathematicians have collaborated with researchers in other disciplines on many difficult heat- and mass-transfer problems. Actual process simulation has been carried out in such areas as heat pump efficiency, pulsed-laser annealing of silicon, solidification in gravity-free environments, solar energy storage, and thermal energy storage for low- and high-temperature applications.

In a different area, ORNL mathematicians have recently become interested in some mathematical questions relating to fractals. Fractals are frequently used to model rough surfaces such as the interface between a metal electrode and electrolyte. Although a fractal model is mathematically tractable and generally explains the observable data, it is not a very realistic picture of a rough surface. Real surfaces do not have the regular self-similar structure that is the basis of the fractal construction but are instead *statistically self-similar*. To more closely approximate this property and thus obtain a more realistic model, our mathematicians have investigated the incorporation of randomness in the model. Random fractals are constructed by allowing the constants in the continued fraction representation of the fractal to be random variables.

Our analysis of random fractals for modeling the impedance across an interface indicates that random fractals accurately model the known asymptotic behavior of the impedance. Generalizations of the fractal dimension to include randomness have also been made. Because the fractal dimension and the impedance can be measured independently, experiments are now under way in the Solid State Division to test the theoretically predicted relationship between the two. If the results of the experiments support our model, we have opened the door on an exciting new mathematical topic.

Statistics

Statistical methods are used at ORNL and throughout DOE to analyze data from research projects and to aid in the planning of experiments and surveys to obtain the best possible results subject to restrictions on resources. Innovative research projects in fields such as materials science, biological sciences, and physics often require innovative research in statistical methods to maximize and summarize the information obtained from the experimental data. The Laboratory has long recognized this fact and has employed an active group of research and consulting statisticians since the mid 1950s. The particular statistical topics that have received research emphasis have changed over the years. However, one of the strengths of the research program remains its depth of knowledge and experience in a large number of statistical areas.

The emphasis of our current research is in computationally intensive methods for statistical applications relevant to the analysis, summarization, or display of complex data sets. Most of our research can be grouped into four areas: computer-aided design of experiments, computer-oriented statistical inference, statistical matrix methods, and data reduction.

The *design of experiments* addresses one of the most fundamental problems in scientific experimentation: the optimal fitting of mathematical models to data. The goal of our research in this area is to develop computer algorithms that find optimal designs (i.e., values for the controllable variables in each experiment) under a variety of criteria using the proposed model and other information provided by the user. This task requires the solution of difficult large-scale combinatorial optimization problems. The algorithm DETMAX was developed at ORNL in the early 1970s by T. J. Mitchell to produce the design that maximizes the precision of the parameters in the model that one intends to fit to the experimental data. This algorithm has been used extensively by researchers in industry, academe, and government laboratories. More recently, we have developed algorithms that optimize designs simultaneously with respect to two criteria: the precision of the model parameters and the ability of the design to reveal deficiencies in the model. A simple example that illustrates our approach is shown in Fig. 3.

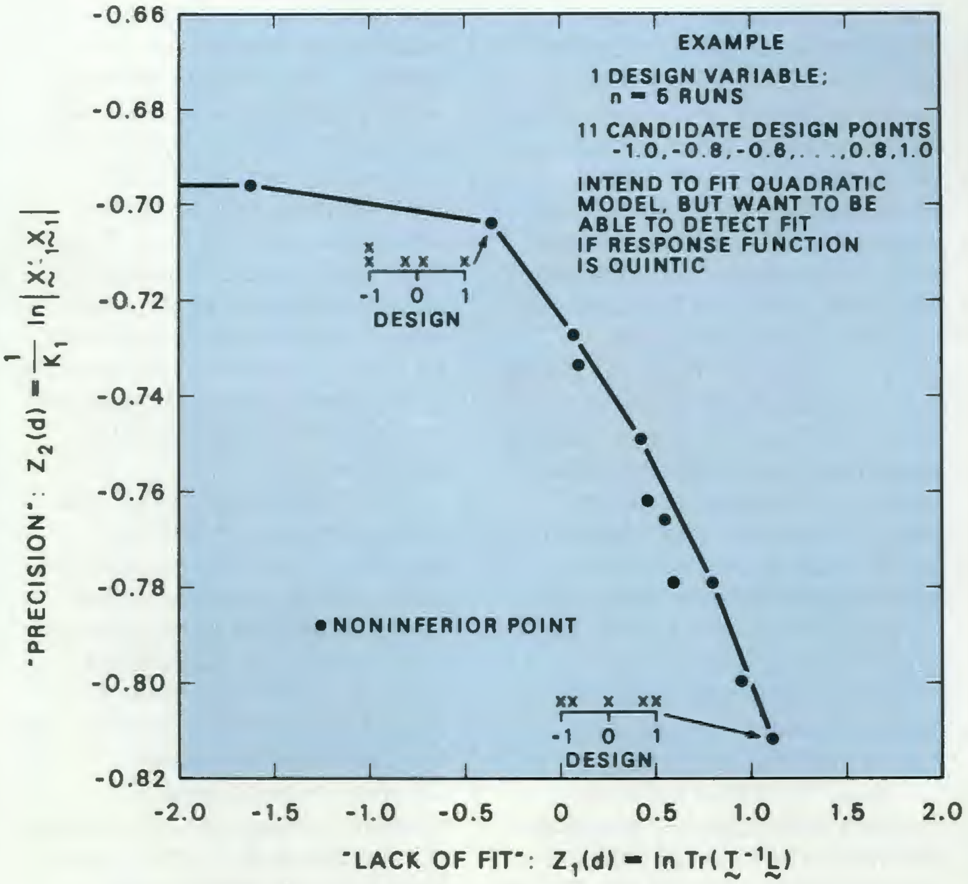


Fig. 3. Illustration of approach to designing experiments that are optimal with respect to two criteria: the precision of the parameters in the model that one intends to fit to the data and the ability of the design to detect lack of fit in that model. In this example, only one controllable variable exists; the objective is to determine a 5-run design in the interval (-1,1) that will be optimal for fitting a quadratic equation and for detecting lack of fit in the event that the true response function is quintic. The complete set of optimal designs corresponds to the criterion values indicated by the closed circles ("noninferior points"). It is usually not feasible to determine all of them. Our approach systematically generates the designs corresponding to the points joined by the solid line segments, by doing a sequence of optimizations with respect to different weighted combinations of the two criteria.

We are also developing algorithms to design experiments that have many controllable variables and that require fewer experimental runs than the number of unknown model parameters. These have application in screening experiments, in which one wants to identify the few most important variables as economically as possible. Another current research project is to develop sequential experimental designs for destructive life-testing studies. The goal of these experiments is to estimate the distribution of times to failure in devices that must be destroyed to determine whether failure has occurred. One of the advantages of these designs is that they greatly reduce the computational problem of determining standard errors for the parameter estimates of interest.

In classical *statistical inference*, hypothesis tests and confidence interval procedures are usually based on the distribution of an appropriate function (test statistic) of the observed data. Our work in this area has centered on the derivation of such distributions. We have determined distributional properties (e.g., percentiles) of such test statistics as the sample skewness and kurtosis and of parameter estimates in the Weibull, Gamma, and generalized Poisson distributions. Although our approach and computational methods have been quite problem-specific, our ultimate goal is to construct a comprehensive computer program that will receive as input the observed data and produce as output the desired properties of the distribution of the test statistic. Such a program would be immensely useful in statistical data analysis, because it would be the basis for hypothesis testing, confidence interval construction, sample size determination, and evaluation of sensitivity of the results to the model assumptions.

A recent initiative in computer-oriented statistical inference is concerned with the computational approximation of posterior distributions. In the Bayesian approach to statistical inference, posterior distributions are used to express uncertainty in quantities of interest. We are developing a system of algorithms that would allow the user to (1) input the selected model, prior distribution of any model parameter, and observed data and (2) output the posterior distribution for the parameter. This would be a very useful tool in evaluating models.

Our research in *statistical matrix methods* has concentrated on developing methods to handle sparse matrix problems in statistical calculations. An algorithm for analysis of variance has been developed that uses modern sparse-matrix technology and the specialized zero-nonzero matrix structure in the calculations to significantly reduce the amount of computer time and storage. Reductions of two or three orders of magnitude have been obtained for most problems, and solutions have been computed for large problems that could not be computed by algorithms in existing statistical packages because of the lack of sufficient computer memory. Significant reductions were also obtained on smaller problems, implying that this new algorithm could easily be used on small personal computers to solve some very large problems. In addition to analysis of variance, we are developing new algorithms for methods related to iteratively reweighted least squares.

Research in *data reduction* involves investigations that reduce the volume of collected data to be analyzed. Our emphasis has been on investigations in variable selection methodology, sampling, and classification. In the first topic, innovative methods using a Bayesian approach have been developed to help investigators determine which of the many "predictor" variables in a large data set have an important (or alternatively, a negligible) effect on a specified response or "dependent" variable of interest. To see how these methods work in practice, we are currently applying the results of our research to data from an ORNL study of a residential weatherization program. In sampling, we have developed methods to analyze data arising from imperfect sampling strategies (undercoverage, overcoverage, duplication, etc.) and the measurement of errors caused by these imperfections. Our future efforts will involve an investigation into combining stratification and sequential sampling to improve efficiency and accuracy of the data analysis. In our multivariate research, we have shown that standard classification methods, which frequently depend on the assumption that the data have a multivariate normal distribution, can perform poorly when that assumption does not hold. We have shown how the performance of these methods can be improved by using transformations to achieve approximate multivariate normality in the distribution of the data and have quantified the amount of improvement.

Our statisticians have a long history involving consulting activities. They have collaborated with research and development personnel in most of the divisions of the ORNL and many of the divisions of the Y-12 Plant, Oak Ridge Gaseous Diffusion Plant, and the Oak Ridge Associated Universities to assist in the statistical design and interpretation of experiments and investigations. They have also aided in the selection, use, and interpretation of computer programs to analyze and summarize data. Some diverse areas of past application of statistical methods include investigation of properties of materials, safeguard studies, reactor safety, validation of computer models, reliability, quality assurance and process control, epidemiological studies, tests on potential carcinogens and mutagens, evaluation of effects of energy-related by-products on the environment, risk analysis, bioassay, energy consumption estimation, and estimation of disease incidence in small animals.

One particular area of significant applied research has been statistical methodology for designing experiments and analyzing data related to health effects (including mutagenicity and carcinogenicity) of chemicals and irradiation. Some of our recent significant research achievements have included the mathematical characterization of the structure of estimation problems associated with sigmoid dose-response curves, which are used in applications such as assessing the toxic or carcinogenic nature of low-dose exposure to potentially hazardous substances; failure assessment based on accelerated life testing in physical applications; the design of optimal sacrifice strategies in experiments to study disease incidence and progression in animals exposed to radiation or chemicals; and the development of regression methods for discrete response variables, as opposed to continuous response variables.

As you can tell, mathematical sciences research and collaboration are indeed alive and well at ORNL, carrying on in the tradition set by Householder in the 1950s. Laboratory computer scientists are leading the ORNL staff into the next generation of scientific supercomputers, mathematicians are producing and analyzing accurate mathematical models of real-world phenomena, and statisticians are producing methodologies that provide quantitative analyses of phenomena for which mathematical and physical theories are still in their formative stages.

The future looks as bright for mathematical scientists now as it did three centuries ago. New algorithms and systems software are needed for current and future parallel computers to provide a programming environment to which scientists are accustomed. New and difficult mathematical modeling problems arise simultaneously with advances in the physical sciences. An exciting new area of research in statistics, the design and analysis of computational experiments, offers the potential for excellent utilization of our statistical expertise.

news notes

Checking installation of the first upper segment of the Advanced Toroidal Facility helical field coils are, from left, Brad Nelson (Y-12 Engineering) and Joe Wright (Y-12 Maintenance). The ATF fusion device is scheduled to begin operation in early 1987.

Advanced Toroidal Facility progressing

Assembly of ORNL's Advanced Toroidal Facility (ATF), a stellarator-type fusion research device, is well under way and is expected to be completed by early 1987. The ATF, a toroidal (doughnut-shaped) reactor, offers advantages over conventional tokamak designs because it allows steady-state (rather than pulsed) operation and because it avoids plasma instabilities that are inherent in tokamaks.

A key test of the ATF's engineering design and assembly procedures was passed in June, when one of the 1400-kg (3000-lb) upper segments of the helical field coil was successfully lowered into place and mated with two previously positioned lower segments. The operation required very precise fabrication and positioning of large, complex three-dimensional parts (precision up to 0.25 mm over distances of about 3 m). The successful design, fabrication, and assembly of these components resulted from a collaboration involving personnel from the Fusion Energy, Engineering, and Computing and Telecommunications divisions, Chicago Bridge and Iron Company (which is manufacturing the parts for the segments), and Y-12 Maintenance.

Magnetic coil testing milestone reached

A series of full-current tests is now under way with the six coils in ORNL's International Fusion Superconducting Magnet Test Facility. Tested first, in mid August, was the coil made by General Dynamics—Convair Division. While the other five coils were charged to an average of 77% of full current to provide a test background field, the General Dynamics coil was operated at full design current (10,200 amperes). It attained a maximum field of more than 8 Tesla, about 150,000 times the earth's magnetic field. The series of tests, intended to bring each coil to its design field strength of 8 T, follows successful individual tests of each coil at full current but at reduced fields, about 6 T.

New research projects funded

Eight new R&D projects and five earlier projects are receiving a total of $3.1 million in fiscal-year 1987 funding from the ORNL Director's R&D Fund, which supports the development of new research areas considered important for the Laboratory's future.

The eight new projects, which are receiving $2 million of the total, are:

- Heavy-Ion Storage Ring for Atomic Physics (HISTRAP) Prototype Studies
- Laser Photochemical Vapor Deposition of Submicron Thin Films and Artificially Structured Materials
- Development of a Prototype Central Solenoid for STX
- Microwave Sintering of Ceramics
- Isotopic Tracers of Global Material Transfers Between Atmosphere, Land, and Water
- Research in Man-Robot Symbiosis
- Application of Advanced Biocatalyst Systems to Waste Treatment
- Biological Markers of Environmental Contamination: Application and Experimental Validation.

New materials irradiation facilities

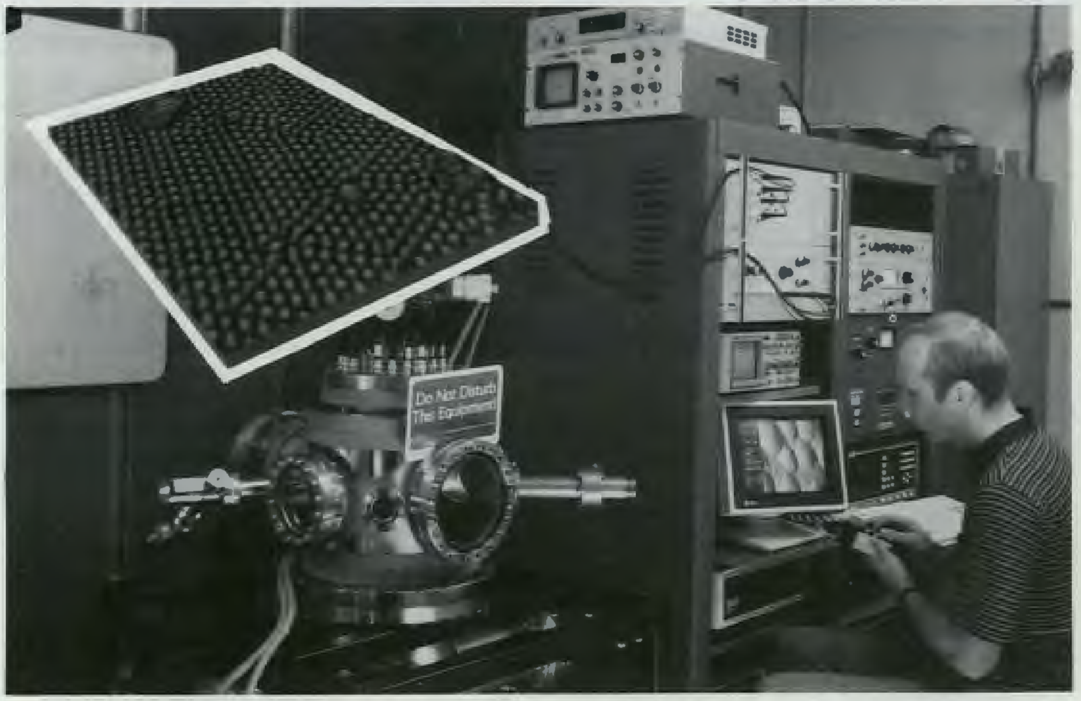
The first part of a two-phase upgrade of materials irradiation facilities at ORNL's High Flux Isotope Reactor was successfully completed in August, when new reactor components designed to allow temperature measurements and temperature control were installed in the reactor. The new components, which will increase the precision of irradiation-effects experiments, were installed during a routine refueling shutdown.

Before the modification to accommodate thermocouples in the target region was made, continuous temperature measurements could not be taken there; instead, peak temperature ranges were determined with passive probes—for example, wires that melt at certain temperatures. The modified components will also allow researchers to control the temperature of test specimens by adjusting the mixture of gases insulating the capsules that contain the specimens.

A second modification to the reactor, due to be completed next summer, will double the number and the size of irradiation positions in the removable beryllium reflector outside the HFIR's fuel elements. Both sets of modifications are designed to facilitate materials irradiation testing, including cooperative U.S.-Japan research on candidate materials for fusion reactors. Materials for fusion reactors must be specially engineered to resist damage from irradiation, which can cause swelling or brittleness in ordinary alloys.

New ORNL microscope singles out atoms

A high-tech microscope that displays the images of individual atoms on a material's surface has recently been assembled and operated at ORNL. Called a scanning-tunneling microscope, this instrument is the first of its type in the Southeast.



R. J. (Bruce) Warmack works at the controls of the scanning-tunneling microscope at ORNL, which recently achieved single-atom resolution. Inset: Image taken from a scanning-tunneling microscope shows the atoms on the surface of a piece of germanium. The large white spots represent defects (e.g., added or missing atoms). The photograph was taken by Warmack at AT&T Bell Laboratories in New Jersey.

The project to produce the complex device was funded by the ORNL Director's R&D Fund and carried out by R. J. (Bruce) Warmack and Tom Ferrell of the Submicron Physics Group in the Health and Safety Research Division with the help of a former colleague now at AT&T Bell Laboratories. Another microscope of the same type is now under construction at ORNL, and demand is growing for additional ones.

Applications may range from studies of the structures of DNA macromolecules and complex proteins like enzymes to analysis of computer microchips that are used to identify harmful impurities or chemical reactions. The microscope already has proven particularly useful for the study of surface physics because it can image impurities, flaws, and details of the atomic structure.

In October 1986 ORNL's scanning-tunneling microscope achieved single-atom resolution. A clean silicon surface was prepared, and a good low-energy electron diffraction pattern was obtained. Then the surface was scanned using the microscope, which obtained clear resolution of single atoms. The instrument has the potential of visualizing a surface detail a hundredth the size of a single atom. Atoms vary in size from one to three angstroms.

The main features of the microscope are a sealed vacuum chamber, tungsten needle, piezoelectric crystals, and computer. The barely visible needle "scans" the surface of the sample—such as a stamp-size slice of silicon— and electrons flow from the tungsten atoms at the needle tip to the surface atoms, a phenomenon called tunneling.

A small voltage put across the tip causes current to flow along the needle controlling a piezoelectric crystal, which expands or contracts in proportion to the current. Current is regulated by the electron flow (tunneling) between the atoms of the needle tip and sample surface. Thus, if the surface atom being scanned is larger than adjacent features, it will be closer to the needle and thus will increase the current. As a result, the crystal contracts, raising the tungsten tip so it can pass over the atom. A drop in current, on the other hand, causes the crystal to expand and lower the tip. Thus, the tip fluctuates much like a phonograph needle in response to a record's grooves.

The computer receives and stores information on the varying tip heights with respect to the surface being scanned. This information, which indicates small differences in elevation on a surface, actually reveals relative positions of different types of atoms. The images of this contour map of a material's surface are displayed on a screen, where they can be enhanced by computer graphics to provide additional detail.

Uranium solidification completed

ORNL has completed a decade-long program for solidifying 1050 kg (2300 lb) of reprocessed uranium fuel by converting it from a liquid solution into an inert, solid oxide form for safer long-term storage. The highly radioactive liquid nitrate solution had been shipped to ORNL in the late 1960s from a fuel reprocessing plant. The liquid waste was concentrated, converted to a dry oxide form, and double-sealed in 401 steel cans.

The complex remote-processing equipment needed for the job took six years to design, fabricate, and install. Completion of the $29-million project in June protects the environment from contamination by liquid wastes and also eases security concerns about the material.

Baby born in U.S. was frozen embryo

The nation's first human birth resulting from the implantation of a frozen embryo occurred in California in June. The basic techniques for embryo freezing, thawing, and implantation were developed in ORNL's Biology Division in 1972 as a way of preserving mouse genetic strains.

According to ORNL's Peter Mazur, one of the developers, the technology has been widely adopted by the cattle industry since the late 1970s. The world's first human birth resulting from frozen embryo implants occurred in Australia.

ORR to demonstrate low-enriched fuel

The Oak Ridge Research Reactor is being used as a test bed for a new, low-enriched uranium fuel that could ease security concerns at research reactors throughout the world. Since it began operation in 1958, the ORR—like most research reactors—has been fueled by highly enriched uranium (>90% fissile uranium-235), which could be used to make an atomic bomb. The low-enriched fuel, which contains only about 20% fissile uranium-235, could not power a nuclear weapon.

DOE funded development of the new fuel at Argonne National Laboratory at the request of the U.S. Department of State. If the year-long experiment at the ORR demonstrates that research reactors can operate effectively with the low-enriched fuel, the fuel could be used at most research reactors at U.S. universities (where security measures are generally less stringent than at DOE facilities) and at other research reactors around the free world.

Army recruits ORNL to study disposal of chemical weapons

Hundreds of thousands of obsolete chemical weapons will be destroyed by the U.S. Army beginning in 1989, and ORNL is playing the leading role in studying the environmental pros and cons of the Army's disposal options. ORNL is producing the environmental impact statement analyzing three alternative disposal plans; the Laboratory is also assisting with public hearings and other information activities related to the disposal program.

The chemical weapons, some of which date back to World War II, are stored at eight Army installations around the nation. The Army plans to destroy the aging weapons by incineration. The three options it is considering are on-site incineration at the eight storage sites; transportation to and incineration at two of the eight sites (Anniston, Alabama, and Tooele, Utah); and transportation to and incineration at a single site (Tooele, where 42% of the weapons are stored).

The weapons disposal program was the focus of a congressional subcommittee hearing in Lexington, Kentucky, in July; a series of public meetings near each storage site began in August. ORNL staff members have been incorporating the congressional and public comments into the final environmental impact statement.

The Army has tentatively identified on-site incineration as its preferred method of disposal. ORNL will recommend to the Army the environmentally preferred alternative in the final environmental impact statement. The Army will make a decision based on the final impact statement and other relevant information in early 1987.

technology transfer briefs:

Tritium shipping containers licensed

Rights to use ORNL-designed shipping containers for the radioisotope tritium have been granted to Ontario Hydro, a quasi-government Canadian utility company that operates two twin-unit nuclear power plants. Tritium, an isotope of hydrogen, is used in luminescent emergency lighting and landing lights for remote airfields. The radioactive gas is produced as a by-product of Ontario Hydro's CANDU nuclear reactors, which use deuterated, or heavy, water as a coolant and neutron moderator.

The shipping containers are approved by the U.S. Department of Transportation for U.S. and international shipments of tritium.

The container design is the fourth ORNL development to be licensed to a private company by Energy Systems since late 1985. Earlier licenses have been negotiated by Energy Systems for high-temperature nickel and nickel-iron aluminide alloys, a fiber-optic luminoscope for detecting organic skin contamination, and an energy-efficient sewage treatment process.

Another ORNL development, ceramics reinforced with silicon carbide "whiskers," was licensed in June to Atlantic Richfield's ARCO Chemical subsidiary for use in cutting tools and other parts requiring wear resistance. For more details, see the story on page 70.

Research in Intelligent Machines at ORNL

By CHARLES R. WEISBIN

Many technologies of interest to the Department of Energy require hazardous operations in which intelligent machines could be used to advantage. Closest to home is the handling of radioactive material around reactors and processing plants, but similar problems arise with explosives and other hazardous chemicals. Underground mining puts humans at risk on a large scale, and underwater operations from exploration to maintenance of equipment and, eventually, to seabed mining has a similar potential. In fact, underwater robots have already been put to use (e.g., Jason Jr., for surveillance of the remains of the sunken *Titanic*).

At a minimum, such a machine should be able to perform a useful task (lift something, cut something, observe something) and move between some staging point and the location of the task. Such goals lead to further required capabilities. The path to the task may be obstructed and the items to be lifted or cut might not be quite the same size or

Charles R. (Chuck) Weisbin is director of ORNL's Robotics and Intelligent Systems Program and the Center for Engineering Systems Advanced Research (CESAR). The mission of the center is long-range, energy-related research in intelligent control systems. He is also head of the Mathematical Modeling and Intelligent Control Section of ORNL's Engineering Physics and Mathematics Division and teaches an introductory course in artificial intelligence for the Computer Science Department of the University of Tennessee in Knoxville. Weisbin is also a member of the Martin Marietta Corporation Artificial Intelligence Steering Committee. He earned an Eng.Sc.D. degree in nuclear engineering in 1969 from Columbia University in New York City, where he completed postdoctoral work a year later. Before coming to ORNL in 1973, he conducted research for three years at Los Alamos National Laboratory in assaying fissile materials for nuclear safeguards and improving the quality of nuclear data. He has contributed to and edited the book *Sensitivity and Uncertainty Analysis of Reactor Performance Parameters* (Vol. 14, *Advances in Nuclear Science and Technology*, 1982). He has extensive experience in data and computer model validation (relying heavily upon sensitivity analysis methods) in fields as diverse as reactor physics, energy modeling, and carbon dioxide effects on climate. His current research interests are robotics, concurrent computation, machine intelligence, decision making, sensitivity and uncertainty analysis, energy-economy modeling, and waste isolation performance assessment. Here, Chuck Weisbin (right) and Bill Hamel examine the HERMIES-II robot that is being used by CESAR for concept demonstrations of artificial intelligence planning and learning algorithms.

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shape or in the same location each time. The machine must therefore have sensors to tell it about its environment, and it must act in appropriate ways upon the information supplied by its sensors (e.g., move left around the pillar and/or cut the pipe closer to the valve). Decisions about which action to take can be made by a human if sufficient time is available and the required information base and reasoning chain are limited. Our long-range goal is to enable the machine to make as many decisions as possible, thus freeing the human to spend more time in a supervisory and review capacity.

ORNL's Center for Engineering Systems Advanced Research (CESAR) is a national center for multidisciplinary long-range R&D in machine intelligence and advanced control theory. Intelligent machines (including sensor-based robots) may be viewed as artificially created operational systems capable of autonomous decision making and action. One goal of the research is autonomous remote operations in hazardous environments.

The long experience at Oak Ridge National Laboratory with the development of control systems (including remotely controlled machines for repairing equipment in reprocessing facilities) makes it a natural place to do research in intelligent machines operating in hazardous, unstructured environments and to develop prototypes with which to test the results of that research. The Center for Engineering Systems Advanced Research (CESAR) was established at ORNL in 1983 as a national, multidisciplinary center for research in machine intelligence and advanced control theory and the application of this research to problems related to energy production and use. Potential benefits include reduced risk to humans in hazardous situations, machine replication of scarce expertise, minimization of human error induced by fear or fatigue, and enhanced capability using high-resolution sensors and powerful computers.

CESAR was created by the Division of Engineering and Geosciences, a part of the Office of Basic Energy Sciences in the Department of Energy. The center's current research objectives include development of methods for real-time planning with sensor feedback, determination of concurrent algorithms for optimal implementation on advanced parallel computers, formulation of a learning theory for enhanced knowledge acquisition and interpretation, modeling the dynamics of flexible structures, generation of automated sensitivity analysis for model simplification and parameter identification, formulation and testing of a comprehensive uncertainty analysis methodology, generation of a machine vision system based on principles of human vision, and inclusion of this research within a systems integration framework encompassing concept demonstration and feasibility.

The kinds of research that are necessary for such a program and the results that we have already obtained will perhaps be more understandable if we first describe the particular machine that we are developing as a testing ground for our research results. Its name is HERMIES (short for Hostile Environment Robotic Machine Intelligence Experiment Series).

THE HERMIES-II ROBOT

The current experimental focus of the CESAR program is the mobile system HERMIES-II. William R. Hamel and Stephen M. Killough of ORNL's Instrumentation and Controls (I&C) Division are the principal architects of the HERMIES evolution into a major research facility. HERMIES-II is a low-cost system developed for initial CESAR experimental activities with autonomous sensor-based robotic systems for use in unstructured work environments. Although limited in its basic performance capabilities, HERMIES-II incorporates mobility and manipulation as well as recently improved sensory feedback functions.

Description. HERMIES is a self-powered mobile robot system comprising a wheel-driven chassis, dual-manipulator arms, on-board distributed processors, and a directionally controlled sensor platform. HERMIES-II is propelled by a dual set of independent wheels having a common axle alignment and driven by separate direct-current (dc) motors (see opening photograph). The on-board computer and electronic equipment are located in an enclosure mounted above the drive chassis, and the dual-arm manipulator torso is located above the computers and electronics. The manipulators are 5-degree-of-freedom (DOF) units manufactured by Zenith/Heathkit and used on the HERO home robot. The torso assembly for the arms also includes a shoulder pitch motion for each arm and a base for single-shoulder rotation. The two-arm shoulder assembly has a total of 13 DOF, and all axes are driven by stepping motors controlled directly by the Z8 microprocessor dedicated to manipulator control.

Sonar scan data are preprocessed on board HERMIES and then transmitted via a 2400-baud RS-232 radio link to either the NCUBE or LMI Lambda computers for navigation planning. A ring of five sensors using sonar, each of which consists of a phased array of four Polaroid transceivers, allows for a narrow effective beam width and rapid scan. The original stepping motor drives for the sensor pan/tilt control have been replaced with high-speed dc servodrives to permit the sonar ring to be stepped quickly. Consequently, the time required to scan a 180° region in front of HERMIES has been reduced from 80 to 7 s.

The dc servodrive of the tilt platform has been designed to accommodate not only the sonar array, but also an infrared range detector and dual Sony miniature charge-coupled-device (CCD) black-and-white cameras. The CCD cameras are part of a new image-processing system obtained to incorporate computer vision into HERMIES' sensor suite. The overall system is an International Robomation/Intelligence P-256 unit, which provides a pixel array of 256 × 256 spatial resolution with 8 bits characterizing possible brightness levels and an integral systolic array processor for reasonably high-speed execution of standard image operations.

Control System Architecture. The HERMIES-II control system consists of a main microcomputer and a satellite microprocessor. The main microcomputer is a single-board computer based on the Intel-8088 microprocessor and the IBM PC backplane. It controls an on-board 320-Kbyte floppy-disk drive and passes commands to a Zilog Z8603 single-chip micro controller, which performs the robot's manipulator control functions. Parameters are passed from the 8088 to the Z8 via a 9600-baud serial link. The dual wheels of the robot are driven independently by two gear-head dc motors that provide a linear speed of 0.154 m/s (0.5 ft/s). HERMIES-II's position is "open-loop" controlled through the on-board 8088 by real-time monitoring of the wheel encoders and on/off control of the drive motors.

The 8088 microcomputer uses the polyFORTH operating system and the FORTH computer language. FORTH is a very flexible language designed for control applications, combining the ease of high-level programming with speeds approaching that of an assembly language. FORTH word definitions have been used to construct a HERMIES command language for controlling the basic functions of the robot. The radio link is used to issue these commands to the on-board 8088 in a direct ASCII format. As an example, the FORTH word command "2 0 FMOVE" causes the robot to move forward 2 ft (0.6 m).

INTELLIGENT MACHINE NAVIGATION

The CESAR research in intelligent machine navigation is currently led by Charles Jorgensen and Gerard de Saussure, supported by Ron Fryxell, Robert Glassman, S. Iyengar, N. Rao, Robert Ricks, Deanna Barnett, and Jim Lucius. Collision-avoidance algorithms fall roughly into two categories: (1) if the position of an obstacle is known, the algorithms attempt mathematically to find optimal paths satisfying obstacle constraints and (2) if the position of an obstacle is unknown, environment-navigation algorithms are usually of the "generate-test-move" variety, in which a tentative path is proposed and tested for potential collisions. The move is executed if no collision is detected; otherwise, a new tentative path is generated.

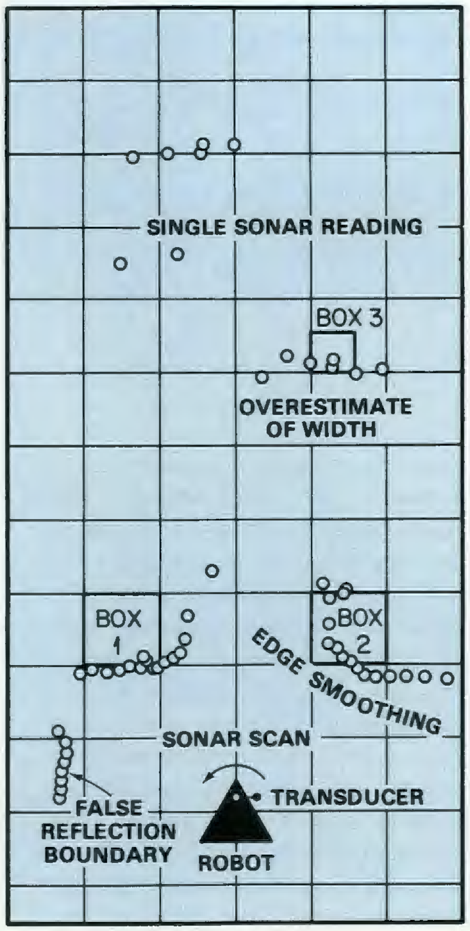


Fig. 1. Sonar recognition of simple obstacles.

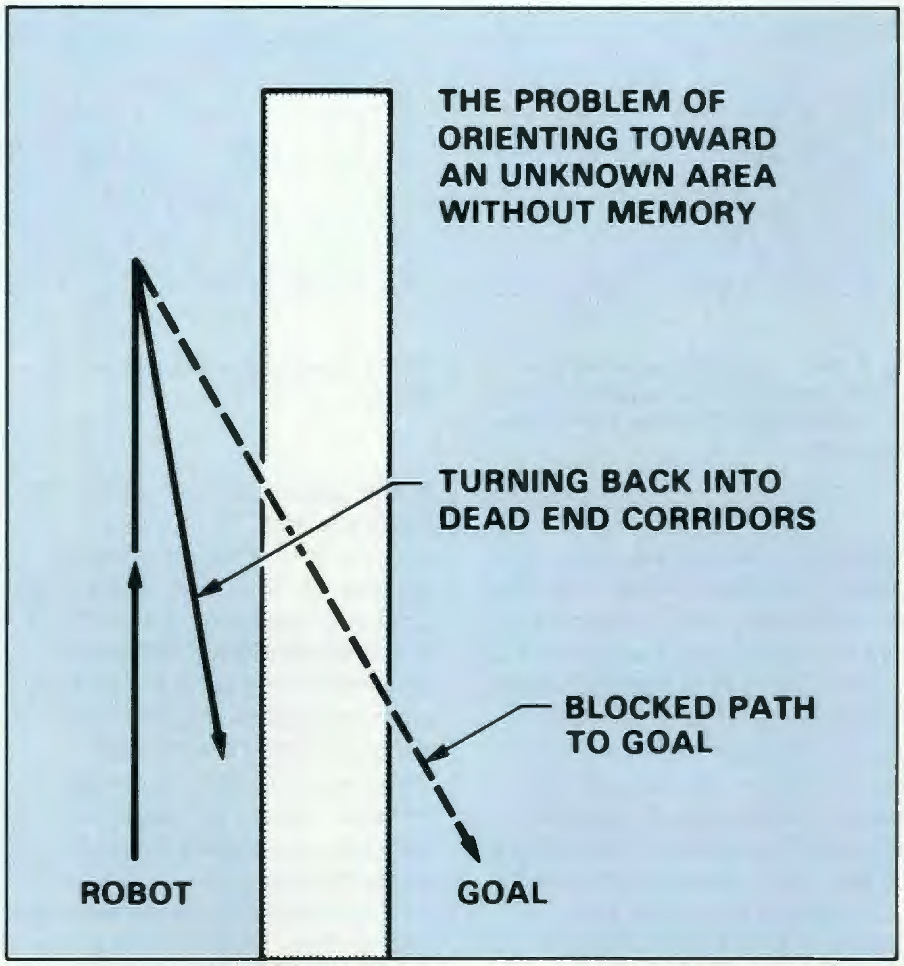


Fig. 2. The need for memory.

Sensory Feedback. Robot sensors include stereoscopic vision systems; fixed and mobile sonar range-finders; laser range-finders; touch, stress, and torque sensors; and collision detectors. Particular attention has been given at CESAR to the sonar systems used extensively for HERMIES-II navigation. Low-cost sonar devices function by sending a multifrequency sound pulse outward from a transducer in a cone-shaped wave front. The difference between time of emission and time of return is measured and an estimated distance calculated on the basis of how far the wave could travel in one-half the period measured.

Several difficulties occur when a robot uses sonar information to construct spatial distance maps from different scanning positions. First, sonar is sensitive to temperature changes. For example, if a sonar were calibrated at 27°C (80° F) and the actual room temperature were 16°C (60° F), a measured range of 11 m (35 ft) would be overestimated by 19.8 cm (7.8 in.) simply because of the temperature difference. Second, sonar is vulnerable to specular reflection and interacts with the texture of materials. The detectability of reflected sonar depends on signal energy and frequency. Frequencies useful in medical imaging are not practical for robotics. An example of this effect occurred in our early experiments using robot manipulators that attempted to grasp polyurethane foam blocks having extremely high sonar absorbency. For all intents and purposes, the blocks become sonar invisible. Other sonar problems result from the typically broad (35°) conical shape of the sonar beam.

A sonar map made by a robot in the CESAR laboratory (Fig. 1) illustrates some of these effects. Current work at CESAR is exploring the use of edge finding with vision image processing as well as sonar.

Navigation Control in Unexplored Terrain. It is not always easy for a robot to recognize a problem situation. Consider a simple maze problem (see Fig. 2) in

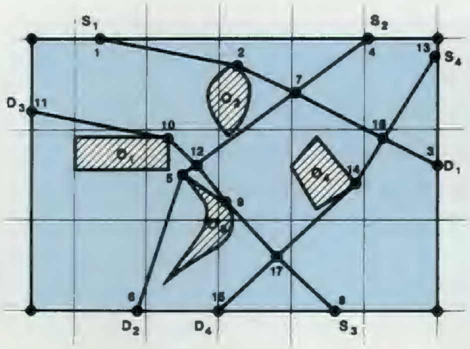


Fig. 3. Four traversals completed from starting points (S_i) to destinations (D_i) around obstacles (O_i) using sensor-based navigation.

which the robot is given this control algorithm: "When in a new area, first turn toward the goal you wish to reach. Take a sonar reading to see if the path is clear. If a path is clear, move. If it is not clear, take the first open path on either side of the line. Go one-half the distance to the goal. When you arrive at that location, turn toward the goal and repeat the process."

At first glance, such an algorithm would appear usable. The clear path nearest to an ideal straight line is always the one taken. The half-distance criterion also ensures that if the robot is far from the goal, it will move to it rapidly and will make smaller, more careful moves as it gets closer. However, the robot has no memory. As Fig. 2 shows, the robot's goal is directly on the other side of the wall. If the robot follows the initial algorithm, it will scan the corridor and after about a 90° left turn, find the first open path halfway to the goal. The robot will begin to move up the corridor away from the goal. After a short distance, the robot will be far enough so that half the distance can be traveled by making a turn back toward the goal. What happens? The robot again moves into the dead-end corridor. In other words, without memory, the robot would loop recursively and never reach the goal. With a memory, previously blocked areas can be designated "off limits" for a time, gradually squeezing the robot out of dead-end situations. Still other problems occur when navigation environments change quickly over time. Traversal may require continuous creation of new goals because unexpected obstacles invalidate previously formed navigation plans.

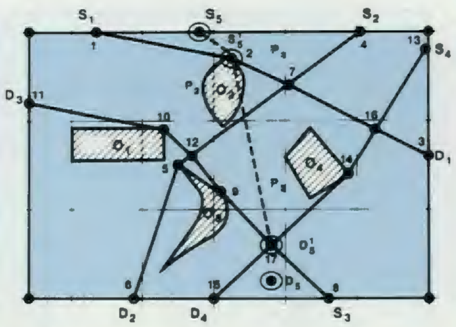


Fig. 4. S_5 source point D_5 destination point.

Learning During Autonomous Navigation. Ideally, an autonomous vehicle should collect information about its local environment and at the same time build or modify a global world model that can be useful for more general purposes. Iyengar and others have developed a method that enables a mobile robot to select and navigate paths in unexplored terrain while systematically acquiring information about the terrain as it navigates.

Learning begins by classifying information about the space a robot explores. Figure 3 illustrates four independent traversals about obstacles whose locations were unknown to the robot before it begins. Traversals are represented using spatial graphs that map the history of robot obstacle-avoidance movements onto a two-dimensional coordinate system composed of edges (the paths traveled) and nodes (stopping points, turning points, or path intersections). The spatial graph provides a real-time data structure to record past movements; however, it is not efficient for planning future movements because no data are retained about the shapes of obstacles, about areas of the room requiring further sensory analysis, or about regions that are clear for maneuvering. Thus, a second type of graph structure called a Voronoi diagram is used to bound obstacles using polygons that can subsequently be labeled and associated with higher-order learning processes.

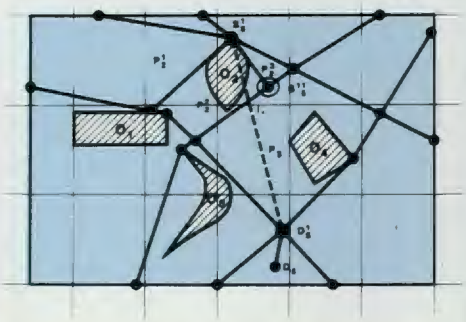


Fig. 5. Exploration of polygon P_2.

Consider determination of a new path from source point S_5 to destination D_5 as in Fig. 4. A virtual source point S_5^1 and destination D_5^1 are found from the Voronoi diagram corresponding to the nearest graph node points from the four previous explorations. The paths from S_5 to S_5^1 and D_5^1 to D_5 are determined using localized sensor-based navigation.

The polygon P_2 contains the source end of the line $S_5^1D_5^1$. The region P_2 is scanned using the sensor, and the polygon P_2 is partitioned into the regions P_2^1, P_2^2, and P_2^3 as in Fig. 5. The regions P_2^1 and P_2^3 are free polygons, and the region P_2^2 is an obstacle polygon with respect to the vertex S_5^1. At this point, the source

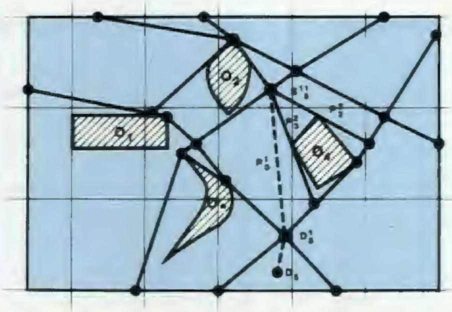


Fig. 6. Exploration of polygon P_3.

end of $S_5^1D_5^1$ is contained in the polygon P_2^2. The robot navigates along the obstacle boundary nearest to $S_5^1D_5^1$ arriving at intersection S_5^{11}. Next, the path $S_5^{11}D_5^1$ is planned. As illustrated in Fig. 6, the polygon P_3, which was previously unexplored, is partitioned (using sensor data) into the regions P_3^1, P_3^2, and P_3^3. P_3^1 and P_3^3 are free polygons and P_3^2 is an obstacle polygon. At this stage P_3^1 contains the source end of $S_5^{11}D_5^1$; the path $S_5^{11}D_5^1$ is directly traversed. The final leg from D_5^1 to D_5 is traversed using sensor-based obstacle avoidance. The final spatial graph of the terrain is given in Fig. 7. Note that the obstacles O_2 and O_4 are bounded by smaller polygons than shown in Fig. 3. Also, the polygons P_2^1, P_2^3, P_3^1, and P_3^3 are declared to be free polygons. Finally, regions P_2^3 and P_3^3 are combined to form a single free polygon. As more paths are traversed, more and more polygons are explored and the spatial graph is consolidated.

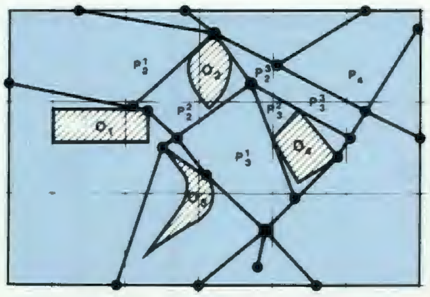


Fig. 7. Terrain model after the path from S_5 to D_5 is consolidated.

Extensions to Navigation Planning. Ron Fryxell, Robert Ricks, Deanna Barnett, Jim Lucius, and Gerard de Saussure are exploring the feasibility of using the PICON (Process Intelligent Control) package as the basis for decision making and robotic control. This software package was written by LISP Machine, Inc., for implementation on its Lambda machine, which includes a dedicated LISP processor running in parallel and asynchronously with a Motorola 68010 processor. The software is partitioned between PICON (the LISP Expert System, which operates on the dedicated LISP processor) and RTIME (written in C and running on the 68010.) RTIME handles routine tasks such as communications with the robot, sensor data analysis, path planning, and unusual-condition sensing, and PICON handles the operator interface, status monitoring, operation sequencing, and problem diagnosis. RTIME continuously monitors the communication channels between it and PICON for commands and passes to PICON information on the status of its operations. In addition, RTIME passes information on unexpected occurrences deduced from sensor data to PICON for high-level analysis and waits for commands on how to intelligently react to these events.

An example navigation problem will illustrate the use of the system. A navigation module written in C is made available to RTIME to be activated by a message from PICON. The module requests information on the robot initial position, the goal position, the navigation algorithms to be used, and the command to proceed; this data is passed from PICON to RTIME.

In each forward movement of the robot, the front fixed sonar is continually activated and, if it indicates an unexpected obstacle within 0.7 m (2 ft), the robot stops and reports the fact to RTIME along with the distance actually moved. RTIME stops the navigation algorithm, reports the situation to PICON, and waits for commands. PICON then requests information from RTIME about the unexpected obstacle: two front sonar readings are taken at a fixed time interval followed by a reading at a higher elevation. RTIME then passes to PICON this information about obstacle characteristics (e.g., size and shape). A diagnostic rule base in PICON is used to determine an appropriate action (see Table 1).

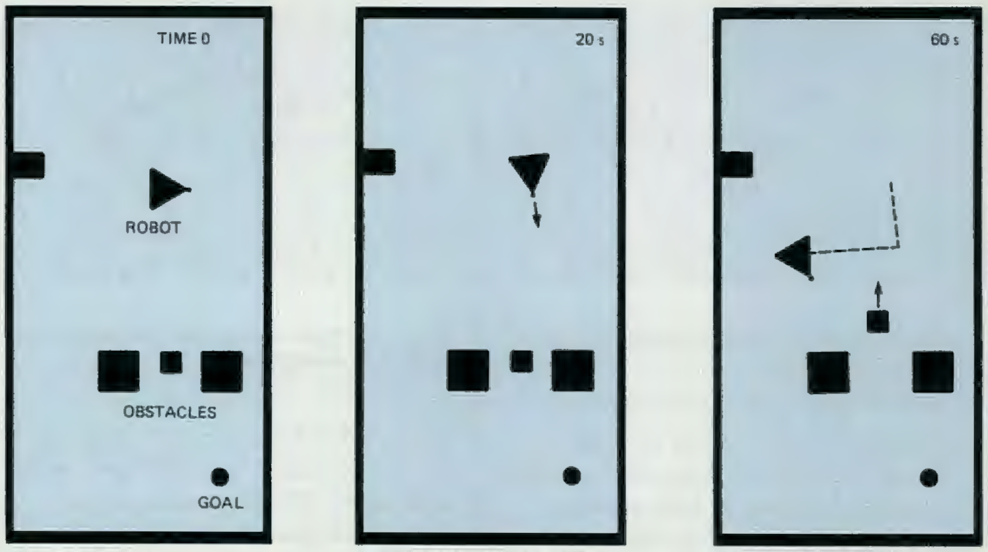
In this way, the robot can respond not only to a changed environment but a dynamically changing one as well. The system is easily modified to activate various robot responses and to accommodate a larger variety of sensors by simply modifying the diagnostic rule base and adding modules to RTIME. A simple robot navigation problem (and possible solutions using a PICON knowledge base of 32 "if-then" rules) is illustrated in Fig. 8.

In another approach toward navigation planning, Matthew Hall, formerly of ORNL's Engineering Physics and Mathematics Division has used an electricity-conduction analogy. Obstructed squares are regarded as insulators, and clear squares are regarded as conductors. A potential difference is placed between HERMIES' current location and the goal, and HERMIES then proceeds along a path based on the line of maximum current density. When this path encounters an unobserved square, a sonar scan is requested, the world model is updated, and navigation continues. The main computational expense of this approach is incurred in computing the current density, which involves solving the Laplace equation. However, this calculation takes only a few seconds. This approach to path planning offers an alternative to the more heuristic approaches.

ADVANCED COMPUTING

To enable a robotic system to work effectively in real-time in an unstructured environment, a variety of highly complex mathematical problems, such as on-line planning, vision, sensor fusion, navigation, manipulation, dynamics, and control, must be solved. The computational requirements of these problems fall into the "supercomputer" class, but ultimately we need to solve them on-board the autonomous robot. Jacob Barhen has led the CESAR effort in advanced computing to exploit concurrent computation, including the capability to dynamically balance the computational load among all processors in the system. He is supported in this effort by Ralph Einstein, Edith Halbert, and Michelle Clinard.

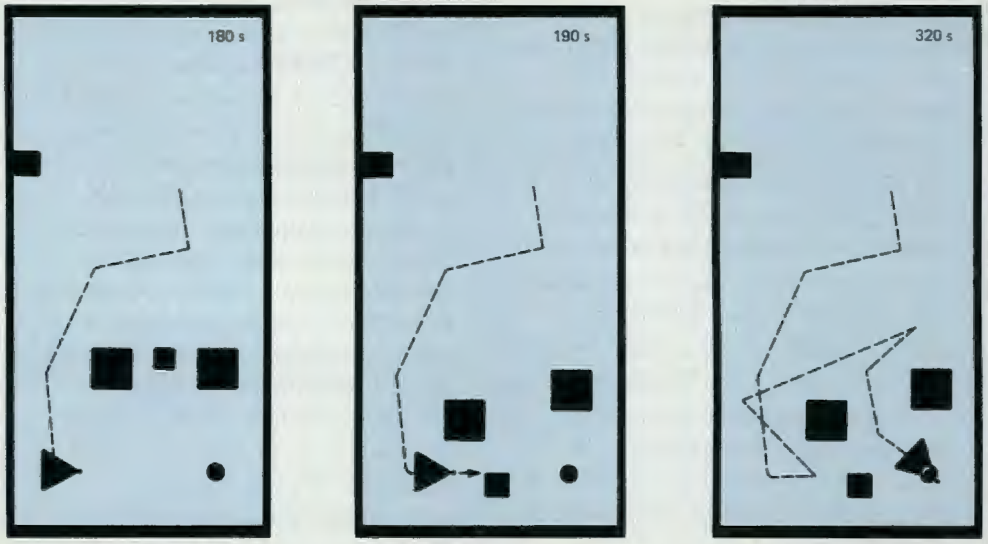
Hypercube Ensembles. Hypercube ensembles refer to a multiprocessor design in which N ($= 2^d$) identical microprocessor nodes are connected in a binary d-dimensional cube topology; each processor has its own local memory and is connected to d nearest neighbors directly. Communication is performed by message passing; the furthest communication distance between any two processors in the ensemble is d. For illustrative purposes, a few hypercubes of low-order are shown in Fig. 9. A hypercube looks topologically identical from the point of view of each node: there are no corner-vs-edge or root-vs-leaf nodes as exist in regular grids or trees. This symmetry is particularly attractive for simplifying the dynamic reconfiguration of the system.



A. INITIAL ROOM CONFIGURATION

B. ROBOT FACES GOAL, FINDS OBSTRUCTION AND STARTS MOVING TO WITHIN 3 ft OF OBSTRUCTION

C. SMALL BLOCK MOVED TOWARD ROBOT. ESCAPE ROUTE FOUND TO THE ROBOT'S RIGHT



D. SMALL BLOCK REPLACED. PATH CHOSEN TO THE ROBOT'S RIGHT

E. OBSTACLES MOVED TO BLOCK CLEAR PATH TO GOAL

F. ALTERNATE PATH CHOSEN TO GOAL

Fig. 8. Sample solution to a navigation problem involving a dynamic environment: (a) initial room configuration; (b) robot faces goal, finds obstruction, and starts moving to within 1 m of obstruction; (c) small block moved toward robot. Escape route found to the robot's right; (d) small block replaced, and path chosen to the robot's right; (e) obstacles moved to block clear path to goal; and (f) alternate path chosen to goal.

The CESAR NCUBE Hypercube. The concurrent computation system now being investigated at CESAR was developed by NCUBE Corporation (see Fig. 10). It contains 64 processors (6-d cube) in its initial implementation; the number of processors that can be accommodated is 1024, each designed to run conventional computer programs at about the speed of a VAX 11/780. Each processor has 128 Kbytes of local memory and can communicate directly with up to ten other processors through direct memory access channels. The importance of

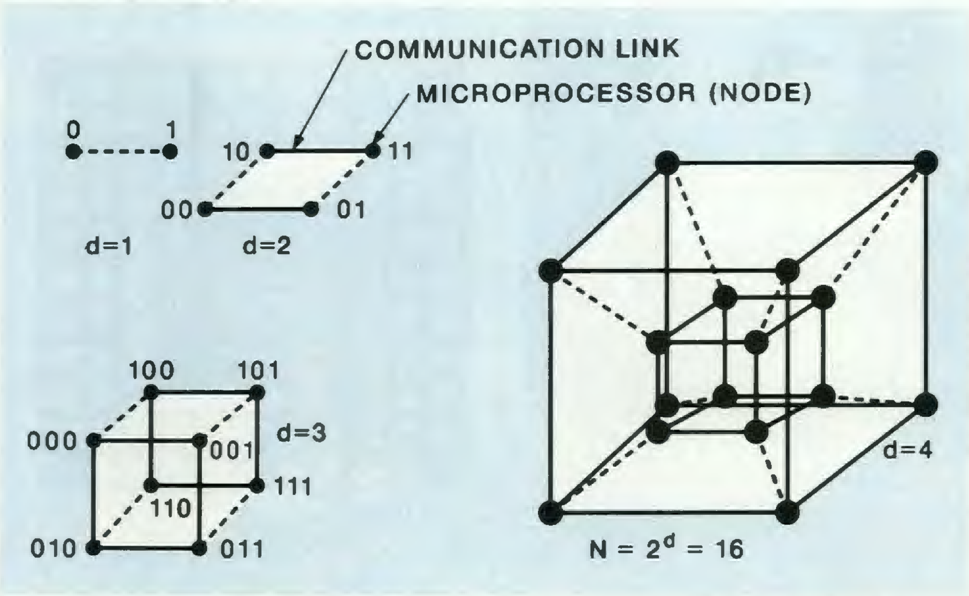


Fig. 9. Hypercube architecture in d dimensions. An order-d hypercube is constructed recursively from two order-(d-1) cubes.

this design for mobile robotics research is that when fully loaded, the hypercube has a capacity of ~500 million floating-point operations/s (500 Mflops) contained within a volume < 1 m^3 (including cooling and power supply) with a power consumption ~8 kW. The system can easily be scaled down for less demanding and more compact applications (e.g., 8 Mflops in something the size of an IBM PC AT). Compilers for FORTRAN-77 and C languages are available. The NCUBE node processor (Fig. 11) is a complex chip of about 160,000 transistors that integrate a memory interface, communication links, and a 32-bit, general purpose processor, including 32- and 64-bit floating point on chip.

Concurrent Algorithms for HERMIES Navigation. Matthew Hall originally developed the NCUBE software for driving HERMIES by partitioning tasks into separate processes: Each process can be executed in a different node on the array board except that processes requiring input-output (I/O) with the outside world must be executed on the controller board. Current HERMIES-II software includes six processes: (1) input of instructions from a terminal, (2) input of data from HERMIES, (3) output of instructions to HERMIES, (4) graphical display of the world model, (5) processing of sensor data and subsequent world modeling, and (6) navigation. Processes 1 through 4 must be run on the I/O board, while processes 5 and 6 can be run on the array board. As the complexity of HERMIES sensor data and environment increase, it is anticipated that processes 5 and 6 will be split into many different processes. Most recently, Judson Jones has extended the NCUBE software capability to allow positioning of the HERMIES-II manipulator arms.

Advanced Operating Systems with Embedded Reasoning. The research in this area is a major long-term endeavor toward implementing machine intelligence through real-time control of a

Table 1. Diagnosis and action on unexpected obstacles

Obstacle characteristic	Action to take
1. Stationary and >1 m tall tall	1. Start the navigation algorithm from the current position
2. Stationary and <1 m tall	2. Move forward to the obstacle, pick it up with the manipulator arms, put it to one side, and proceed to the original destination. Anything shorter than 1 m is guaranteed to be light enough to lift
3. Has moved out of the way	3. Proceed to the original destination
4. Is moving away from the robot	4. Wait for the obstacle to clear the path and proceed to the original destination
5. Is moving toward the robot	5. Check to the left and right with sonar, if clear, move out of the way. If both sides are blocked, go back to starting position and recheck escape routes to left and right

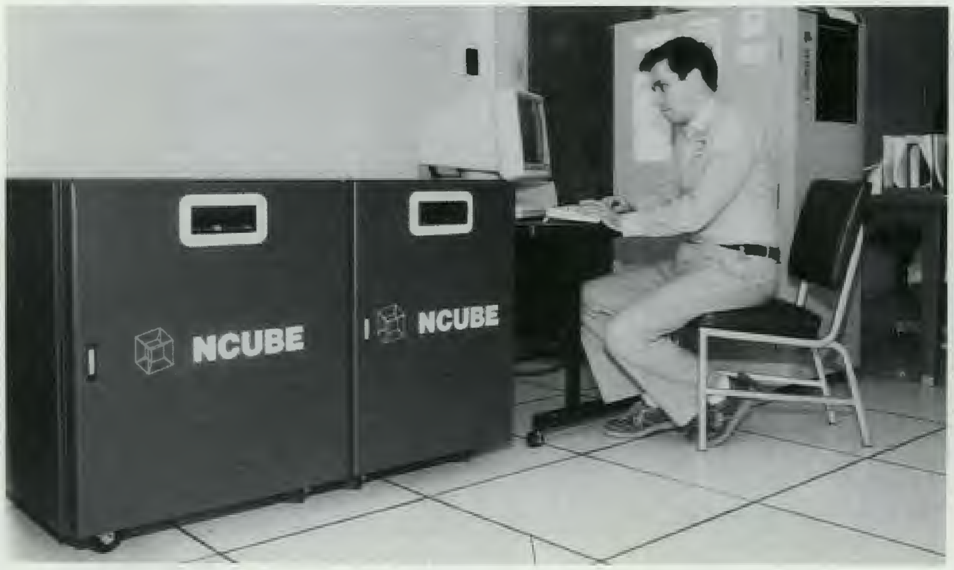


Fig. 10. Jacob Barhen operates the NCUBE concurrent processor in the CESAR Laboratory for Machine Intelligence. Up to 1024 processors, each having about the power of 1.5 Vax 11/780, can be enclosed in the left-hand-side box (i.e., in a volume <1 m^3).

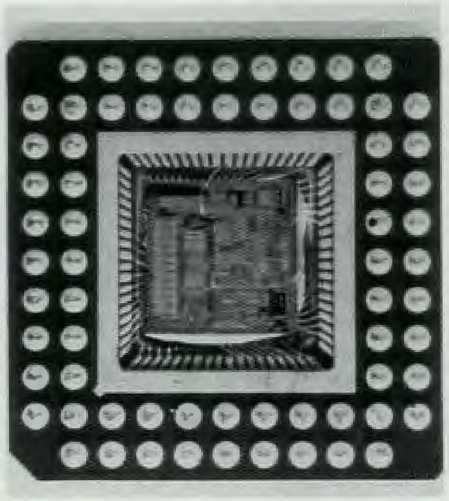


Fig. 11. The NCUBE node processor.

dynamically reconfigurable multiprocessor architecture. Reasoning and control functions are intimately associated with an operating system that provides for interrupt capability, priorities, communication, scheduling, etc. This development includes all research in the four tasks discussed below.

Treatment of Precedence Constraints (ROSES). The ROSES system is being developed to schedule precedence-constrained tasks for computation by an ensemble of concurrent processors. This endeavor is particularly difficult when the number of tasks required exceeds the number of available processors or when the interconnection topology of the task graph differs from the interconnection topology of the computation ensemble. Multiprocessor scheduling has been studied extensively; excellent reviews can be found in the literature.The task of multiprocessor scheduling is to determine, given a number of tasks and their associated precedence constraints, the appropriate sequence of tasks for assignment to available resources. The ROSES approach seeks near-optimal solutions by combining heuristic techniques to minimize scheduling time as a function of the number and relationship of tasks with data structures to most efficiently use available computer memory and algorithms to control the search process and eliminate dead ends.

Hard-Real-Time Capabilities. Many tasks in intelligent autonomous systems are expected to have stringent execution deadlines. Such tasks are said to induce "hard-real-time" constraints on the system, and these present major difficulties in the design of the scheduling algorithms for a distributed operating system.

When previously unanticipated tasks, which must be completed prior to some absolute deadline, arrive at a processor node, methods must be developed to guarantee such compliance. The first attempt is to find an open window within the computation schedule already developed for that processor. If this cannot be accommodated, task shuffling within that schedule is considered (i.e., a check to determine whether already-scheduled nonperiodic tasks can be rescheduled at an earlier time to guarantee that the newly arriving task be completed prior to its deadline). Finally, internode task-bidding is considered for guaranteeing successful task completion. Algorithm development for such scheduling capability is currently under way.

Virtual Time. In multiprocessor systems in which task computations are migrated among processor nodes to improve efficiency, one cannot guarantee that messages intended for a particular process will arrive in the temporal order in which they were sent. A "virtual time" paradigm is being developed as a synchronization mechanism to cope with this problem. The research builds on a version of the Caltech hypercube simulator made available to CESAR.

The Caltech simulator as received by CESAR was such that (1) all nodes executed the same program, (2) message-passing was assumed to occur only between nearest neighbors, and (3) all messages were received in the sequence they were sent. Because the CESAR emphasis is toward problems characterized by structures irregular in time and space, modifications were made such that (1) nodes can now execute totally different programs, (2) message-passing is from any process to any other at any time, and (3) tasks are initiated after the necessary messages have been received. The next phase of research involves the implementation of the virtual time algorithms (including modification of tentative plans based on new messages from other processors that invalidate previous assumptions) into the NCUBE VERTEX operating system.

Simulated Annealing. To address the load-balancing problem, Barhen has proposed using a simulated annealing method. Simulated annealing has been proposed as an effective method for determining global minima of combinatorial optimization problems involving many degrees of freedom. In analogy with statistical mechanics, each processor n could correspond to a lattice site in d dimensional space, and each process i would correspond to a particle. The kinetic energy of particle i is identified with the non-message-passing portion of the execution time of the corresponding process. A potential energy V_i represents the total time spent by process i for communication. To induce processes to spread out, a repulsive potential is introduced corresponding to the difference between the specific processor computational load and the average. The total energy of the system is then minimized to determine appropriate task allocations among processors.

Hypercube Algorithms for Robot Dynamics. The pioneering work of J. Y. S. Luh and C. S. Lin of Clemson University on scheduling of parallel computations for a computer-controlled mechanical manipulator has served as a benchmark for subsequent R&D of parallel algorithms for robot dynamics. Barhen and Einstein have examined the same problem using a modified version of ROSES, and results for the forward recursion (base-to-tip equations of motion) involving 144 tasks indicate that the speed of computation increases with the increasing number of processors—but only up to a point. Beyond that, adding more processors is a waste of computing resources.

Direct running-time comparisons is not appropriate because of the different hardware used by Lin and the CESAR group; the individual NCUBE nodes were designed by NCUBE to be about an order of magnitude faster than previously used microprocessors. Timing studies are under way now to verify these assertions.

However, the load balance reported by Barhen and Einstein for the most unbalanced node in this benchmark was about 95% for four processors, compared with 5% reported by Luh and Lin in an architecture in which one processor is assigned for each joint.

MACHINE VISION BASED ON HUMAN NEURAL MECHANISMS

The CESAR team has initiated a research effort to develop a robot vision system based on principles of human vision (e.g., massive parallelism, dynamic feedback, and multilayer pattern recognition). During the first year, led by Charles Jorgensen and Richard Gawronski, the modeling effort concentrated on understanding the electrochemical processes in the retina which follow photochemical conversion of the light impinging on the human eye. Two types of neural models were considered. The first represents neural layers in terms of static two-dimensional linear equations using a linear matrix and linear feedback. The second considers dynamic two-dimensional nonlinear processes using matrices of nonlinear differential equations. The first set of equations was parameterized using psychophysical data drawn from subjective judgments about the intensity of three visual illusions (see Fig. 12). The experimental results were used in a Fourier solution process, which was then applied to new illusions and compared with human subjective results through dimensional plots of transformed pixel intensities. The second set of equations was studied using a computer simulation operating on digitized picture matrices.

Although near-term generation of neural-based processors is still out of reach, the development of systems having silicon-based neurons at the front end and pattern recognition technologies at the higher levels may be feasible. A transition from static to dynamic models and models for higher-level perception, remain to be developed.

Finally, appropriate task decomposition of image processing algorithms for asynchronous parallel operation will be essential to achieve the required speed improvements. Current CESAR research in machine vision and multisensor integration using the NCUBE is led by Judson Jones and Reinhold Mann.

CESAR RESEARCH MANIPULATOR

The CESAR research manipulator (CESARM) is being developed by Scott Babcock and Bill Hamel to support their studies in robot dynamics and control (see Fig. 13). The CESARM incorporates several fundamental characteristics important for mobile operation. Mobility requires that overall

Fig. 12. Judson Jones (left) and Charles Jorgenson test the new CESAR machine vision system being developed for the U.S. Army Human Engineering Laboratory. The project explores the feasibility of applying human neural models to advanced robotic vision systems.

weight and power consumption be minimized; thus, manipulators must be designed with low weight-to-capacity ratios. The manipulator being developed weighs approximately 68 kg (150 lbs) and can lift about 13.6 kg (30 lbs)—a weight-to-capacity ratio of approximately 5, a factor of 4 improvement over typical industrial manipulators. Drive motors for the upper arm roll; elbow pitch; and wrist pitch, yaw, and roll are centralized at the shoulder to minimize the inertia and the actuator size (see Fig. 14). Note that the 3-DOF wrist is cable-driven.

Complex tasks will require high dexterity. The CESAR research manipulator has 7 DOF plus the parallel jaw gripper to be used as the initial end-effector. The manipulator's low-friction drive train, together with the redundant degree-of-freedom, provides an ideal research tool for dexterous manipulation. The manipulator incorporates a unique 3-DOF spherical wrist whose singularities occur only at the extremities of motion. A flange interface between the wrist and the parallel jaw gripper will facilitate research using other end-effectors, such as multifingered hands.

The CESAR experimental manipulator design is based on teleoperation technology developed at ORNL as part of DOE's Consolidated Fuel Reprocessing Program. The CESARM control system is designed around the VME bus. The initial implementation uses three Motorola 68010 processors and the FORTH programming language. Plans include upgrading to Motorola 68020 processors when practical and eventually interfacing CESARM to the CESAR hypercube.

Currently, mass and inertia properties of the manipulator are being determined experimentally for use in a mathematical model, and a simple torsional pendulum has been built for use in determining individual link inertias. The remaining model parameters, such as compliance and friction, will be identified from manipulator test data. This effort will provide a verified model with complete parametric data that should be useful to the entire robotics research community.

Near-term plans include experimental verification of controller structures similar to recently formulated inverse-dynamics position control and position/force control algorithms for manipulators having compliant drive trains. This is important because the cycle time of typical industrial manipulators is limited by vibrational characteristics associated with drive train compliance and current industrial robotic control is based on rigid-body dynamics. Our long-term goal is the coordinated control of two compliant manipulators mounted on a mobile platform.

SENSITIVITY AND UNCERTAINTY ANALYSIS

Ed Oblow leads the CESAR effort in developing methods for automated derivative generation and systematic uncertainty analysis. First derivatives (sensitivities) are required for model-simplification studies and parameter identification of complex calculations such as robot

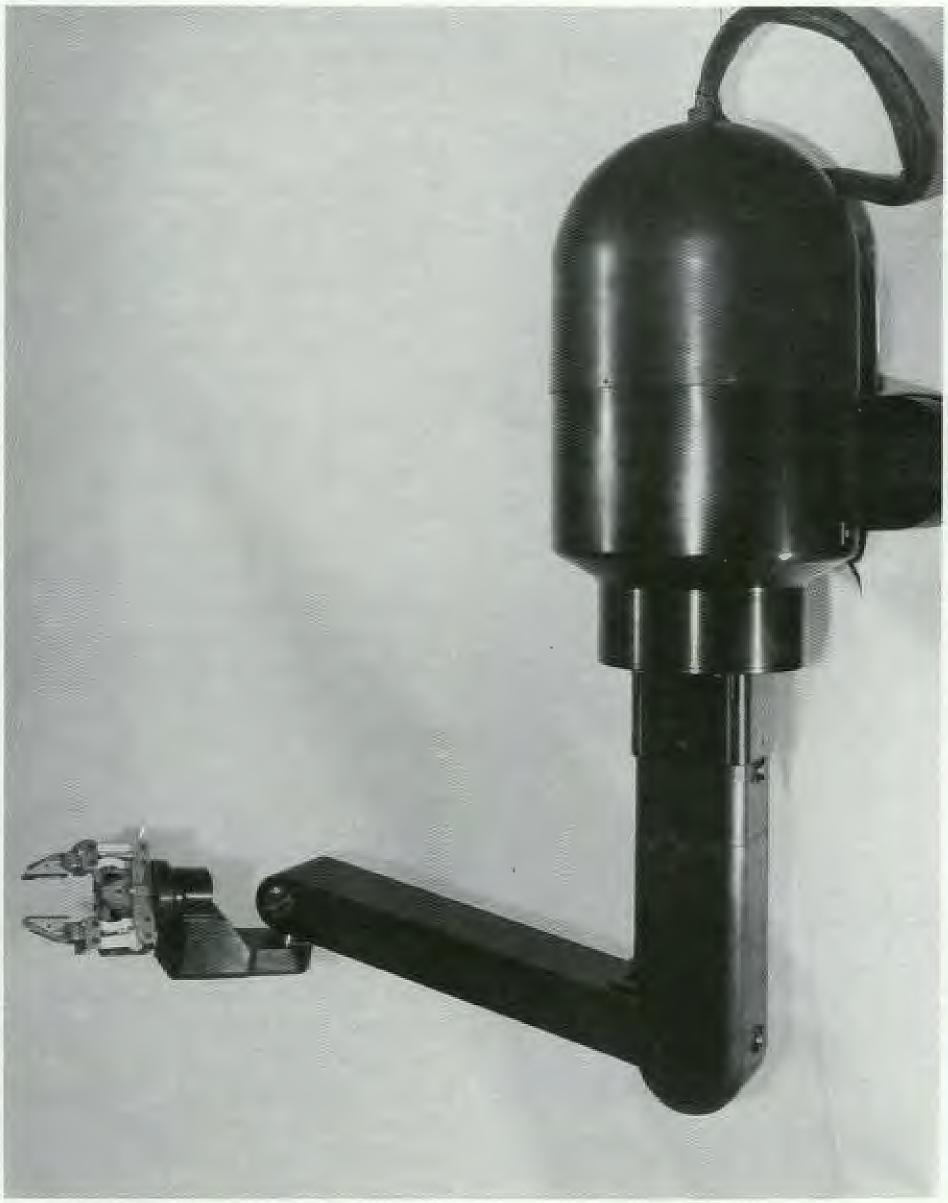


Fig. 13. The CESAR Research Manipulator.

dynamics. A comprehensive uncertainty analysis is required to handle numerical data uncertainties (such as occur in sensor measurements), rule and heuristic uncertainties (for searches and decision), and structural uncertainties for vision and language problems. Each of these uncertainties must be properly represented and combined for use in different decision-making environments. This work is jointly sponsored by DOE's Office of Nuclear Waste Isolation, and the principal investigators are Francois Pin and Brian Worley.

Sensitivity Analysis. Sensitivity theory has been used in many fields over the past two decades to assess the importance of variations in modeling data and parameters on calculated model results. Sensitivity determination based on reruns is usually unwieldy for complex programs having large data bases. Statistical methods suffer from lack of comprehensiveness and associated a priori engineering judgment of importance for much of the data set. Adjoint methods have required significant code development prior to implementation.

Oblow, Pin, and Worley have developed and validated an automated procedure for performing sensitivity analysis. The procedure uses a new FORTRAN precompiler that has computer calculus capabilities. The new compiler is called GRESS (Gradient Enhanced Software System); in it each FORTRAN line corresponding to storage operations is analytically differentiated, and total first derivatives are propagated using the chain rule. The GRESS system has now been successfully tested on several major codes. The major advantage of the GRESS language is its ability to process the model source program as data; no special effort is needed to specify the model.

Uncertainty Analysis. Oblow has also developed a theoretical framework for uncertainty analyses that can be used in artificial intelligence domains. The result is a hybrid uncertainty theory (O-Theory) developed to bridge the gap between Fuzzy Set Theory and Bayesian Inference Theory. The intersection operator proposed combines belief from independent sources into a new belief set in a manner previously thought only to be possible in a probability framework using Bayes' theorem.

The basic operations defined for O-Theory include dominance and order, union, intersection, complement, and general mappings. The formal connection between mass and probability derived by Oblow suggests that the distinctions between Dempster-Shafer Theory (DST) and probability theory are far less consequential than previously believed. The DST conception of

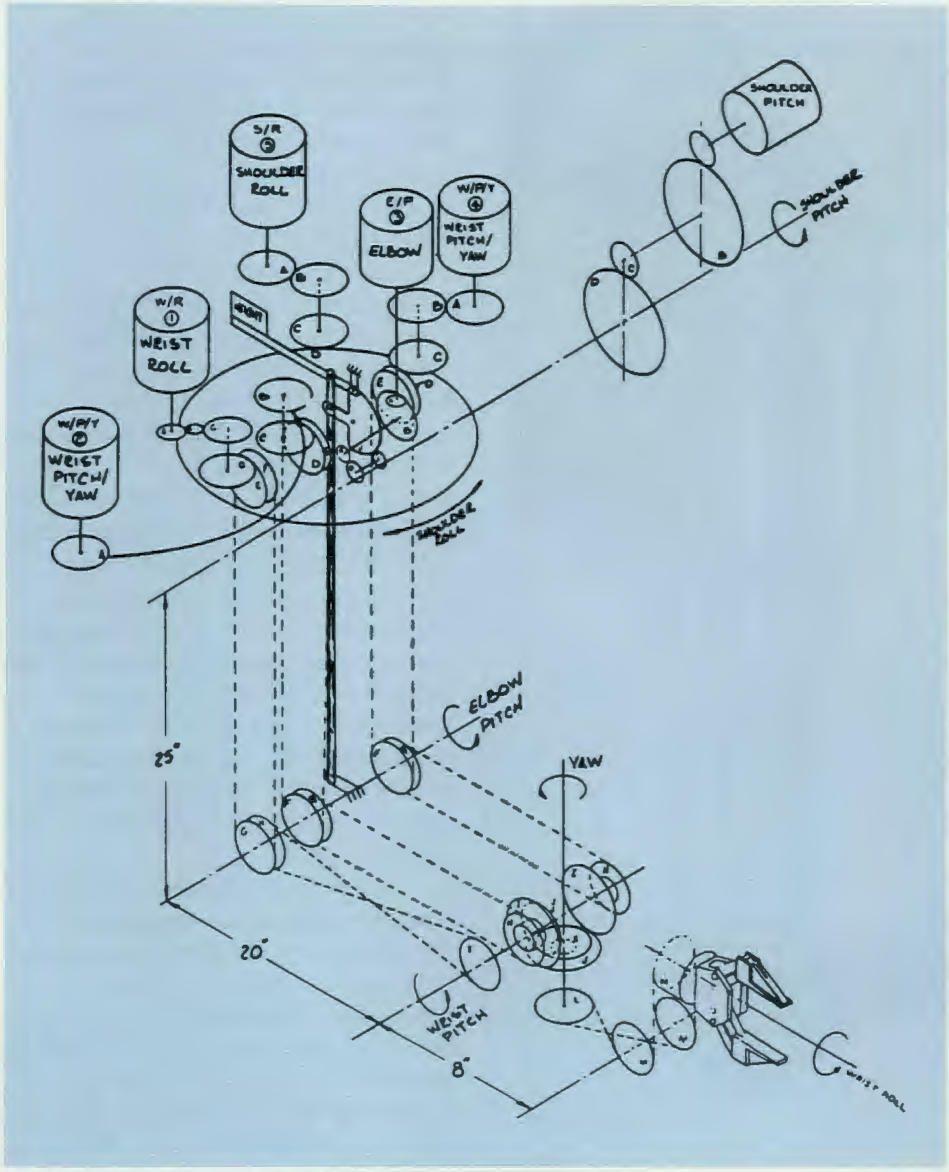


Fig. 14. CESAR Research Manipulator Power Transmission.

uncommitted belief was shown to be compatible with classical probability theory. O-theory is currently being tested within an expert-system framework by Mike Guth.

CESAR ACHIEVEMENTS

CESAR has organized and led two major national workshops. In November 1983, a workshop entitled "Research Needs in Intelligent Machines" was held to develop long-range goals and priorities. In August 1985, CESAR conducted a second workshop, "Planning and Sensing for Autonomous Navigation," in conjunction with the International Joint Conference on Artificial Intelligence.

Based on R&D results to date, other federal agencies have elected to participate in the sponsorship of CESAR. The U.S. Army Human Engineering Laboratory (HEL) is supporting research in soldier-machine system development, which has applications for projects that require dexterous manipulation in hazardous environments, such as explosive ordnance disposal and vehicle refueling and decontamination. HEL is also supporting research that explores the feasibility of applying human neural models to advanced robotic vision systems.

In addition, the Air Force Wright Aeronautical Laboratories is sponsoring research in concurrent computation that exploits the potential speed, compactness, and versatility offered by the CESAR hypercube ensemble machine.

A summary of CESAR's achievements through FY 1986 are presented below.

- The directionally controlled sensor suite of our HERMIES-II mobile robot was upgraded to include a phased array of sonar sensors and a new vision system. HERMIES-II now has full duplex communication with our NCUBE hypercube ensemble computer as well as a dedicated LMI LISP machine and has been controlled by both as distributed brains in various experiments involving near real-time task planning, path planning, and vision.
- Navigation algorithms have been successfully generated and augmented using learning techniques that record and synthesize information from multiple journeys and allow for continuous transition from local- to global-path optimality. Deterministic navigation approaches based on analogy to electrical conduction (i.e., obstructing squares regarded as insulators) have been implemented and offer an alternative to existing heuristic search techniques.
- A new research manipulator (CESARM) adapted from the Consolidated Fuel Reprocessing Program has been designed and built and now allows our analytical work on the modeling and control

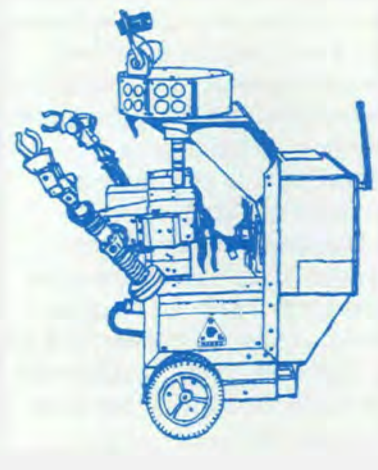
of manipulators to be experimentally verified. The manipulator weighs approximately 68 kg (150 lbs) and can lift approximately 13.6 kg (30 lbs), a weight to capacity ratio of about 5, a factor-of-4 improvement over typical industrial manipulators (which are necessarily heavy and rigid so they can precisely perform repetitive operations).

- A computer design based on a hypercube architecture is currently being investigated by CESAR. Up to 1024 32-bit processors developed by NCUBE Corporation, each processor designed to have the power of about one and a half VAX 11/780's, can be connected to their nearest neighbors; however, because VLSI technology is used, the total physical volume of the NCUBE machine is less than 1 m^3. The initial CESAR configuration is a six-dimensional cube that became fully operational in January 1986. Current research focuses on generalizing the simulated annealing global optimization methodology to systems having a varying number of degrees of freedom and on exploring its applicability to the static and dynamic load balancing of large-scale, message-passing hypercube multiprocessors. A significant effort is under way toward development of operating system concepts such as "virtual time." In addition, the development of parallel algorithms for machine vision is receiving increasing attention. In particular, work was initiated to study the applicability of human neural mechanisms to robotic vision. Mathematical models were developed that describe the first three layers of the retina; these models were evaluated using psychophysical experiments to parameterize the retinal equations and independently test their validity.
- Our GRESS calculus precompiler is now being used for automated derivative generation that supports model-simplification studies parameter identification. Each FORTRAN line corresponding to storage operations is analytically differentiated, and total first derivatives are propagated using the chain rule. The GRESS system has now been successfully tested on several major codes. The major advantage of the GRESS language is its ability to process the model source program as data; no special effort is needed to specify the model.
- A new uncertainty theory (O-Theory) has been developed in an attempt to combine and synthesize the strengths of Dempster-Shafer (DST), Fuzzy-Set (FST), and Bayesian Inference Theory (BIT) to retain the probabilistic basis of BIT, the beliefs and possibilities of DST, and the mathematical diversity and rigor of FST. The theory is now examined with respect to the PICON expert system for use in planning and decision making.

In making the transition from the teleoperated systems of today to the autonomous systems of tomorrow, CESAR is completing preliminary plans for HERMIES-III. This robot will have two dexterous arms (dual CESARMs instead of the one CESARM of HERMIES-II) and will outperform HERMIES-II in sensing the environment, thanks to high-resolution vision and a laser scanner. HERMIES-III will also be smarter than its predecessor. Its brain will be a mobile hypercube parallel computer, which has enormous processing power for rapid reasoning, learning, and decision making.

CESAR's long-range goals include allocating tasks and facilitating cooperative problem solving among humans and machines. We will be a step closer to these goals when we complete the Intelligent Machine Operating System, which more fully exploits the hypercube processor for scheduling tasks, load balancing, and synchronization. We will continue research on modeling the human visual process at higher levels (e.g., colinearity, periodicity, etc.) and for time-varying imagery. This research will be merged with conventional vision methodology for high-level scene analysis and with information from other types of sensors (sensing force, pressure, etc.) CESAR will also study control theory for dual-armed, closed-loop manipulation.

We hope that the long-term nature and continuity of the program will enable us to build common-sense knowledge representations, to deal wisely in using limited fast memory (what shall we allow the robot to forget?), and to develop algorithms to allow the robot to learn from experience. Finally, we expect to augment expert systems for robot control to include a measure of uncertainty used in decision making.



The physics of highly charged ions has been said to be the newest frontier in atomic physics. A group in ORNL's Physics Division has been studying collisions of multiply charged ions for just over 10 years. Although this research activity has been supported primarily by the controlled thermonuclear fusion program, where such processes play a key role, it has also uncovered important basic information about the nature of atomic interactions using state-of-the-art equipment.

Collisions of Low-Energy Multiply Charged Ions

By RON PHANEUF

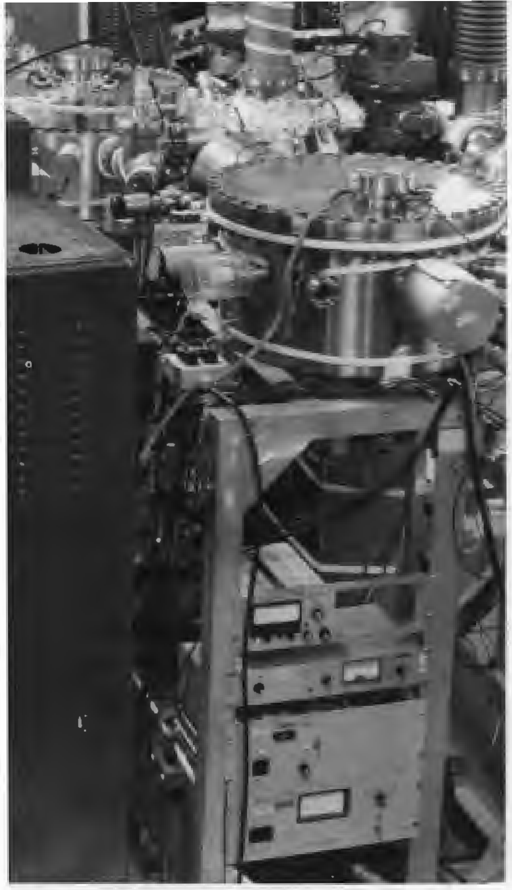
An ion is created when an electron is ejected from a neutral atom or molecule, leaving it with a net positive electrical charge. Removal of more than one electron yields a multiply charged ion whose net charge is proportional to the number of electrons removed.

Our group in the Physics Division of Oak Ridge National Laboratory has been studying collisions of multiply charged ions for just over 10 years. Although this research activity has been supported primarily by the controlled thermonuclear fusion program, where such processes play a key role (see box on page 153), it has also uncovered important basic information about the nature of atomic interactions. It has been said that the physics of highly charged ions represents the newest frontier in atomic physics. This article will characterize some ORNL research in this area and highlight a few of the more important results.

Multiply Charged Ions

Our atmosphere consists primarily of neutral atoms and molecules. The ionized state represents a departure from the minimum-energy equilibrium configuration of these neutral particles. Additional energy must be supplied to the atom to cause it to be stripped of its bound electrons. This energy is usually transferred to the atom when it collides with other particles or interacts with light. The disturbances produced by a lightning bolt, by an arc welder, or in the upper atmosphere by our sun are examples of situations in which such an energy transfer can occur and cause ionization. The minimum energy required to remove a bound electron from a neutral atom or ion is called its binding energy, or ionization potential.

Ions are commonly found in nature—in flames and aurorae, for example—and also play an important role in many areas of research. Because of their net electrical charge, they can be accelerated by electric fields, focused, and formed into beams by methods analogous to those used



Ron Phaneuf (second from right) is manager of the Atomic Physics and Plasma Diagnostics Development for Fusion Program in ORNL's Physics Division. He received his Ph.D. degree in experimental atomic physics from the University of Windsor in Canada in 1973. As recipient of a National Research Council of Canada Postdoctoral Fellowship, he went to the Joint Institute for Laboratory Astrophysics (JILA) of the National Bureau of Standards and the University of Colorado, in Boulder. As a research associate there, he spent two years working on electron-ion, crossed-beams experiments. Phaneuf joined ORNL's Thermonuclear Division on a half-time basis in 1975 to perform diagnostics on the ORMAK tokamak fusion device. In his first year at ORNL, he also continued his appointment with JILA on a half-time basis, helping to establish a fruitful and continuing research collaboration on collisions of electrons with multiply charged ions. This ORNL-JILA collaboration developed the first crossed-beams experiment involving multiply charged ions and reported the first cross-section measurements for electron collisions with such ions. Phaneuf joined the Physics Division in 1976. Since then he has conducted experiments on collisions of multiply charged ions. Since 1983 he has also served as manager of the fusion-related activities there, which include the Controlled-Fusion Atomic Data Center and an advanced plasma diagnostics program that applies laser technology to develop devices for monitoring fusion plasmas. Here he enjoys the company of current members of the experimental atomic physics for fusion group. From left to right are Charlie Havener, Fred Meyer, Jerry Hale (seated), Phaneuf, and Don Gregory.

for propagating light in optical instruments (e.g., telescope lenses). Ions in motion are deflected by magnetic fields according to their charge and mass and, consequently, can also be conveniently sorted, counted, and identified. Beams of a particular ionic species can be prepared in the laboratory and accelerated over a wide range of velocities. Ion beams are employed for a variety of research purposes, ranging from the study of the basic properties and interactions of matter to the modification of the surface characteristics of materials by ion implantation.

The removal of more than a single electron from an atom to create a multiply charged ion requires the input of considerable energy. As electrons are successively removed, the screening of the positive charge of the atomic nucleus by the remaining electron cloud of the atom is reduced. Thus, the attractive force binding each remaining electron to the nucleus increases, raising the binding energy of the ion. For example, removal of the first electron from a carbon atom requires 11.2 electron volts (eV) of energy. (An eV is the energy a single free electron gains when it is accelerated through a potential difference of one volt.) The energy required to remove the last (sixth) electron from carbon (whose nucleus contains 6 protons) is 490 eV. The total energy required to strip all six electrons from a carbon atom is 1030 eV. This total corresponds to the sum of the binding energies of the individual electrons that have been removed. (See Fig. 1.)

One method of imparting the energy necessary to create a multiply charged ion is to accelerate a singly-charged ion beam to energies of millions of electron volts and pass it through a very thin solid foil or a gas. Violent collisions in the foil or gas cause a large number of electrons to be stripped from the ion. This technique is widely used to generate fast beams of multiply charged ions and is central to much of the research of the accelerator-based atomic collisions group (see Sheldon Datz's article, which follows this one).

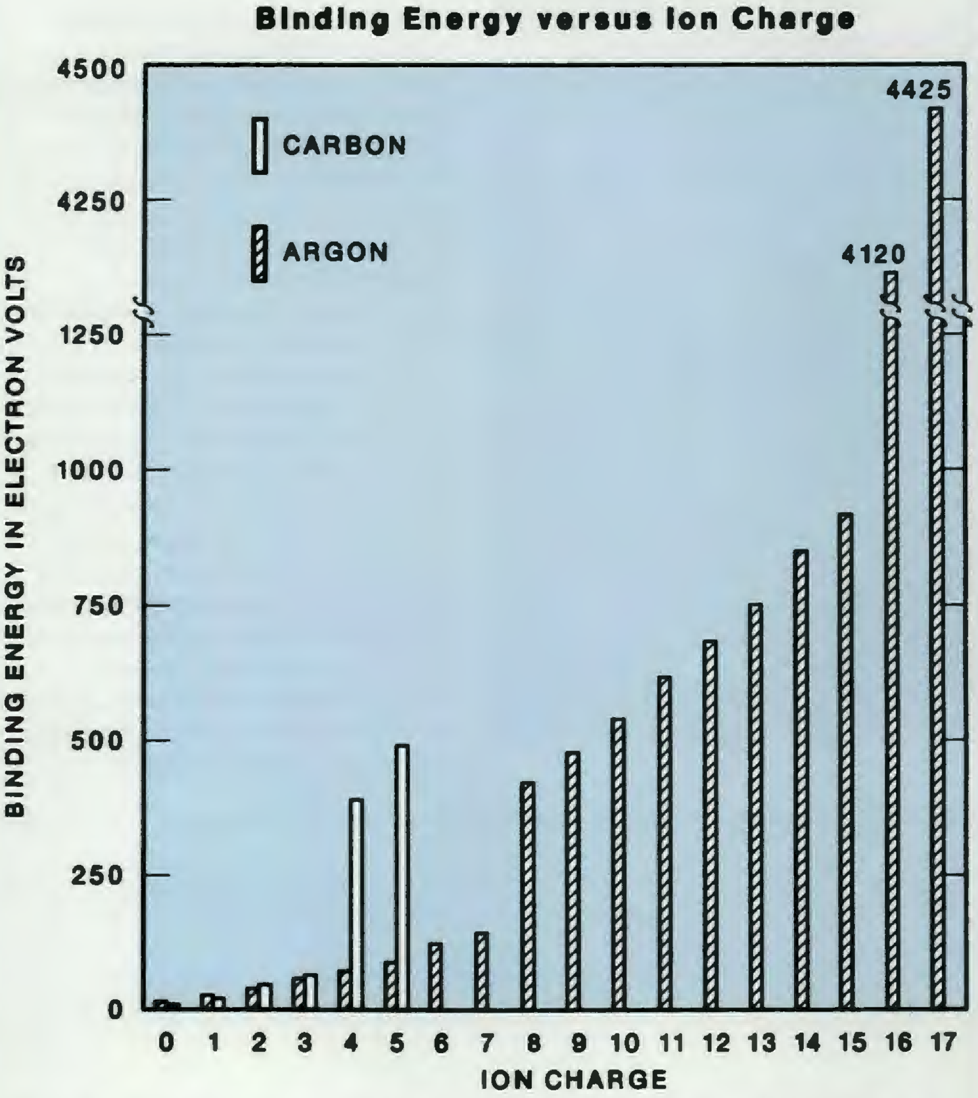


Fig. 1. The electron binding energy, the energy required to remove an electron from a neutral atom or ion, increases with each successive ionization stage of a given element. Here, the binding energies of carbon (nuclear charge of +6) and argon (nuclear charge of +18) are compared. The abrupt jumps at charge +4 for carbon and at charges +8 and +16 for argon are manifestations of the shell structure of the atom. The minimum total energy required to create an ion in a given charge state is equal to the sum of the binding energies of the removed electrons. For example, formation of a bare carbon nucleus requires at least 1029 electron volts (eV) of energy, whereas 14,393 eV must be supplied to an argon atom to remove all 18 of its electrons.

The production of slower multiply charged ion beams requires special ion sources to strip the ions of electrons before they are accelerated to form a beam. One such device is called a Penning Ionization Gauge (PIG) ion source, so-named because its arrangement of fields and electrodes is like that first used by F. M. Penning in his low-level gas detectors. In the PIG source, multiply charged ions are produced in a magnetically confined arc discharge, into which about 2 kilowatts of electrical power are applied. Our group takes qualified pleasure in telling visitors that the ORNL-PIG (pronounced Oar-null-Pig) has been the workhorse in our laboratory for about ten years. The qualification comes from our recollection that the PIG is a feisty beast at best and that production of some ion beams has been like taming a warthog. The PIG source is an inherently dirty device, requiring partial disassembly and cleaning on almost a daily basis. Many of the connotations arising from animal husbandry are surprisingly accurate and, therefore, all the more irresistible. The group has a tall list of PIG lore and has accumulated a large collection of PIG posters and cards over the years, many of which were sent to us by colleagues from around the United States and abroad.

We have also used pulsed lasers to produce multiply charged ion beams for collision experiments. Focusing an intense laser pulse to a small spot on a solid surface produces an expanding spark-like discharge that contains multiply charged ions. Although the average ion-beam intensity from such a laser source is quite low, it has proved sufficient for some experiments, allowing us to achieve higher ion charge states and lower beam velocities than we could obtain with the PIG source.

In 1984, an advanced multiply charged ion source was implemented for atomic physics research in our laboratory. Designed by Fred Meyer of our group and built at ORNL, this Electron Cyclotron Resonance (ECR) Multicharged Ion Source has dramatically increased our capabilities for producing low-energy beams of highly charged ions. Funded by the Office of Fusion Energy of DOE, it is one of about a dozen such sources in existence (three in the United States) and is the only advanced multicharged ion source that is now totally dedicated to atomic physics research. Apart from a substantially increased ion charge-state capability compared with the PIG source, the ECR source boasts higher beam intensity, improved beam stability, and almost maintenance-free operation. It is also capable of readily producing intense beams of metallic ions, which are important in fusion research and in astrophysics. (See box on pages 148–149).

Electron-Impact Ionization

ORNL has a strong tradition in the study of ionization phenomena produced by light (photoionization), led by Tom Carlson and Manfred Krause of the Chemistry Division.

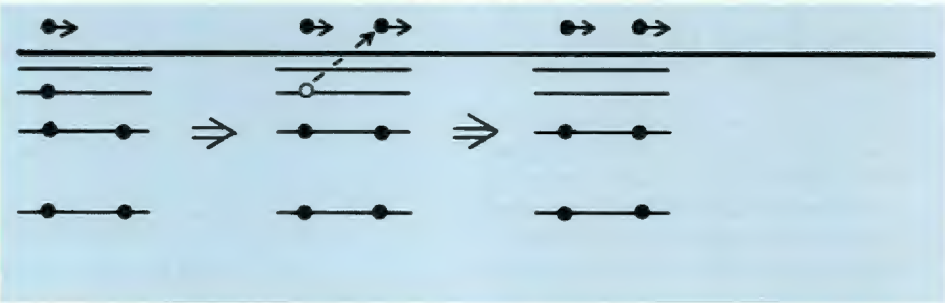
The ejection of electrons from ions by electron impact is a fundamental physical process that our group has been investigating for about a decade. For ions, such collisions are usually studied by the intersecting-beams technique. In our laboratory, in experiments led by Don Gregory, a beam of electrons is made to intersect a multiply charged ion beam inside an ultrahigh vacuum chamber. Collisional ionization is detected by measuring the fraction of ions whose charge has increased after passing through the electron beam. The standard physical measure of the likelihood of a particular collision process is the collision "cross section," which may be thought of as an effective area surrounding the target ion into which the projectile must penetrate for the process to occur. The smaller the cross section, the smaller the probability that an ionization event will occur, just as the probability that a marksman will hit his target depends on its size.

In general, the more tightly an electron is bound to an ion, the smaller the cross section for its ejection in a collision. An approximate scaling law derived from simple classical theory predicts that the cross section for ionization will be proportional to the inverse-square of the binding energy. As noted earlier, the energy binding an electron to an ion increases with the ion's charge. Thus, for multiply charged ions, one would expect that an ionization cross section would decrease strongly with increasing ionic charge. Such a trend has been documented in our experiments on a large number of multiply charged ions. This scaling is quite reliable for the process known as direct, or "knock-out," ionization. This kind of ionization may be thought of simply as a billiard-ball type of collision of the incoming projectile electron with a single bound electron, in which enough energy is transferred to the bound electron to allow it to escape the ion [pathway (a) of Fig. 2].

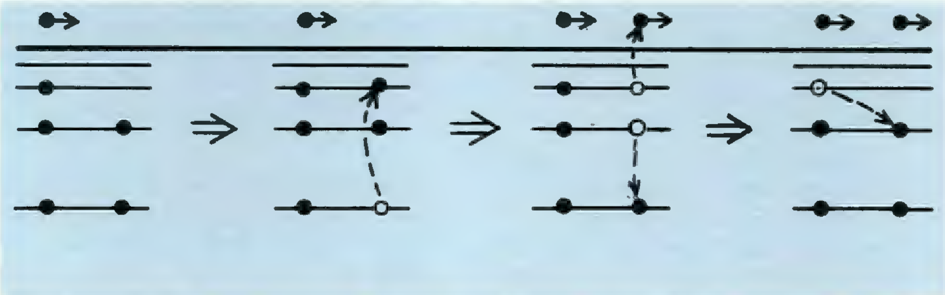
However, these same experiments have shown that, as the charge of an ion increases, the cross section for this direct process becomes smaller and other collision mechanisms begin to make important contributions to the ionization cross section. Such mechanisms often produce distinctive signatures in the variation of the ionization cross section with the velocity or energy of the projectile electron.

One important example of such an "indirect" ionization mechanism

(a) Direct Ionization



(b) Excitation Autoionization



(c) Ionization Autoionization

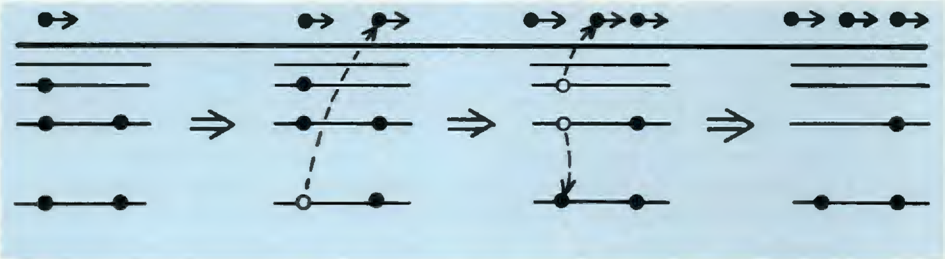
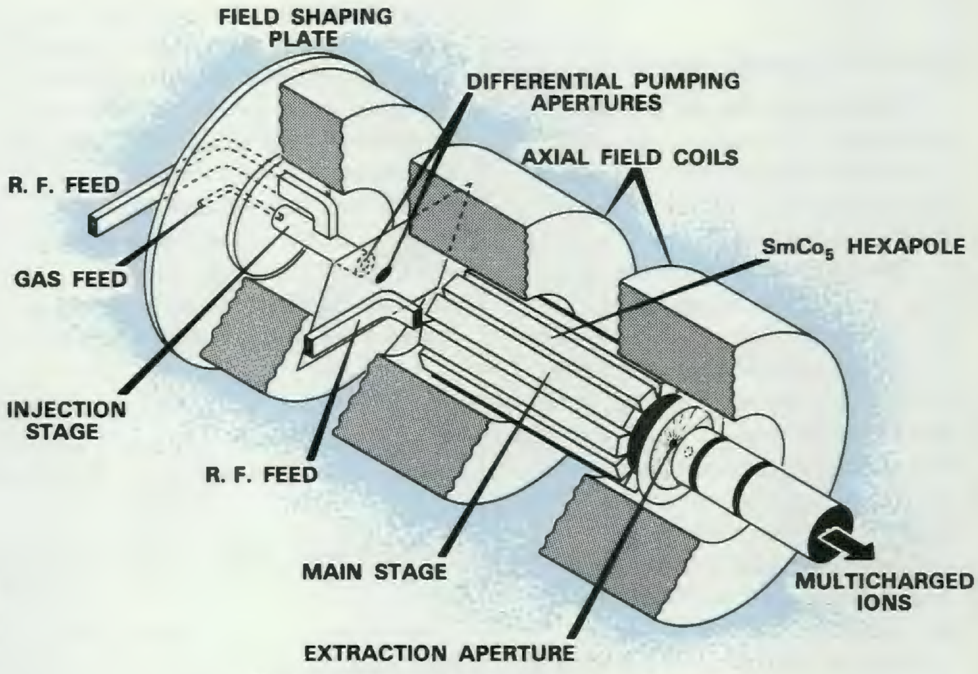


Fig. 2. Three different ionization pathways are depicted schematically for a 5-electron atom or ion. Solid circles represent electrons and open circles represent vacancies left behind as electrons are ejected or promoted (excited) to a state of higher energy. The continuous line at the top represents the ionization limit, above which electrons are unbound or free. In the example, processes (a) and (b) lead to single ionization, while process (c) leads to double ionization. Other pathways are also possible; these involve different levels and combinations of the steps shown here.

The Electron Cyclotron Resonance Multicharged Ion Source

The job of ORNL's electron-cyclotron-resonance (ECR) multicharged ion source, developed by Fred Meyer of the Physics Division, is to produce positively charged ions by colliding electrons with atoms of a specific element, thus stripping each atom of electrons. In such a multicharged ion source, three basic operating conditions must be satisfied. First, free electrons must be produced and "heated" to high energies. Second, ions must be allowed to collide with these hot electrons over a long enough period for the ions to be successively stripped of many electrons. Third, the operating gas density in the source must be low enough that the ions do not recapture electrons from neutral atoms and molecules before they are extracted to form a beam.



ORNL ECR Multicharged Ion Source

A cutaway view of the ORNL electron-cyclotron-resonance (ECR) multicharged ion source. The main stage of the source is a magnetic bottle in which electrons are confined and heated by microwave power. Atoms and singly charged ions from the injection stage drift slowly through the main stage, where they become multiply ionized by successive collisions with these hot, confined electrons. The multicharged ions are removed through the extraction aperture by an electric field and formed into a beam.

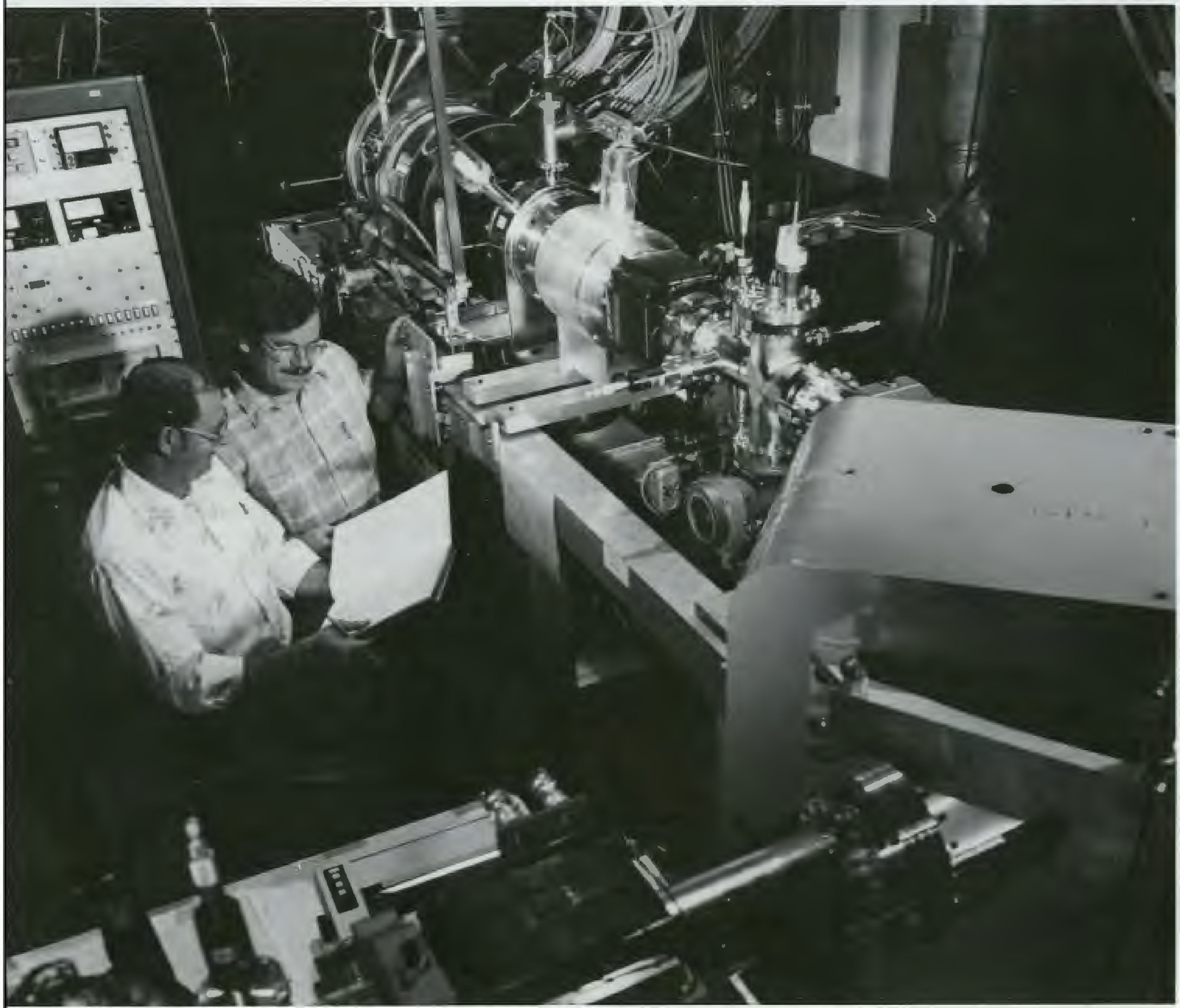
The ECR-heated ion source was first conceived about 15 years ago by R. Geller in France. The main component (see figure) is a "magnetic bottle" in which electrons are trapped and heated by microwave radiation. The main-stage magnetic bottle is created by the superposition of two magnetic fields. An axial magnetic mirror is created by two solenoidal coils, which produce a field along the axis of the source; the field is larger at the two ends than in the center, impeding the leakage of electrons out the ends. In the transverse or radial direction, an array of 12 permanent-magnet bars surrounding the main stage produces a six-sided "hexapole" field that has the characteristic of being zero along the axis and increasing radially outward. Thus, electrons are impeded from moving out radially from the axis as well. The combination of the axial and radial magnetic fields confines the electrons.

Into this magnetic bottle about a kilowatt of microwave power is injected. If the microwave frequency and magnetic fields are chosen appropriately, electrons on a cigar-shaped surface inside the bottle are resonantly heated by the microwave field. This surface is defined by the condition for cyclotron resonance:

$f = eB/2\pi m$,

where f is the microwave frequency, e is the electronic charge, B is the magnetic field strength, and m is the electron mass. In our source, the frequency f is 10.6 GHz, roughly four times that used in a conventional microwave oven. Electrons may be resonantly heated in such a structure in much the same way that a pendulum or a swing increases its amplitude and maximum velocity if repetitively given a push at just the correct time.

Once a magnetic bottle is created to contain the hot electrons, the atoms to be ionized can be injected. In the preionizer or injection stage, the desired atomic species is admitted into a small ECR region (created by a third solenoidal coil) into which a small amount of microwave power is injected, producing efficient preionization. Ions from the injection stage then drift into and slowly through the main stage and undergo successive collisions with the hot, confined electrons. About a millisecond later when they reach the



Jerry Hale (left) and Fred Meyer measure an ion charge-state distribution from the ORNL-ECR multicharged ion source.

extraction region where a beam is formed, these ions have been stripped of many of their electrons and have become multiply charged. These liberated electrons are also available for heating by the resonant microwave field and contribute further to the stripping process.

One advantage of the ECR source over some other multi-charged ion sources is its inherent ability to operate continuously rather than being limited to a pulsed mode. This is a significant advantage for many research applications such as colliding-beams experiments, which require large average beam intensities.

The ECR source at ORNL (see figure) has produced beams of bare ions for a number of different atoms—that is, it has stripped away all the electrons of these ions. The heaviest of the bare ions produced at ORNL is neon (nuclear charge of +10). Argon ions in this source have each been stripped of 16 electrons, leaving only 2. The highest charge-state beam that has been accelerated and identified so far is xenon after being ionized 29 times (its nuclear charge is +54).

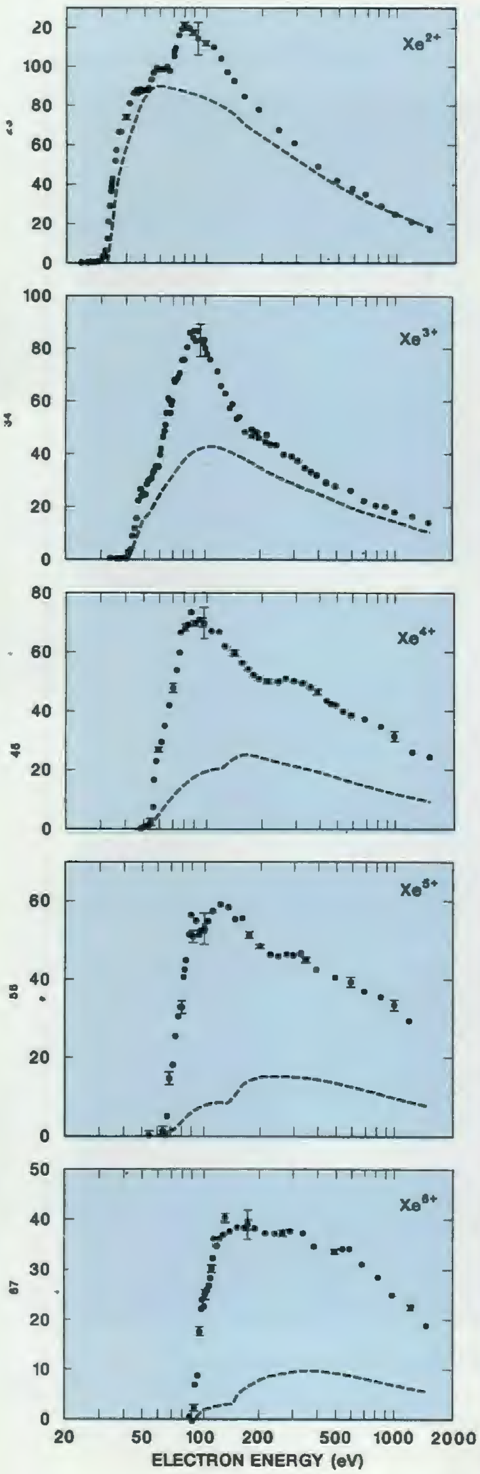


Fig. 3. The probability, or "cross section," for electron-impact ionization varies strongly with projectile electron energy. Here, experimental data are shown for an isonuclear sequence of multiply charged xenon ions. The electron energies at which the cross sections "turn on" represent the binding energies, or ionization potentials, of the ions. The dashed curve in each case is the prediction of a semiempirical formula for the direct ionization cross section. This direct process accounts for less and less of the total cross section as the initial charge of the ion increases. Our experiments have shown this to be a general characteristic. The abrupt changes in the curves are signatures of indirect ionization mechanisms, which are activated at specific energies. The overall shapes of these features, or "bumps," in the ionization cross sections give information about the nature of the excitation processes that lead to ionization.

is the collisional promotion, or "excitation," of a tightly-bound, inner-shell electron from one quantum state of the ion to a higher-energy state. Ions in such excited states can have energies greater than that required to remove an outer electron and can relax (return to normal) by giving the excess energy to two electrons, one of which falls back to fill the inner-shell vacancy, while the other leaves the ion with a well-defined kinetic energy. This spontaneous process is called "autoionization," or "Auger decay," after the physicist who first recognized it.

The time scale for autoionization is typically very short (picoseconds or less) compared with flight times of the ions in the experiments (microseconds); therefore, it is registered as simultaneous with the collision. The complete process is called excitation-autoionization [pathway (b) of Fig. 2]. In some of our experiments, we have shown that this type of indirect ionization occurs up to 20 times as frequently as direct ionization. By carefully measuring cross sections for electron-impact ionization of multiply charged ions at different projectile electron energies, we have been able to both identify and quantify the roles of excitation-autoionization, as well as other more complex ionization mechanisms.

Another process that we have studied is multiple ionization, in which more than one electron is ejected from an ion in a single collision. In most of the cases that we have investigated, the cross section for multiple ionization is dominated by the direct ejection of a single tightly bound, inner-shell electron by the projectile [pathway (c) of Fig. 2]. Additional electrons may be subsequently released by the autoionization process, as the inner-shell vacancy is filled by an outer electron. The result of such a collision is a net multiple ionization. The interaction of the projectile with more than one target-ion electron is a less likely process in general, although we have unambiguously identified its important role in at least one case—the triple ionization of xenon in which Xe^{6+} becomes Xe^{9+}.

By systematizing our investigations, we have been able to more readily identify mechanisms and trends. An approach that we have found to be particularly effective is to study a number of ions whose structure is not too different. We have concentrated on sequences of ions having either the same number of bound electrons but a varying nuclear charge (isoelectronic sequence) or the same nuclear charge but a varying number of electrons (isonuclear sequence). The implementation of our new ECR multicharged ion source about a year ago has opened up many exciting new possibilities for such experiments and allowed us to tie together many loose ends and extend previous studies. (See Fig. 3.)

A parallel theoretical effort led by Chris Bottcher of ORNL and consultants Don Griffin of Rollins College and Mitch Pindzola of Auburn University has contributed substantially to our understanding of the ionization process. *Ab initio* calculations of ionization cross sections for ions having many electrons are very sophisticated and require extensive computing

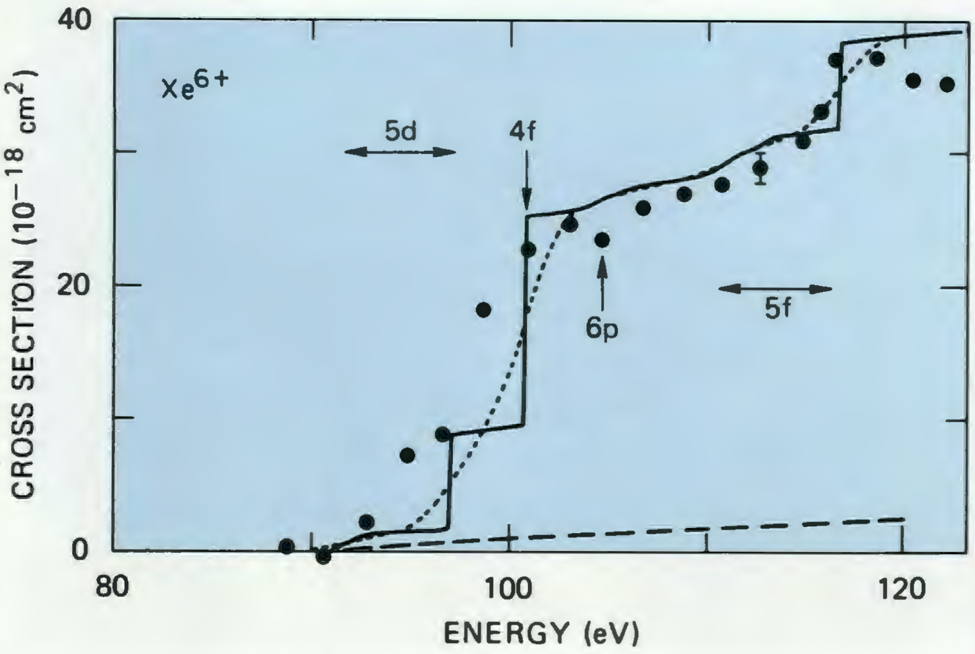


Fig. 4. Indirect mechanisms often dominate the ionization of multiply charged ions by electron impact. Specific information about these mechanisms can frequently be obtained by comparing experimental data to theoretical calculations. Here is a blowup of the cross section for electron-impact ionization of xenon (Xe^{6+}) in the low-energy region. The long-dashed curve is a semiempirical estimate of the direct ionization cross section. The solid curve represents detailed quantum-mechanical calculations by the ORNL theory group, which include the indirect ionization mechanism of excitation of an inner-shell ionic electron to various levels. As an outer-shell ionic electron fills the inner-shell "hole" left by the excited electron, another ionic electron is released by a process called autoionization. The short-dashed curve takes the energy resolution of the experiment into account, and is what the experiment would be expected to yield if the theory were correct and complete. The arrows and labels denote the quantum states to which a 4d inner-shell electron is excited and the projectile energies at which the excitations "turn on." In answer to the obvious question, our theory and experiment do not always agree so well, but we almost always learn some new physics when they don't.

capabilities but are necessary for valid comparisons of experiment and theory (see Fig. 4). These studies have been made possible by access to the supercomputers of the National Magnetic Fusion Energy Computer Center at Lawrence Livermore National Laboratory.

The relationship between our experimental and theoretical efforts has been a symbiotic one in which the theorists suggest the collision systems that may reveal the most important new information and the experimenters try to provide the benchmarks against which their calculations may be tested. Frequently, of course, the most interesting ions from a theoretical standpoint are the most unattractive ones for the experimenter, and vice versa. For example, toxic species such as arsenic and antimony are frequently on theorists' shopping lists of interesting follow-ups to existing studies. (Fortunately, the computer is immune to the nasty properties of some elements, so that simulated experiments can be run on toxic species when actual testing is impractical.) So far, each side has managed to adapt to the needs and capabilities of the other, and this close coordination of experimental and theoretical efforts has helped us to maintain a leadership role in the study of collisions between electrons and multicharged ions.

Electron Capture Collisions

So far, we have discussed only the collision processes that increase the positive charge of a multiply charged ion by removing its electrons. Because such an ion carries a large positive charge, it exerts an attractive force on both free electrons and electrons in other atoms. The most probable way for the charge of a multiply charged ion to be reduced is by a collision process called electron capture (or charge exchange), in which a multiply charged ion collides with a neutral atom or molecule, capturing one or more of its electrons. Cross sections (probabilities) for such collisions are relatively large and increase with the initial charge on the ion. For the ions and energy ranges that we have studied, electron capture cross sections are typically about 100 to 1000 times as high as those for ionization by electron impact.

ORNL has a pioneering heritage in the investigation of electron-capture collisions. Recent studies in our group have focused on low-velocity collisions, in which the electron clouds of the colliding particles have plenty of time to interact with each other. Such collisions are difficult to treat theoretically because of the large number of possible states in which electrons may be captured. Most of our studies have concentrated on electron capture by multicharged ions from hydrogen atoms, which each possess only a single electron. Use of hydrogen simplifies the theoretical treatment considerably.

The experiments we have performed to study such collisions are relatively straightforward. A beam of multicharged ions is directed through a gas target cell containing hydrogen atoms. The

Fig. 6. Charlie Havener adjusts the charge-analyzing magnet of a merged-beam apparatus in which slow electron-capture collisions of multicharged ions with hydrogen atoms are investigated. An atomic hydrogen beam is formed by passing a beam of negatively charged hydrogen ions through a laser beam, which neutralizes the ions by photodetachment. The multicharged ion and atomic beams are merged by electric fields in the large ultrahigh vacuum chamber at center.

cross section is determined by measuring the fraction of ions that capture an electron as a function of the hydrogen atom density. The major complication arises from the fact that hydrogen exists in the molecular state (H_2) at ordinary temperatures, so we used a special gas target cell to break the hydrogen molecules into atoms. Our cell is a tungsten tube heated to about 2000°C—about the temperature of the filament in a 25-W light bulb. When normal molecular hydrogen is admitted into this tube, about 90% is dissociated into hydrogen atoms.

Our studies have attempted to characterize the electron capture process and develop generalized theories and scaling laws. The recent implementation of our new ECR multicharged ion source has allowed us to be the first group to systematically investigate collisions of bare multicharged ions with hydrogen atoms. In such a collision, two nuclei compete for only a single electron. From the perspective of atomic physics, this represents a true three-body interaction, one of the simplest problems that cannot be solved exactly in physics. In a recent series of experiments led by Meyer, anomalies (oscillations) in the scaling of electron-capture cross sections with ionic charge for bare ions were explained on the basis of a simple model for the interaction (Fig. 5). An interpretation of the basic features was made possible by the fact that only a single electron takes part in the collision. Thus,

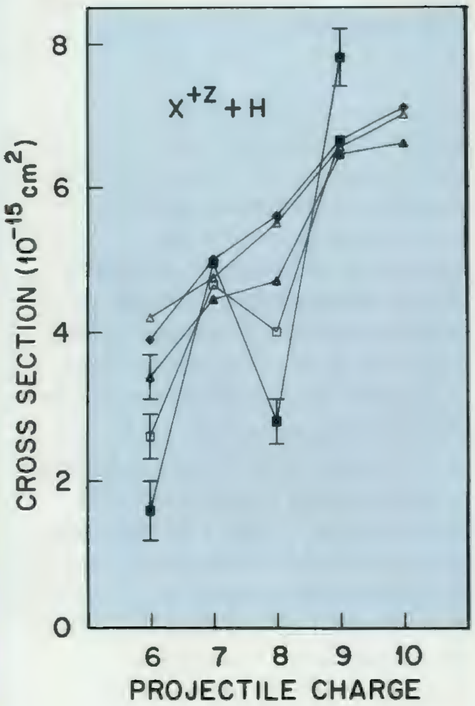


Fig. 5. The probability that a multiply charged ion will capture an electron in a collision with a neutral particle is large and increases with the charge of the ion. Here the measured variation with ion charge of capture cross sections for bare ions (X^{+z}) colliding with hydrogen atoms (H) is shown at five different collision velocities. The solid squares are for the lowest velocity, and the open triangles are for the highest. The pronounced oscillatory structure is progressively dampened as the collision velocity increases from 11 to 56% of the mean orbital speed of the electron on the hydrogen atom. The structure is the result of variations in the availability of quantum states into which the electron may be readily captured. As the velocity increases, the capture becomes less state-selective, and the oscillations eventually disappear.

Multiply Charged Ions in Fusion

The most important practical applications of research on collisions of multiply charged ions are found in fusion energy research. In fact, our group in the Physics Division is a part of the ORNL Fusion Program, and a major portion of our financial support comes from the Department of Energy's Office of Fusion Energy.

The goal in fusion research is to confine and heat heavy isotopes of hydrogen (deuterium and tritium) to temperatures so high that their nuclei collide violently and fuse together, releasing enormous amounts of energy in the process. The temperatures required are in the millions of degrees, well beyond the vaporization limits of any materials. In fact, such temperatures are high enough to completely strip most atoms of their electrons. The hot ionized gas, or plasma, must therefore be confined by some other means.

The most promising methods employ magnetic fields to confine the hydrogen ions, in ways similar to that used to confine hot electrons in our ECR ion source. The Advanced Toroidal Facility (ATF) currently being developed in ORNL's Fusion Energy Division is a device based on these principles (see article by John Sheffield in the ORNL *Review*, Number Three, 1984).

One of the most important obstacles to be overcome in designing an energy-producing fusion reactor results from the inability of magnetic fields to perfectly confine a hot plasma. Energetic particles escaping from the plasma core strike the interior wall of the containing vessel, sputtering materials from the wall surface into the plasma. Stainless steel is the usual wall material in fusion devices, and common impurities are iron, nickel, and chromium, which make up the wall material, as well as oxygen, which sticks to metal surfaces.

The temperatures in a fusion device are high enough that collisions in the plasma will quickly strip away many of the electrons from these impurities, creating multiply charged ions. As we have seen, this stripping or ionization process requires considerable energy; thus, the impurities cool the hydrogen plasma. Further cooling occurs because impurities that have lost some but not all of their electrons have other extremely efficient ways to dissipate energy, such as emitting light. A plasma can lose considerable energy if it contains as little as 1% iron (nuclear charge of +26). Although such emissions of energy from impurities are deleterious to plasma heating, they can be measured, thus providing a diagnostic to understand fusion plasmas just as astronomical measurements help us determine the characteristics of stellar plasmas.

The study of charge-changing collisions of multiply charged impurity ions thus plays an important role in fusion research. Accurate cross-section data are required to model the ionization and movement of impurities in the plasma. Because it would be impossible to measure cross sections for all the impurity species and charge states present in a plasma, we have attempted to systematize our studies along ionic sequences to identify scalings and trends and to provide benchmarks against which atomic theory may be tested. With the rapid advances being made in supercomputer technology, the eventual generation of a complete and reliable data base is not out of the question from a theoretical standpoint, provided that some experimental data are available to check the theoretical tools as they are developed and applied to more and more complex problems. ORNL's Controlled Fusion Atomic Data Center is operated by our group and has the mission of compiling, evaluating, and recommending atomic collision data to the fusion research community.

Other Key Players

In addition to those mentioned, a number of individuals have made substantial contributions to the research on collisions of low-energy, multiply charged ions. Dave Crandall (now with DOE) and Clarence "Barney" Barnett were responsible for establishing this area of research at ORNL and have provided sound leadership and inspiration over the years. Our long-standing collaboration with Gordon Dunn and his group at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado, has been a most productive one. Finally, our senior technologist, Jerry Hale, keeps our laboratory running smoothly and holds the record for time spent in the cage wrestling with the PIG source.

only hydrogen and hydrogen-like ions are involved. Because the structure of hydrogenic systems can be calculated exactly, the role of the dynamics of the collision could be directly addressed. Even the most sophisticated quantum-mechanical calculations of cross sections for these "simple" collisions differ from each other and from the experimental results by as much as 50% at the lowest collision velocities, emphasizing the fact that much remains to be learned about ion-atom collisions.

Electron-capture collisions of partially stripped multicharged ions are even more complex from a theoretical standpoint. Accurate experimental data are needed at even lower collision velocities than shown in Fig. 5 to test critically our understanding of these processes. During the last few years, Charlie Havener and I have been developing a new experimental approach in which a beam of multicharged ions is merged with a beam of hydrogen atoms (see Fig. 6). The scenario is similar to the exchange of a baton in a relay race. If the velocities of the beams are made to be nearly equal, very low relative velocities between the beams can be achieved by this method and very slow collisional interactions can be studied. The technology of such experiments is demanding, and we are just beginning to obtain definitive results.

Sheldon Datz is head of the Atomic Physics Section of ORNL's Physics Division. Born in New York in 1927, he received his B.S. and M.A. degrees in physical chemistry from Columbia University and his Ph.D. degree in physical chemistry from the University of Tennessee. He has been at ORNL since 1951 and has held various positions, including associate director of the Chemistry Division. He has been awarded a Fullbright Senior Research Fellowship and is a Martin Marietta Corporate Research Fellow. He has held guest professorships at the FOM Institute for Atomic and Molecular Physics in Amsterdam, Netherlands; Aarhus University, Denmark; Max Planck Institute for Plasma Physics, Munich, Federal Republic of Germany; University of Paris, France; University of Chicago, and Texas A&M University. In 1955 he pioneered the technique of crossing molecular beams for the study of mechanisms of chemical reactions; the technique was recognized by the 1986 Nobel Prize in Chemistry, which went to three men who refined the Oak Ridge technique. Datz's work has also included inelastic scattering and surface scattering. He has edited a number of books on atomic collision phenomena. His work now centers on accelerator-based atomic physics and has included gas phase ion-atom collisions, ion-electron collisions, ion-surface scattering, and interactions of penetrating energetic particles with crystalline solids.

High-Energy Atomic Physics

By SHELDON DATZ

High-energy atomic physics generally involves the use of multiply charged ions, atoms that have had some or all of their electrons removed, generally by violent collisions with electrons or atomic nuclei. The natural environment for these species is therefore in regions of very high energy density. On a macroscopic scale, multiply charged ions exist in equilibrium in stellar atmospheres, in magnetically confined thermonuclear plasmas, or briefly in inertially confined plasmas and nuclear explosions.

On a microscopic scale, a nuclear fission event gives rise to fragments that are energetic multiply charged ions. The slowing down of these ions in solids by atomic collision processes results in heat such as that used in nuclear power plants to generate electricity. In fact, most of the multiply charged ions generated by human activity are formed in the fuel elements of fission reactors. Currently, the world's generating capacity is ~260 GWe. With a thermal efficiency of ~30%, ~200 MeV per fission, and two multiply charged fragments per fission, this works out to be ~9000 amperes of highly charged ions!

Energetic multiply charged ions are also found in accelerators dedicated to nuclear and particle physics research. For acceleration purposes, the higher the charge on the ion, the better: the energy that ions can attain through a given electrical impulse and the ease with which they can be manipulated by electric or magnetic fields are directly proportional to their charge. In the study of nuclear reactions, the ions pass through targets where many more atomic events than nuclear ones take place; hence, an understanding of atomic physics is needed for nuclear experimentation.

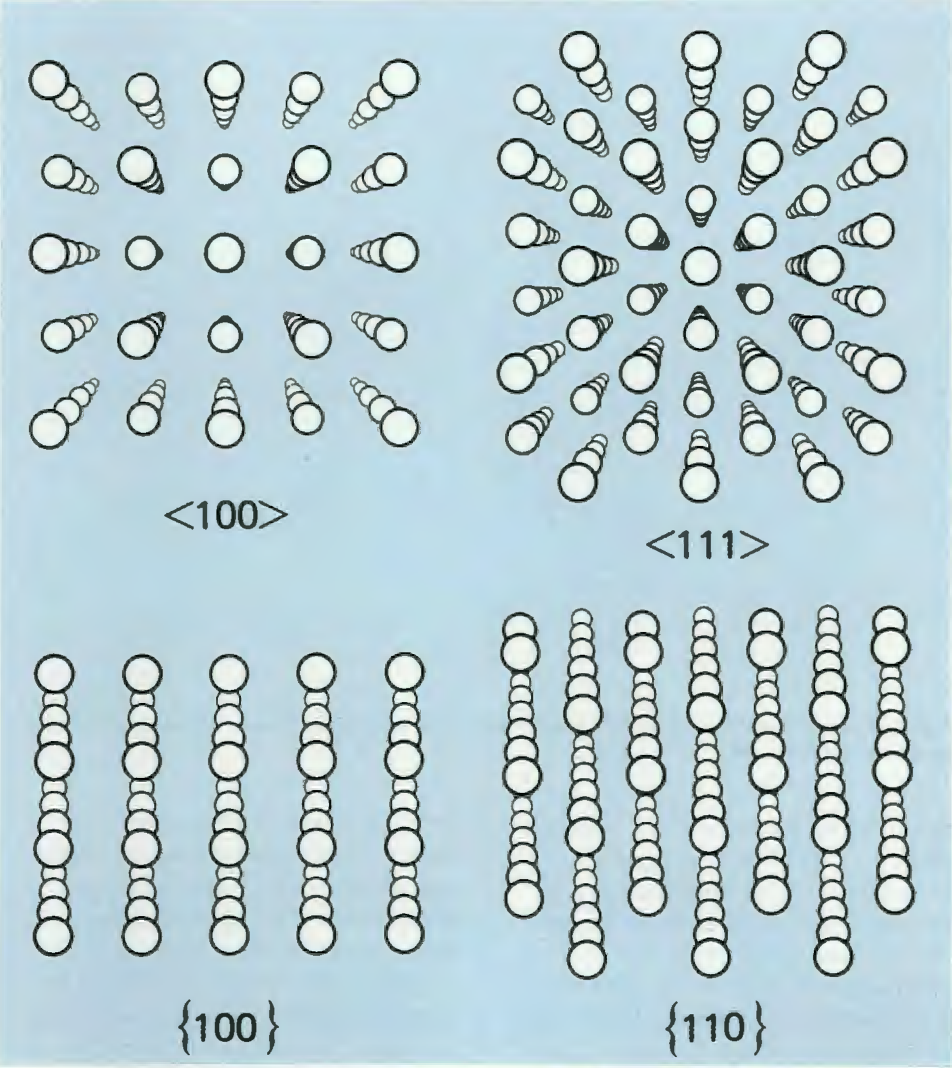


Fig. 1. A simplified model of a face-centered-cubic crystal showing the open axial and planar directions (channels).

High-energy atomic physics research at ORNL includes studies of ion channeling in crystals, which provides information about crystal forces and the penetrating ions, as well as studies of the electron-ion recombination that occurs when beams of electrons and ions are merged. The proposed Heavy-Ion Storage Ring for Atomic Physics is also discussed.

The relationships between atomic physics and nuclear physics, plasma physics, and energy technologies suggests why the interactions of ions with atoms, electrons, and solids is a proper subject for research at Oak Ridge National Laboratory. However, the diversity of investigative paths that have evolved from the use of accelerators to study atomic physics is surprising. These approaches include the study of (1) ion channeling in crystals, (2) the various paths for the formation of inner-shell vacancies in ion-atom collisions (including the formation of "quasi-molecules"), which lead to the production of X rays, (3) the correlation of electrons in pairs when they transfer from a target atom to a highly charged ion, and (4) the delicate recombination processes that occur in plasmas, as simulated by merging electron beams with ion beams that have been accelerated to tens of millions of electron volts (eV). In this article I will concentrate on the first and the last of these topics.

Heavy-Ion Channeling

Actually, our ventures into heavy-ion atomic physics began more than 20 years ago, when Charlie Moak and his co-workers in the Physics Division found that they could make beams of bromine and iodine in our EN-tandem Van de Graaff accelerator with energies up to 110 MeV. These beams could be used to simulate the action of fission fragments.

In 1963 I returned to ORNL's Chemistry Division following a sabbatical in Amsterdam, where I had demonstrated the single-atom nature of energetic ion collisions with surface atoms and had observed that the effect was enhanced when the ion beam was headed into an "open" direction in the crystal (see Fig. 1). Also about that time, the phenomenon of "channeling" was discovered in the computer calculations of Mark Robinson and Dean Oen of ORNL's Solid State Division. They found that ions moving in a crystal were repelled not by single collisions with the atoms in the solid but by the collective action of the atoms in the close-packed rows ("strings") and planes of the crystal. The analytical description for the "string effect" was given about a year later by Jens Lindhard of Aarhus, Denmark.

Joining forces with Tom Noggle of the Solid State Division, Charlie Moak and I showed that when energetic heavy ions penetrate through a thin (2000 Å) crystal of gold in a channeling direction, they lose only about half the energy they would lose going through the same thickness in a random direction. Penetrating ions lose energy mainly through collisions with electrons, and the reduction in energy loss for channeled particles occurs because the gentle pushing by the "strings" or "planes" keeps the ion away from the atomic cores where the electrons are concentrated.

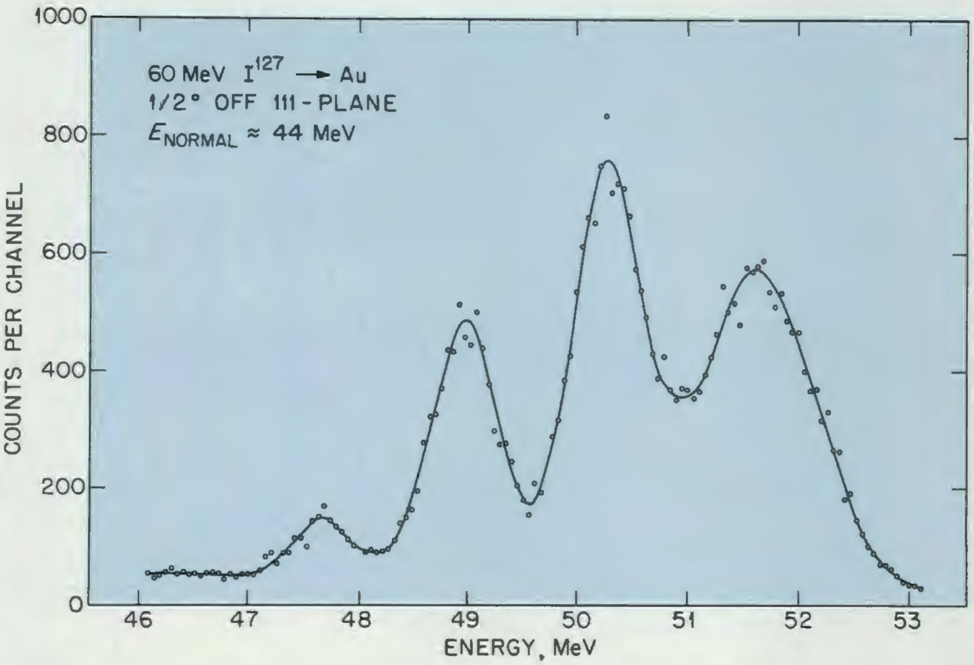


Fig. 2. Energy spectrum of 60-Mev iodine ions after they have passed through a channel in a thin gold crystal.

When we looked harder at planar channeling and concentrated on ions emerging in the forward direction, we found structure in the energy-loss spectrum (see Fig. 2). This structure occurs because the paths of the ions inside the crystal depend on where they enter it. The ones that enter closer to the atomic planes are pushed harder and undergo more frequent oscillations than the ones entering farther away. Moreover, the ones entering closer to the planes penetrate regions of higher electron density and therefore lose more energy. This change in energy loss varies continuously with the ions' entrance point.

We had no control over where an ion entered; yet we saw structure. The reason for this is shown in Fig. 3. The angle at which the ion leaves the crystal depends on the wavelength of its motion in the channel; that wavelength decreases as the amplitude (and energy loss) increases. Because we made our observations in the forward direction, only those ions leaving the crystal in that direction (integral member of wavelengths) could be detected; the ones in between having intermediate energy losses simply missed the detector.

This discovery led to the possibility of determining new information about crystals, such as the crystal forces felt by penetrating particles and "stopping powers," the ability of crystal atoms to stop penetrating ions, as functions of ion distance from an atomic row or plane. In collaboration with Hans Lutz (now a professor in the Federal Republic of Germany), Mark Robinson, Bill Appleton, and John Barrett, we were able to arrive at potential maps for crystals (see Fig. 4).

This experiment also revealed something about the state of the ion moving in a solid. This was (and is) an important question that has not been completely solved. How can we describe the state of an ion that is colliding with about 10^8 atoms over a centimeter path length (or for ions moving at high speeds, about 10^{17} collisions per second)? Can we say anything about particles that may be changing their states so often? It turns out that by using channeling as a tool, we can say quite a bit. For example, when we shot energetic (e.g., 30-MeV) oxygen ions, which were either bare of electrons or had one or two bound electrons, through channels in thin crystals, we found that a large fraction of the ions neither lost nor captured electrons. Why? First, because the ions moved through regions of relatively low electron

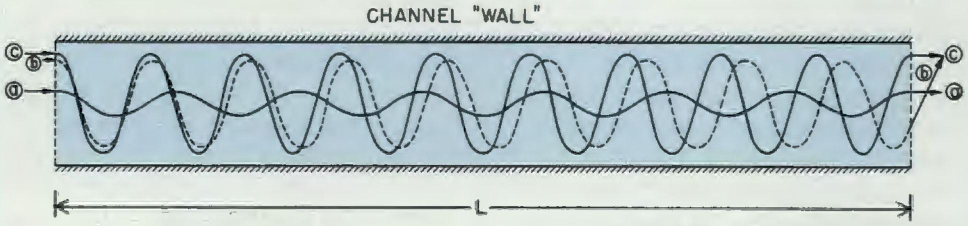


Fig. 3. Trajectories of ions entering a planar channel at three different points. Particles a and c will reach a detector in line with the entering beam; particle b will not.

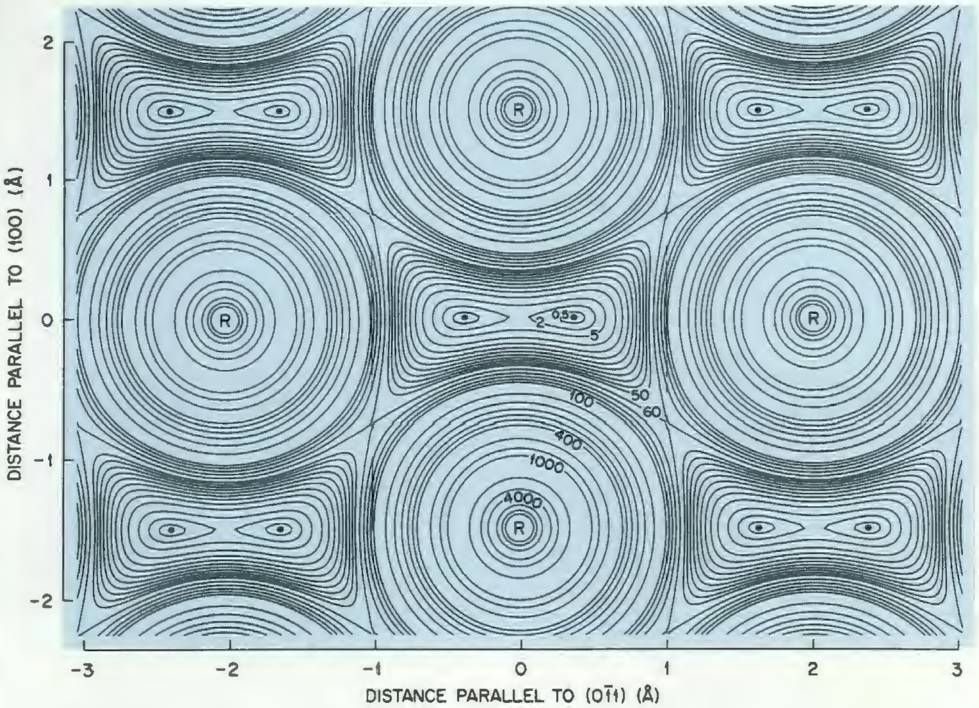


Fig. 4. Potential map of a crystal showing energy contours.

density, there was little danger of their electrons being stripped through collisions. Second, because the electrons they interacted with had a much lower velocity than the ion velocity, electron capture was difficult.

Using these ions with "frozen" charge states, we could measure the dependence of the projectile nuclear charge on the stopping power of atoms in the crystal, the effect of bound electrons on screening the nuclear charge, and many other aspects of penetration phenomena.

Resonant Coherent Excitation

By far the most delicate and precise measurement of the states of penetrating ions came from our experiments on "resonant coherent excitation." So far, we have been considering the motion of ions determined only by the rod-like (axial) or sheet-like (planar) channels. But atomic physicists at ORNL and elsewhere have also wondered about the effect of the "beadiness" of the strings on ions. Each time an ion passes an atom in a string, it receives an impulse from the local electric field (see Fig. 5). Because the atoms are evenly spaced along the string, the ion receives a periodic impulse of a frequency equal to its velocity divided by the distance between atoms in the string. Now, if an ion moving in a crystal is indeed in a well-defined (ground) state and can be excited into another well-defined state, it is logical that a velocity exists at which a resonant frequency is achieved that can cause a transition from the ground state to an excited state.

An experiment to test this hypothesis was possible because the electron in an excited state can more easily be removed during its passage through the channel than can one in its ground state. In a series of experiments, we used ion beams of boron, carbon, nitrogen, oxygen, and fluorine from our EN-tandem accelerator and from the Holifield Heavy-Ion Research Facility tandem accelerator. An example of the results is shown in Fig. 6. Here we used a beam of fluorine ions that had been stripped of all but one electron. We passed the beam through a channel in a 1600-Å-thick gold crystal at different velocities and measured the fraction of the ions that got through without losing their sole electron. We found that a velocity exists at which the surviving fraction suddenly decreases, suggesting that many more sole electrons were excited to the point of being removed. This velocity is very close to that at which a resonant excitation from the ground (1*s*) state to the excited (2*p*) state of the ion would occur *if* the ion were in a vacuum. The slight but measurable difference between the vacuum state and the crystal state results from the effect of the crystal field and the response of the "electron gas" through which the ion is traveling. Spectra of this type give highly detailed information on

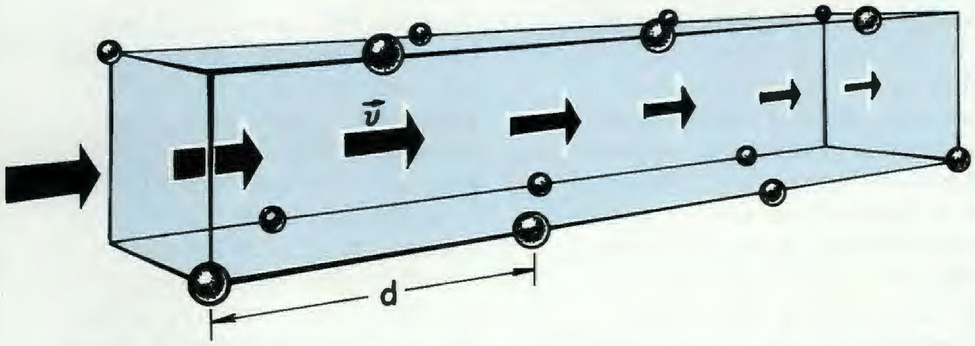


Fig. 5. An ion moving down a channel receives periodic impulses from the atoms lining the channel.

the interactions of fast ions with solids. The detailed interpretation of these spectra is continuing. In addition to Charlie Moak and me, the work on resonant coherent excitation was carried out by Herb Krause, Oakley Crawford, Phil Miller, John Biggerstaff, and George Gomez del Campo of ORNL in collaboration with Helge Knudsen and Preben Hvelplund from Denmark and Nebojsa Neskovic from Yugoslavia.

Electron-Ion Recombination

In a hot plasma (as in a fusion device), ions are continually bombarded by electrons; such "jostling" of ions can result in the excitation of electrons bound to each ion and in the loss of electrons (ionization) from some ions. The free electrons may also recombine with an ion so that the number of electrons remaining on an ion at any one time depends on the competing rates of ionization and recombination.

Recombination is actually a rather delicate process because the potential energy gained when an electron falls into a bound state must be gotten rid of somehow or it will break free from the ion. The situation is much like rolling a marble into a smooth depression; on the way down it gathers speed and, in the absence of frictional loss, it will roll up the other side and out again. Two processes are known to be important in recombination: radiative recombination in which a quantum of light is released with an energy exactly equal to the potential energy gained and "dielectronic" recombination in which the unbound electron kicks one of the already bound electrons into a higher state (further from the nucleus) and, in so doing, loses just enough of its own energy to be itself captured into a bound state. Because this latter process for recombination involves the cooperative action of *two* electrons, it is called dielectronic.

Remarkably, until about three years ago none of these recombination processes had been studied under controlled conditions. At that time we began reporting on dielectronic recombination of multiply charged ions using an apparatus in which we merged a beam of electrons with a beam of ions coming from our EN tandem Van de Graaff accelerator. (The apparatus used is shown schematically in Fig. 7.) An electron beam from a spherical heated cathode (2 cm in diameter) is compressed and contained in a solenoidal magnetic field over a length of about 1 m, after which it expands and is dumped. The ion beam coming from the accelerator enters the electron beam through a small hole in the cathode. It interacts with the electron beam over the merged length and passes on to another region, where it is analyzed to determine if it has captured an electron. If a recombination has occurred, the ion's positive charge will drop by one unit. Because dielectronic recombination requires very specific collision energies, we can measure the energy dependence of the fraction of ions that have captured an electron.

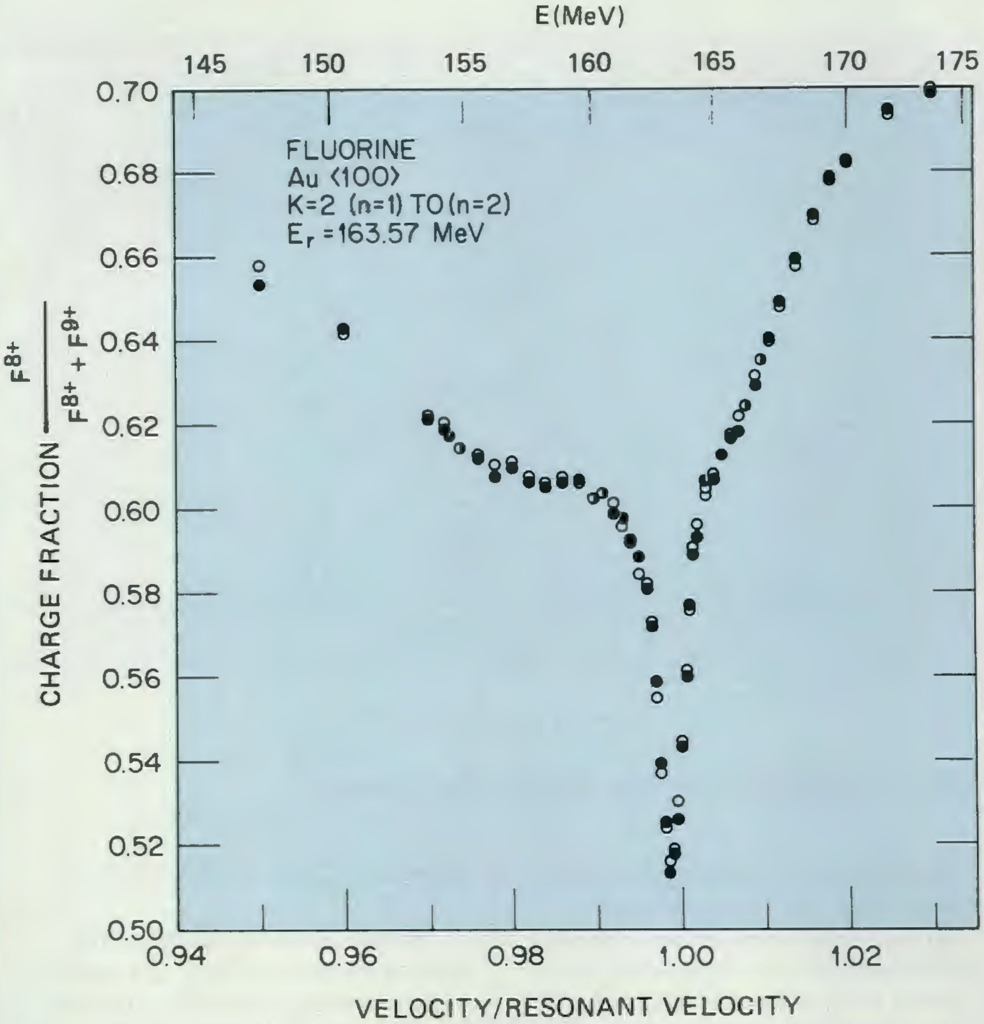


Fig. 6. The fraction of one-electron-containing fluorine ions that survive passage through a 1600-Å-long channel in gold as a function of ion energy (top scale). Plotted along the bottom is the ion velocity divided by the velocity calculated to give a resonance assuming that the ions' state in the crystal is the same as that in vacuum.

In Fig. 8 such a measurement is shown for sulfur that had been ionized five times (S^{5+}). These ions resemble neutral sodium atoms in that they contain a single electron in the outermost *3s* shell. The incoming electron excites the *3s* electron to a *3p* state and is itself caught in some high but bound state of the now S^{4+} ion. There are many of these bound states, each with its own characteristic energy, but we observe only a single envelope because our energy resolution is insufficient to see them as separated lines. The two solid curves shown represent the extremes predicted by theory depending on the effects of the local electric field in the merged-beam region. We have measured about a dozen ionic systems and have established some systematics, which now require further refinements of theory for their explanation.

In the merged-beam technique, both the electron and the ion beam are moving at very high velocities in the laboratory system but at low velocities relative to each other. The collisions are much like those in the car-chase scenes that inevitably occur in many movies. The cars are careening on the city street at a breakneck pace, but only small crunching sounds are heard when one car hits the other in the rear. In the collision, only the relative velocity counts. Because an electron is much lighter than an ion and about 2000 times lighter than a proton, it takes less energy to bring it to the same velocity as an ion. For example, an oxygen ion has a mass 16 times that of a proton. To match the velocity of an oxygen ion of 32 MeV, an electron needs an energy of only about 1 keV. (The electrons used in a TV picture tube have energies of 20 keV).

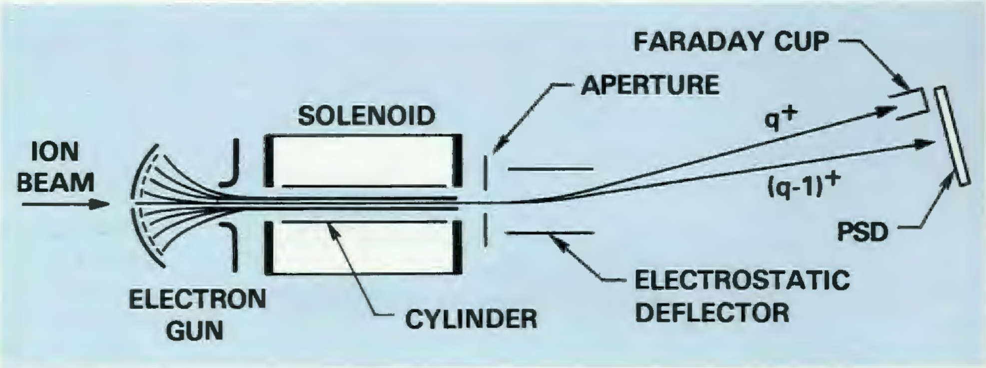


Fig. 7. Schematic diagram of the multiply charged ion-electron merged beam apparatus used to measure recombination.

In our experiments we fix the energy of the electron beam and vary the relative energy by changing the velocity of the accelerated ion beam. In Fig. 8 the horizontal scale, shown at the bottom, represents relative collision energy in eV; at the top is given the corresponding sulfur-ion beam energy in MeV. Note that to change the relative energy by just 1 eV at 10-eV relative energy, a 0.4-MeV change in ion energy is required. Because the ion energies can be measured with good precision, this demagnification effect can lead to very high precision measurements of the relative energy.

Why do we use merged high-energy beams rather than crossed low-energy ones? Reasons include the ready availability of multicharged ions, increased electron beam currents, and strong reduction in background signals that result from interactions with trace amounts of gases remaining in the vacuum system.

By using this merged-beam technique, we were the first to make recombination measurements on multiply charged ions. Besides me, the members of the group that developed and applied this difficult technique were Pete Dittner, Phil Miller, Charlie Moak (now retired), Paul Stelson, Gerald Alton, and Bill Dress (all from ORNL), and C.M. Fou from the University of Delaware.

Much remains to be done in this area of atomic physics. For example, we can learn a great deal from measurements of the individual resonances that make up the bump in Fig. 8. Dielectronic recombinations that are dominant in very high-temperature plasmas involve higher-energy excitations but have too low a probability in single collisions to be measured with current techniques. Radiative recombination, which has never been measured for complex ions,

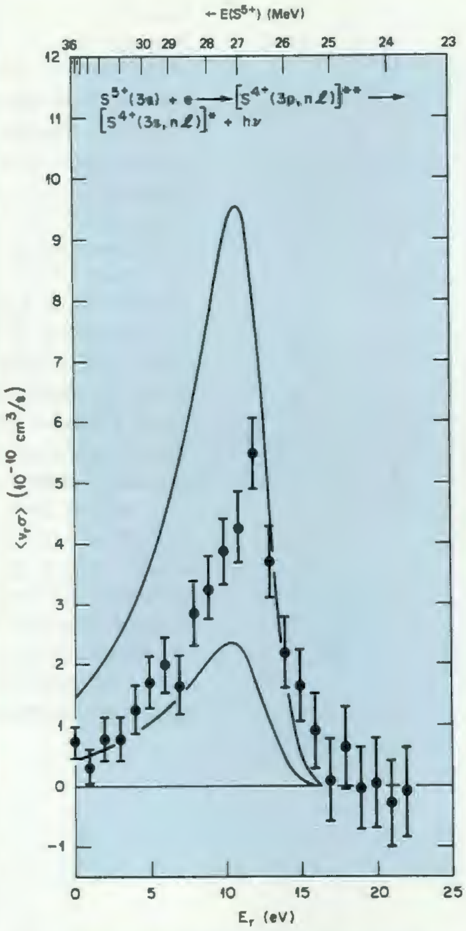
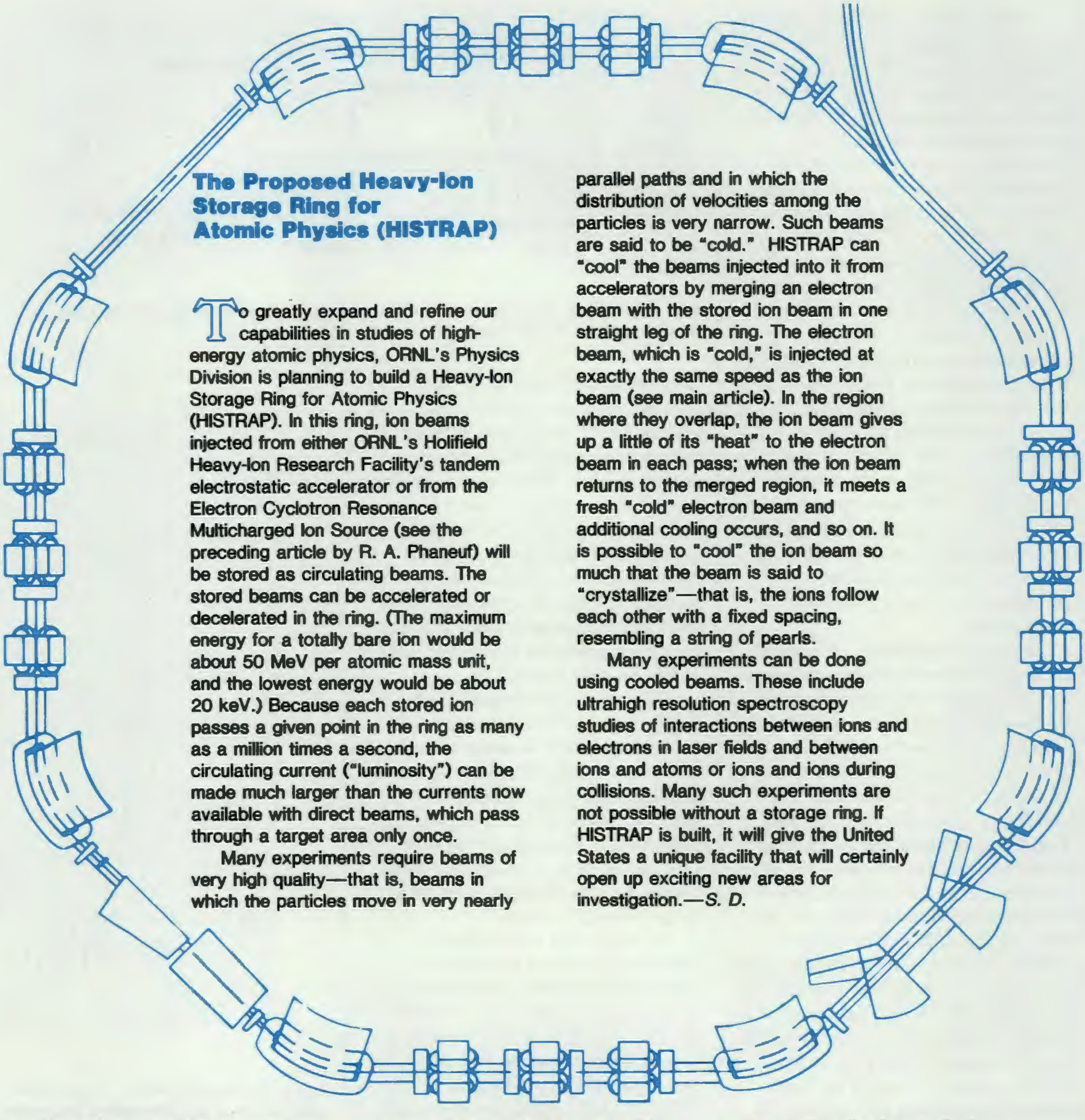


Fig. 8. The rate at which S^{+5} recombines with electrons as a function of ion energy (top) and relative energy (bottom). The solid curves give limits on the theory.

requires relative collision energies very close to zero, which are difficult to obtain with our present electron beam. To open these and other areas of investigation will require the development of more advanced merged-beam techniques. Investigations of electron-ion collisions represent one area that can be opened up using ORNL's proposed Heavy-Ion Storage Ring for Atomic Physics (HISTRAP) facility (see sidebar).

I have chosen the two examples used in this article to demonstrate the broad range of applicability of accelerator-based atomic physics and the complementarity of the scientific results obtained with other disciplines (solid-state physics) and other techniques (low-energy atomic collision physics). In between exist many other areas of atomic collision physics that can be investigated with accelerated ions when we have the capability of producing ion beams of higher quality and intensity and in more highly ionized states.



The Proposed Heavy-Ion Storage Ring for Atomic Physics (HISTRAP)

To greatly expand and refine our capabilities in studies of high-energy atomic physics, ORNL's Physics Division is planning to build a Heavy-Ion Storage Ring for Atomic Physics (HISTRAP). In this ring, ion beams injected from either ORNL's Holifield Heavy-Ion Research Facility's tandem electrostatic accelerator or from the Electron Cyclotron Resonance Multicharged Ion Source (see the preceding article by R. A. Phaneuf) will be stored as circulating beams. The stored beams can be accelerated or decelerated in the ring. (The maximum energy for a totally bare ion would be about 50 MeV per atomic mass unit, and the lowest energy would be about 20 keV.) Because each stored ion passes a given point in the ring as many as a million times a second, the circulating current ("luminosity") can be made much larger than the currents now available with direct beams, which pass through a target area only once.

Many experiments require beams of very high quality—that is, beams in which the particles move in very nearly parallel paths and in which the distribution of velocities among the particles is very narrow. Such beams are said to be "cold." HISTRAP can "cool" the beams injected into it from accelerators by merging an electron beam with the stored ion beam in one straight leg of the ring. The electron beam, which is "cold," is injected at exactly the same speed as the ion beam (see main article). In the region where they overlap, the ion beam gives up a little of its "heat" to the electron beam in each pass; when the ion beam returns to the merged region, it meets a fresh "cold" electron beam and additional cooling occurs, and so on. It is possible to "cool" the ion beam so much that the beam is said to "crystallize"—that is, the ions follow each other with a fixed spacing, resembling a string of pearls.

Many experiments can be done using cooled beams. These include ultrahigh resolution spectroscopy studies of interactions between ions and electrons in laser fields and between ions and atoms or ions and ions during collisions. Many such experiments are not possible without a storage ring. If HISTRAP is built, it will give the United States a unique facility that will certainly open up exciting new areas for investigation.—*S. D.*

Platinized Chloroplasts: A New Bioelectronic Material Developed at ORNL

When plants photosynthesize carbohydrate from carbon dioxide and water, an elaborate electron-transport system links the two light-activated reactions that drive the process. In a new bioelectronic system developed at ORNL, colloidal platinum precipitated onto the surface of a spinach-derived, photosynthetic thylakoid membrane short circuits the transfer of electrons and splits water, yielding hydrogen and oxygen instead of carbohydrate and oxygen.

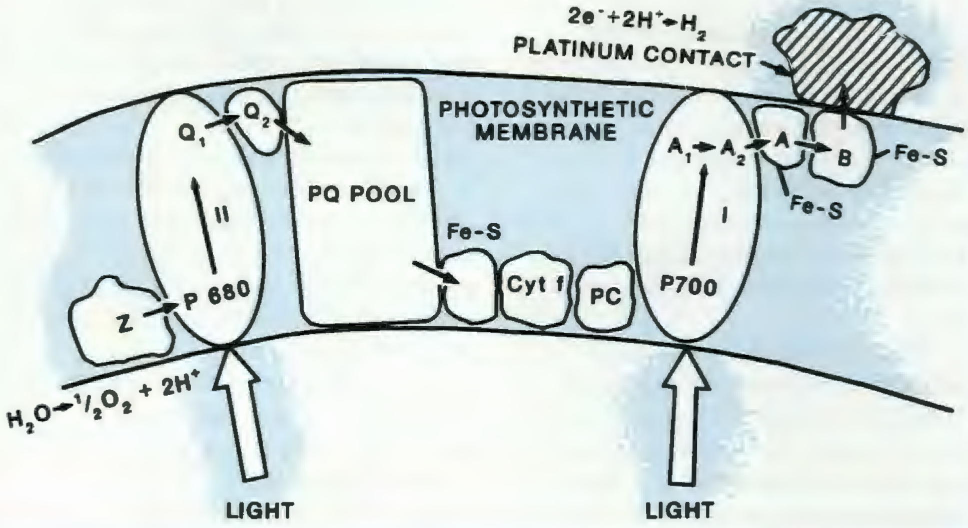
In 1985 Perry Eubanks and I discovered this material, which we call "platinized chloroplast," in our search for efficient photosynthetic methods of producing hydrogen fuel from water. This new development has successfully combined approaches from the field of biotechnology with the nonbiological methods of molecular engineering.

Data on the platinized chloroplast system demonstrate electron flow across the membrane-metal interface while maintaining charge continuity. In addition to its electrical properties as a metal, platinum is a highly efficient cathode for the electrosynthesis of hydrogen. The moistened platinized chloroplast is capable of sustained simultaneous photoevolution of hydrogen and oxygen when irradiated with any wavelength of light in the chlorophyll absorption spectrum.

In determining which specific ionic species could be used for preparing the bioelectronic material, we acquired additional information about the electrostatic properties of the Photosystem I reduction site on the membrane surface. Hydrogen was produced when we used platinum precipitated from the hexachloroplatinate(IV) ion, which bears a net charge of minus two (2−). When we used platinum precipitated from the positively charged (2+) tetraammineplatinum(II), no hydrogen activity was detected. This result suggests that the 2+ ion is repelled by the Photosystem I reduction site which, presumably, bears a net local positive electrostatic charge. This interpretation is logical, considering that the protein amino acid composition in the vicinity of Photosystem I is rich in lysine residues, which would be positively charged at physiological pH.

We first used the conventional method for precipitating elemental platinum onto a substrate (i.e., treating an aqueous salt solution of the metal with a chemical reductant) to prepare platinized chloroplasts. Recently, however, we have discovered that the Photosystem I light reaction of photosynthesis itself can serve as the source of reductant. This method of platinizing chloroplasts has the unique advantage of depositing the metal colloid particle at the site of electron emergence from the thylakoid membrane; thus, the particle can serve as a marker for the Photosystem I reduction site.

Platinized chloroplasts are an example of an artificial photosynthetic material in which the energy-rich product is molecular hydrogen rather than a carbon dioxide fixation compound (the normal product of photosynthesis). A near-term goal of our research in the Chemical Technology Division is to effect other energy conversion reactions, such as the synthesis of ammonia or methane, by contacting selected metals and catalysts with the energy-rich electrons emerging from the photosynthetic membrane. Photoreactions of this type are clearly of scientific interest for the production of fuels and chemical feedstocks from renewable organic resources.—*Elias Greenbaum, Chemical Technology Division.*



Photosynthesis consists of two light reactions, Photosystems I and II, that are linked in series by an electron-transport chain. The photosystems, as well as the electron-transport chain, are embedded in a thin (70-Å) membrane, which also contains the light-harvesting chlorophyll molecules. In normal photosynthesis, the electrons emerge from the membrane and flow to the Calvin cycle enzymes for the chemical reduction of carbon dioxide to carbohydrate. The platinum contact short-circuits the electron flow and serves as an electrode for the photoelectrosynthesis of hydrogen from water.

Learning to separate one substance from another has been an important activity at ORNL from the beginning. Early separation research was directed at problems in nuclear technology, but today it has broadened to include fossil fuels, the environment, waste management, and biotechnology. This overview explores current R&D in separation science at ORNL.

Separation Science and Technology

By CHARLES F. BAES, JR., and
DAVID J. PRUETT

What is now Oak Ridge National Laboratory was established as part of the Manhattan Project in 1943 primarily to demonstrate the production of plutonium by the irradiation of natural uranium with neutrons in a chain-reacting "pile" (the Graphite Reactor) and then to separate this new element in pure form. The separation of one substance from another has remained an important part of ORNL's programs in all the years since.

The amounts of material separated by processes developed at ORNL have ranged from very large to very small. Solvent extraction on a scale of thousands of tons has recovered uranium from its ores, purified spent nuclear reactor fuels, and removed hafnium (a neutron absorber) from zirconium metal (used for cladding nuclear fuel). Many different methods have been used to separate gram quantities of radioisotopes and stable isotopes, and chromatographic procedures routinely separate submilligram amounts of artificial transplutonium elements produced at the High Flux Isotope Reactor (HFIR). Laser-excitation analytical techniques developed at ORNL have even separated and identified a single atom of one isotope in a mixture of isotopes.

Research and development activities on many aspects of separation science and technology are continuing at ORNL. In this article we will review current studies involving solvent extraction, chromatography, electromagnetic separation, laser-based separation techniques, and bioseparations.

Solvent Extraction

In the late 1940s, processes were developed at ORNL to recover uranium from the stored wastes of the plutonium pilot plant. These processes involved the rapidly developing technology of solvent extraction in which a desired substance is separated by extracting it from a water solution and transferring it into a second, non-water-soluble liquid. Attention then turned to the general problem of learning how to process nuclear reactor fuels to recover usable uranium and plutonium from spent fuel (for possible reuse in reactors)

Charlie Baes is leader of the Separations Chemistry Group in ORNL's Chemistry Division. He obtained his Ph.D. degree in physical and inorganic chemistry at the University of Southern California in 1950 and came to ORNL in 1951. His initial research was conducted on the chemistry of solvent extraction processes related to recovery of uranium. In the years since, his research centered on the chemistry of liquid solutions in nuclear reactors and, later, in the environment. In 1976 he and Robert E. Mesmer (also of ORNL) published a book on the hydrolysis of metal ions in aqueous solutions. In his current position, he has returned to his original interest, the basic chemistry of solvent extraction processes. He is a fellow of the American Association for the Advancement of Science.

Dave Pruett is a member of the Chemical Development Section in ORNL's Chemical Technology Division. A native of Pontiac, Michigan, he earned his Ph.D. degree in analytical chemistry from Michigan State University in 1978. Upon graduation he came to ORNL to investigate the chemistry of the actinide and fission product elements and, in particular, their separation behavior in nuclear fuel reprocessing. In 1985 he authored a broad review of separation science and technology and its role in the programs and mission of ORNL. His current interests include continued investigations of the separation chemistry of the actinide elements and the application of advanced computer technology, especially artificial intelligence, to separation science.

Here Pruett (left) and Baes look at output from preparative high-pressure liquid chromatography, a separations technique.

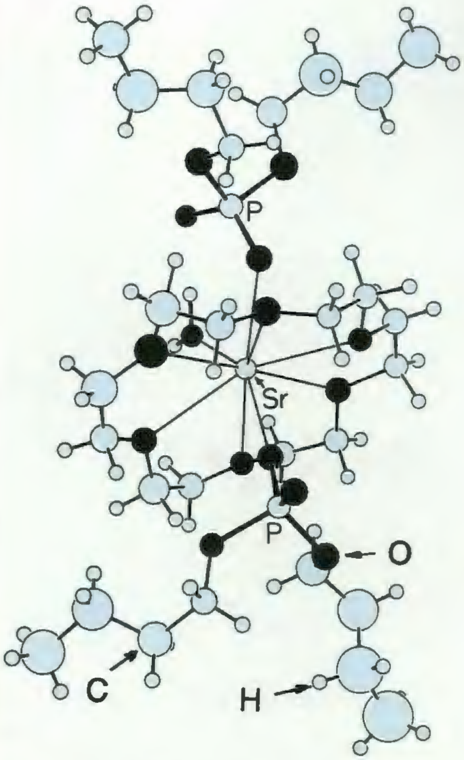


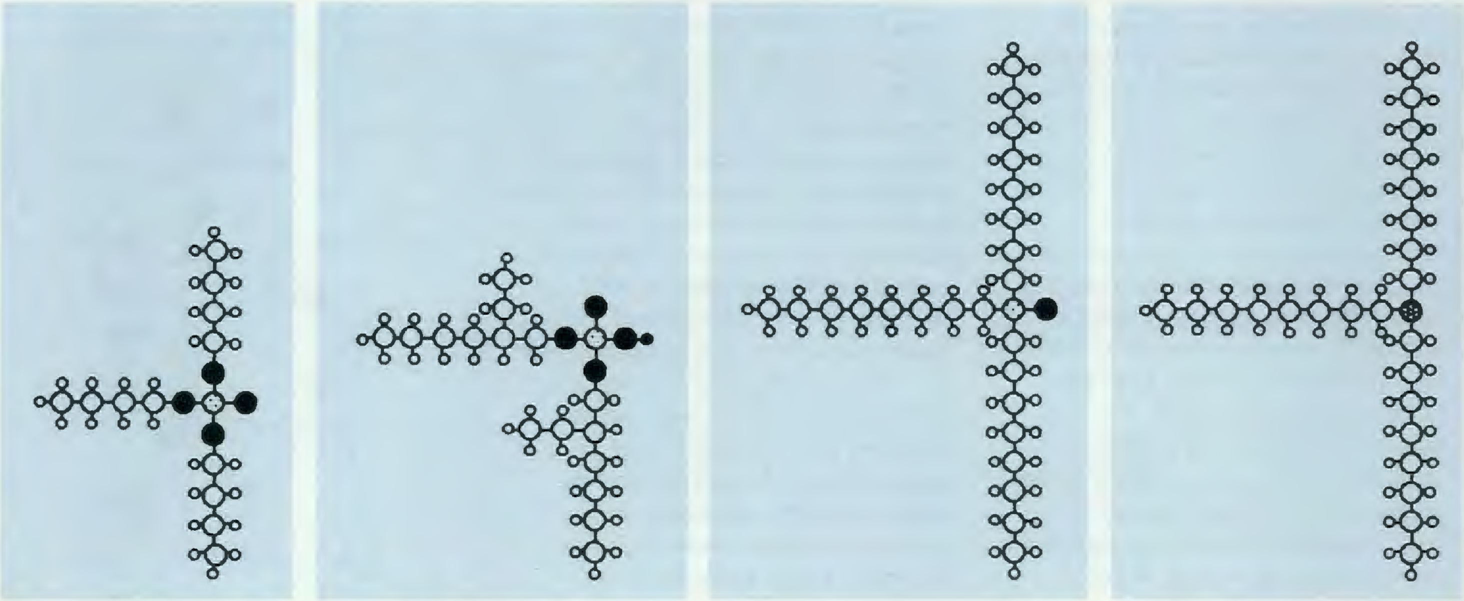
Fig. 1. The determination of the structure of this molecule advanced the understanding of how solvent extraction works. The extraction of strontium ions (Sr^{2+}) from water into an organic solvent containing a crown ether (see Fig. 3) and a dialkylphosphoric acid (similar to DEPA in Fig. 2) produces a molecular complex in which the Sr^{2+} ion is surrounded by the crown ether and the two dibutylphosphate anions. These groups neutralize the charge and give the neutral complex an organic coating, thus rendering it soluble in the organic phase. The molecular structures of complexes such as this one are being determined by John Burns and his co-workers in the Chemistry Division. The structure of the solid complex is determined by X-ray diffraction analysis of carefully grown crystals, and its structure in solution is confirmed by infrared and nuclear magnetic resonance spectroscopy. X-ray diffraction does not show the position of hydrogen atoms (the small open circles in the figure), but their position can be inferred by other means.

and to separate radioactive fission products from the fuel rods and concentrate them to reduce the volume of radioactive material requiring storage or disposal.

In the early 1950s, the only readily available sources of natural uranium were the pitchblende deposits in the Belgian Congo (now Zaire) and the tailings (waste) from gold mining operations in South Africa. A group was established at ORNL under the leadership of Keith Brown to develop improved methods of recovering uranium from the large deposits of lower-grade uranium ores in the United States. These ORNL-developed processes are still in use for recovering much of the uranium mined around the world. In uranium recovery and in the reprocessing of nuclear reactor fuels, the new technology of solvent extraction was employed very successfully.

In solvent extraction, a material is transferred from one liquid to another when the two are shaken together vigorously. The immiscible liquids separate upon standing into two liquid phases, as oil and vinegar do. The material of interest will be distributed between the two phases according to its chemical affinity for each.

The concept is at once simple and versatile. One liquid is almost always a water (aqueous) solution, and the other (called the extractant phase) can be any one of many possible immiscible organic liquids. Originally the organic liquid was a single compound. The important development that occurred during the war years was the addition of a reagent that could combine chemically with the material of interest and extract it more strongly into the organic liquid. Subsequently, it was found that extraction often could be further improved by adding a "modifier" to increase the rate of phase separation or to prevent the unwanted formation of a third solid or liquid phase. Finally, it was discovered that certain other additives ("synergists") could play a



Tributylphosphate (TBP)

Di(2-ethylhexyl)phosphoric Acid (DEPA)

Tri(n-octyl)phosphineoxide (TOPO)

Tri(n-octyl)amine (TOA)

Fig. 2. These molecules, shown schematically, are typical solvent extraction reagents consisting of hydrocarbon chains bound to a central polar group. TBP, long used for the reprocessing of nuclear reactor fuels, binds to metal ions at the exposed oxygen (black) atom. The extraction complex also includes anions to neutralize the charge on the metal cation. DEPA can bind metal ions at a similar site by exchanging its acidic hydrogen (small shaded) ion to form a salt. No other anions are required. TOPO, like TBP, binds through a neutral oxygen atom, but often more strongly. TOPO and DEPA in synergistic combination form a very stable complex with uranyl ion which, in a process developed by Fred Hurst and co-workers at ORNL, is used to recover uranium during the conversion of phosphate rock to fertilizer. TOA can bind a hydrogen ion to its polar nitrogen atom to form a cation that can combine with anions, such as sulphate, and cations, such as uranyl, to form neutral extraction complexes.

direct role in the extraction process and greatly enhance the extraction of the desired substance.

In its present form, solvent extraction is an extremely versatile tool for chemical separation. Perhaps its most important advantage over other separation techniques, the one that led to its early application in the nuclear enterprise, is that the liquids involved are more easily handled than solids and gases. Unlike solids, liquids separate spontaneously upon standing. Unlike gases, they can be confined without use of pressure. Furthermore, when the composition of the two liquid phases is varied, it can strongly affect the distribution of dissolved substances between them. The large number of composition variables provided by the two liquids makes solvent extraction particularly versatile.

To appreciate the capabilities of solvent extraction as a separations technique, consider the state of substances being extracted in each of the liquid solutions involved. Some substances, such as sugar, are present in water as molecules that can be extracted into an organic liquid without an appreciable change in their structure. The extent of extraction is determined by so-called solvation interactions of the extracted substance with each liquid.

Other substances exist in aqueous solutions as ions (i.e., atoms and molecules with an electrical charge). When ions are extracted into another liquid, electrical neutrality must be preserved either by the coextraction of ions of opposite charge or by back extraction of ions of the same charge (ion exchange). Generally, ions "prefer" an aqueous to an organic environment because the water molecule has a large dipole (a separation of charges) that interacts strongly with ions. Organic solvents are much less polar, so to induce ions to move into them, it is usually necessary to replace the water molecules surrounding the ions with ions of opposite charge and with organic molecules supplied by the extracting phase. The resulting structure, called the extraction complex, is electrically neutral—polar on the inside and nonpolar on the outside (Fig. 1).

The extraction complex may consist simply of an extracted metal ion and oppositely charged ions derived from the extractant. Additional (synergistic) molecules are often required to fully enclose the metal ion with a polar environment and to complete the nonpolar exterior. If the metal ion has been accompanied by aqueous ions of opposite charge, these are involved in the extraction complex as well. The complex may contain one metal ion surrounded by coordinating polar groups and an outer nonpolar covering, or it may be a large polymer involving many metal ions bound intricately by ions and molecules.

Clearly, the great versatility of solvent extraction comes at the price of complexity. The solvent extraction systems that have found application as practical separations processes have employed an extractant, often a modifier, and sometimes a synergist in the organic phase. The chemistry of such mixtures can be quite complicated. In the past, full resolution of these complications has often been beyond the capabilities of the tools of chemistry and, as a consequence, progress in the application of solvent extraction has been largely empirical, often as much an art as a science.

The solvent extraction reagents in current use at ORNL illustrate many of the features of a successful solvent extraction system. Perhaps the most venerable reagent is tributylphosphate (TBP). It consists of a phosphate (PO_4) group to which three hydrocarbon chains of four carbon atoms each are attached (Fig. 2). The phosphate ends of two TBP molecules can bind strongly to an aqueous uranyl ion (UO_2^{2+}). Two aqueous nitrate ions are also bound to make a neutral extraction complex having a hydrocarbon exterior that can enter either pure TBP or a solution of TBP in a hydrocarbon diluent such as kerosene. TBP is used in the Plutonium Uranium Extraction (PUREX) process, which was invented at ORNL to recover uranium and plutonium from nuclear reactor fuels.

Another type of extractant was developed to recover uranium from ores in the western United States. These are the so-called alkylamines (Fig. 2). Here, the polar part of the extractant molecule is a nitrogen atom to which one or more hydrocarbon chains are attached. The nitrogen atom can bind a hydrogen ion (H^+) when exposed to aqueous acid solutions to form an amine cation. With the coextraction of aqueous anions (usually sulfate), an amine salt is formed in the organic phase, often in the form of aggregates containing many amine anions and cations. This amine salt can, in turn, extract UO_2^{2+} ions and additional anions. Surprisingly, the degree of aggregation of the organic complex often seems to depend on how vigorously the mixture is agitated during the extraction.

As a final example, a synergistic combination of two extractants is used in the DEPA-TOPO process developed at ORNL by Fred Hurst and co-workers in the Chemistry Division to recover the small amount of uranium (typically 100 parts per million) from the phosphoric acid produced in huge quantities during the processing of phosphate rock into fertilizer. Both are organophosphate compounds like TBP, but each differs from it in an important way (Fig. 2). One (DEPA) is formed by attaching two hydrocarbon chains and a hydrogen ion to the phosphate group, producing an acid that can extract uranyl ions by ion exchange. The other reagent (TOPO) is formed by attaching three hydrocarbon chains directly to the phosphorous atom. The one oxygen atom attached to the phosphorous can bind strongly to certain metal ions. The extraction complex formed with UO_2^{2+} has not been identified fully, but probably contains two DEPA anions and one or two TOPO molecules. It has the extreme stability necessary to extract uranium from concentrated aqueous phosphoric acid into kerosene.

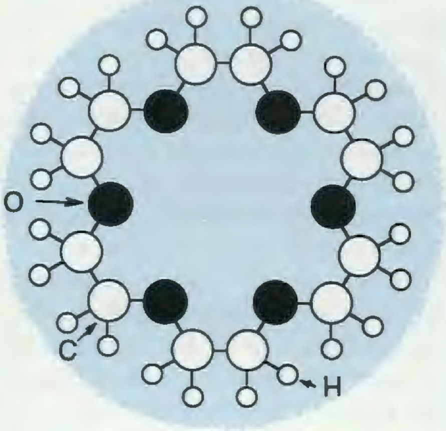
The main goal of current solvent extraction research at ORNL is to develop improved extractants and accurately predict their behavior. Of special interest are the so-called macrocyclic reagents. These molecules are in the form of rings that provide a cavity or cage into which the extracted metal ion can fit snugly and be surrounded by polar groups. The most important class of such reagents at the moment are the so-called crown ethers (Fig. 3), in which oxygen atoms linked by hydrocarbon chains form the ring. Because such molecules are neutral, formation of an extraction complex requires anions either from the aqueous phase or from a synergistic organic additive. Jack McDowell and co-workers in ORNL's Chemical Technology Division have found that when organic acids having long hydrocarbon chains are used as synergists, the crown ethers become very effective and selective extractants for the ions of groups I and II of the periodic table (i.e., sodium, potassium, beryllium, calcium, strontium, barium, and radium).

John Burns and co-workers in ORNL's Chemistry Division have been determining the structure of extraction complexes by the scattering of X rays and neutrons from crystals (Fig. 1) and from solutions. Only by learning how extraction complexes are put together and what structural characteristics are most important in determining their stability can we hope to understand solvent extraction behavior and to improve it as a separation tool.

Most of the compounds currently being used as extractants were synthesized originally for other purposes. Researchers in the Chemistry Division are now designing and synthesizing new extractants. Oak Ridge Associated Universities postdoctoral fellows Rich Kessler and Rick Sachleben have been trying to improve the extraction properties of crown ethers by adding side chains that contain phosphoryl groups (P = O) Charlie Baes is trying to synthesize a cyclic compound in which the polar groups are carbon-oxygen ($>C=O$) linkages of a type that has proven very effective in simpler extractants.

The usefulness of a solvent extraction process depends not only on the amount of material distributed between the phases but also on the speed of distribution. Unfortunately, the factors that control the rate of mass transfer between phases are difficult to control and study and so remain poorly understood. Charles Byers, Bob Wham, and others in the Chemical Technology Division are examining these factors in an elegant apparatus that allows them to suspend a single drop of an aqueous solution in a column of organic liquid. They are then able to study the rate of mass transfer between the organic and aqueous phases under many different chemical and physical conditions using a variety of sophisticated chemical, video, and computer-enhanced analyses (see Fig. 4 and sidebar by Bob Wham).

The thorough study of a solvent extraction system requires many kinds of measurements. These include the distribution of the extracted component as a function of composition to determine the nature of the reactions taking place, vapor pressure of the organic liquid to determine the degree of aggregation of its constituents, X-ray and neutron diffraction studies to determine their structure, and infrared spectra to determine the type of bonding involved. Finally, the interpretation of all these results to obtain a clear picture of the extraction process is often a difficult task that requires computer modeling techniques. All of these activities are being pursued by the Separations Chemistry Group in the Chemistry Division.



A Crown Ether

Fig. 3. Crown ethers such as the one shown schematically here can accommodate metal ions in the central cavity and surround them with polar oxygen atoms (black). Jack McDowell and his co-workers in the Chemistry Division have found that when crown ethers with attached organic groups are used in combination with organic acids to supply anions in an organic solvent, they will extract a variety of metal ions from aqueous solution that otherwise are difficult to separate. The molecular complexes formed in the organic phase are believed to have structures similar to those shown in Fig. 1. The strength of extraction is influenced strongly by how well the metal ion fits into the macrocyclic cavity, by the organic groups attached to the crown ether ring, by the organic acid used, and by the type of metal. Systematic studies of such combinations of crown ethers and organic acids suggest the possibility of a number of separations involving alkali metals (e.g., sodium, potassium, and cesium) and alkaline earth metals (e.g., calcium, strontium, and barium) that may have important technological and medical applications.

Chromatography

Chromatography differs from solvent extraction in that one of the two phases being contacted is stationary and often a solid rather than a liquid. The moving phase may be a liquid or a gas, and its constituents are separated by virtue of their differing chemical affinities for the material of the stationary phase. The stationary phase is usually contained in a cylindrical column and can be separate particles, a liquid coating on solid particles, or a coating on the inner wall of the column.

A moving fluid phase cannot be contacted with a stationary phase as efficiently as two liquid phases can be contacted with one another; hence, chromatography generally is limited to lower processing rates than is solvent extraction. Another important consequence of one phase being stationary is that separations must usually be done in batches—that is, the sample is introduced at the inlet of the column containing the stationary phase, and the separated components emerge sequentially at the other end. An important step in overcoming this limitation was the development of a continuous chromatograph (Fig. 4). In 1978 Chuck Scott and his co-workers in ORNL's Chemical Technology Division received an I•R 100 award from *Research & Development* magazine for this invention, which is now being used in a number of research and industrial applications.

Perhaps the greatest advantage of the chromatographic technique is its tremendous power to resolve the components of a mixture by the use of small particles and long columns, equivalent to many hundreds of separate equilibrium stages. For these reasons chromatography has found its greatest use as an analytical technique or for the purification of relatively small amounts of material.

Ion-exchange chromatography is a technique that shares some common features with solvent extraction. In this case, however, the "extractant" is not a liquid

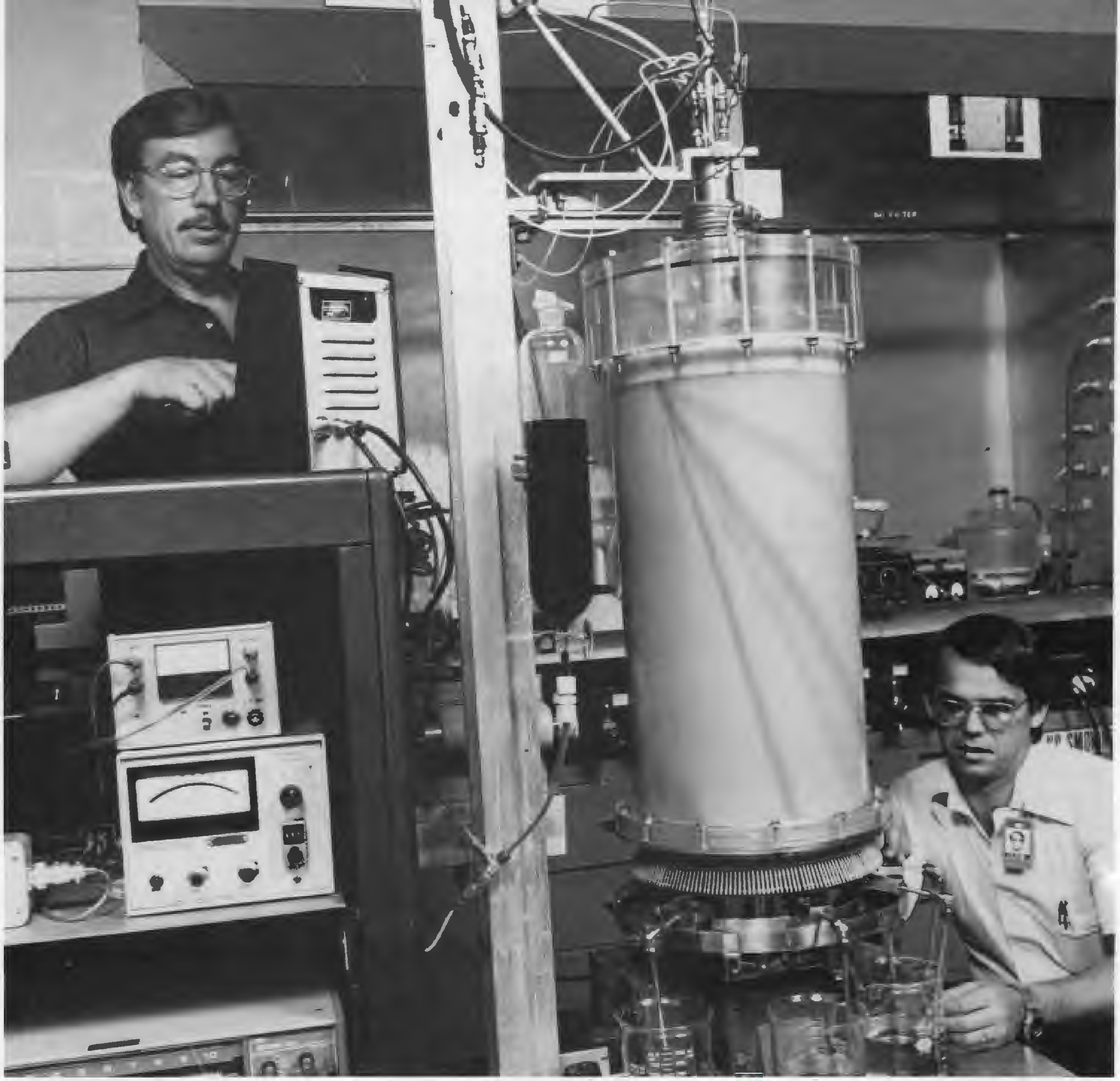


Fig. 4. Chromatography is an especially powerful separation technique because it uses hundreds or even thousands of separation stages in a small volume. In this way, substances having very similar chemical properties can be separated by multiplying the small separation achieved in only one stage through many stages. Traditional chromatography, however, is a batch technique that can be used on only relatively small samples and is difficult to scale up. The continuous annular chromatograph was developed at ORNL to do chromatographic separations continuously, making it suitable for large-scale production operations. Here, Warren Sisson and Ron Canon perform an early test of the unit in 1978. Since that time, the device has been tested and used by several industrial firms to produce new products and purer products more economically than could be done with traditional batch methods.

phase but rather an active group that has been attached to a solid support. The solid support is usually in the form of small beads of an organic polymer, called an ion-exchange resin. The active groups may be chemically bonded to the resin after it is produced or they may be an integral part of the polymer itself. As with solvent extraction, a separation can occur either by the exchange of ions (thus the name) between the active group and the aqueous phase, or it can occur by the coextraction from the aqueous phase of both the ion of interest and counter ions to balance the charge.

The chemistry of ion exchange has been well characterized for decades, but important developments in their form and application have occurred recently. The size of the resin beads has been decreasing, greatly improving the resolution of columns because of the increasing reaction rates and the decreasing length of a stage.

One limitation of using resins based on organic polymers is that they quickly break down when exposed to high temperatures, radiation fields, and many organic solvents. Historically, ion-exchange chromatography was developed using inorganic materials as the solid phase, but these were soon replaced when organic polymers proved to be much simpler to produce and use. More recently, however, advances in chemistry and in materials science have made it much easier than it was to synthesize and use inorganic ion-exchange materials. The importance of these improvements has been demonstrated during the cleanup of the damaged nuclear reactor at Three Mile Island. Joe Knauer, Dave Campbell, and their co-workers in the Chemical Technology Division developed methods for using these inorganic ion-exchange materials to remove large amounts of radioactive isotopes from the contaminated water that partially filled the reactor building.

Another recent development, called ion chromatography, employs resin beads having active groups only on their surface. Although they have low capacity, columns of such resins are capable of tremendous resolution and selectivity. They are being applied with considerable success to chemical analysis by Don Palmer and Ed Drummond of the Chemistry Division.

Ion-exchange chromatography is ideally suited to small-scale rapid chemical separations such as those carried out at the Transuranium Research Laboratory to isolate short-lived radionuclides for study before they decay. An interesting application of ion-exchange resins has been made by T. L. Rucker in the Low-Level Radiochemical Analysis Group of the Analytical Chemistry Division (Fig. 5). In Rucker's system, as many as ten environmental water samples can be analyzed simultaneously.

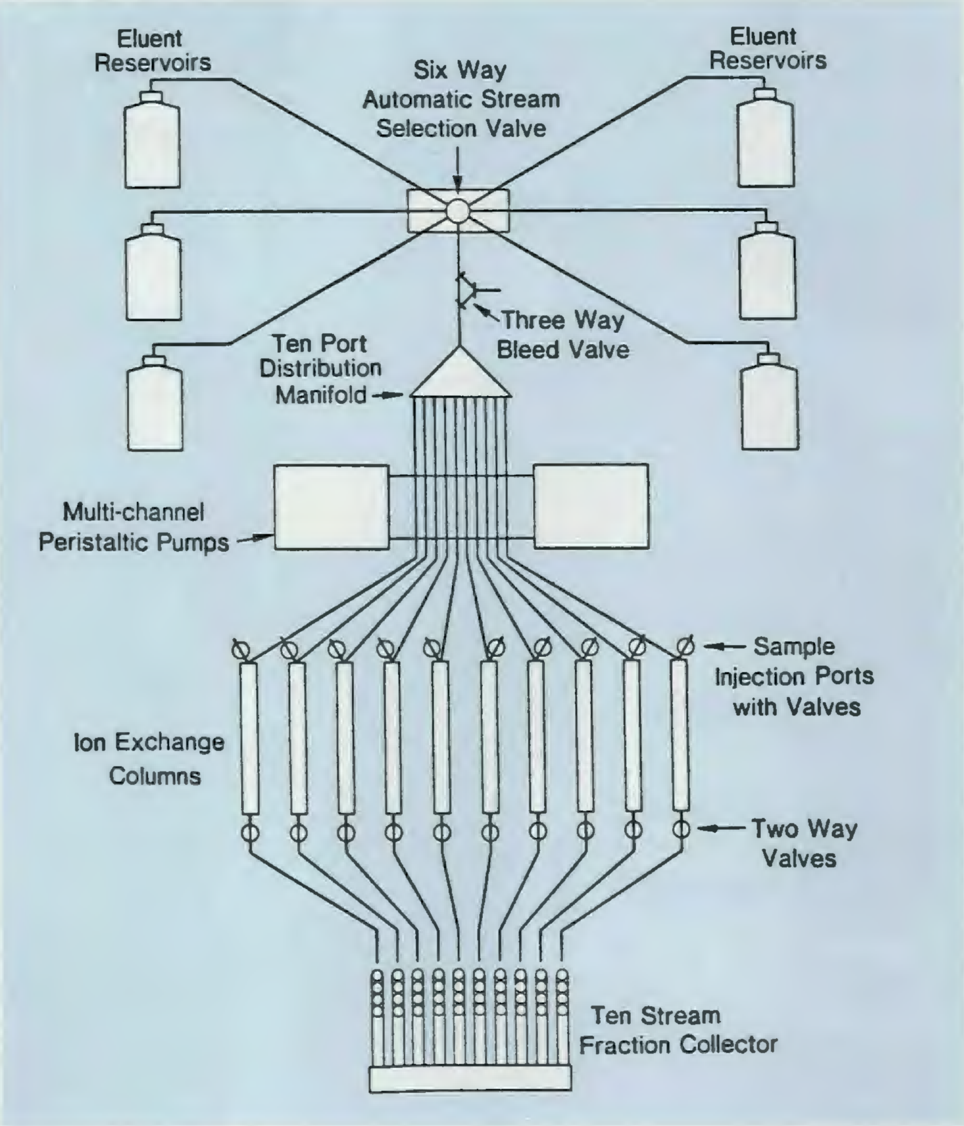


Fig. 5. Ion-exchange chromatography is a valuable and commonly used technique for the separation of transuranic nuclides from each other prior to their assay by alpha counting. Analyses done in this way are rapid, sensitive, and relatively inexpensive. Nearly 2000 such determinations are performed annually on environmental samples by the Low-Level Radiochemical Analysis group at ORNL. A separation scheme developed by T. L. Rucker of the Analytical Chemistry Division is shown here. The samples are introduced at the three-way valve. As many as six different solutions are then passed in an appropriate sequence through the ten parallel columns, permitting the separation and determination of the elements in up to ten samples simultaneously. The effluent from each column is collected in a series of fractions, which are then counted to determine the amount of each radionuclide. The whole process is automated and controlled by a programmable computer.

Many other forms of chromatography have also become routine laboratory procedures. In gas chromatography a gaseous sample is passed through a long capillary tube coated on its interior with a film of liquid with which it can equilibrate. In high-pressure liquid chromatography the sample is liquid, and the column is packed with a finely divided active solid which, in turn, may be coated with an active liquid. Finally, in gel chromatography, the stationary phase consists of gel particles that can react with a liquid sample.

Electromagnetic Separation

Electromagnetic separation is a technique used to separate and identify molecules, molecular fragments, and atoms. Instruments known as mass spectrometers are routinely used in analytical laboratories to determine the molecular weight, structure, and identity of compounds. These instruments vaporize the sample to be analyzed, convert the individual atoms or molecules in the vapor to ions in an electron beam, and then accelerate them through a magnetic field. Molecules that pass through the electron beam not only acquire varying charges but also break into pieces that are characteristic of the individual compound. Because the magnetic field deflects the ions differently depending on their mass and electrical charge, they take different paths through the magnetic field and can thus be separated. Very small samples, sometimes only a few micrograms, can be analyzed in this way.

Larger versions of these same instruments are used to prepare isotopically pure samples of many elements that are used in medicine, chemistry, physics, materials science, biology, geoscience, and engineering. These large-scale mass spectrometers, known as calutrons, were first developed by E. O. Lawrence at the University of California (hence the name). ORNL operates a large calutron facility at the Oak Ridge Y-12 Plant to produce the isotopically enriched elements that have become critical to many applications such as scans of heart patients.

The electromagnetic isotope separation process is as old as the Oak Ridge complex itself. The production of kilogram amounts of fissionable uranium-235, which makes up only about 0.7% of natural uranium, was crucial to the success of the Manhattan Project. Producing ^{235}U was a formidable challenge, however, because the physical and chemical properties of ^{235}U are almost identical to the properties of ^{238}U, which makes up the other 99.3% of natural uranium. It was known that small amounts of these isotopes could be separated electromagnetically in a mass spectrometer, but it was not at all certain that the process could be scaled up to produce kilograms of highly enriched ^{235}U. In 1943 the top-secret Y-12 plant, which housed 1152 calutrons, began producing ^{235}U for the first time. The success of the effort was dramatically demonstrated on August 6, 1945, when the first atomic bomb to be used in warfare, powered by uranium that had been enriched in the Y-12 calutrons, exploded over Hiroshima, Japan. This electromagnetic separation process (like the solvent extraction process discussed earlier that was employed to obtain the plutonium used in the first atomic bomb test at Alamogordo, New Mexico, and in the bomb dropped on Nagasaki, Japan) is an example of a separation method that fundamentally changed the nature of warfare and the history of mankind.

The calutrons are no longer used to produce enriched uranium. A second technique, called gaseous diffusion, was developed at the same time as the calutron as a backup method for obtaining enriched uranium for the war effort because of the uncertainty about the success of electromagnetic separations. Although it took longer to come on line, the gaseous diffusion method proved to be more efficient and, in 1945, a decision was made to shut down the Y-12 facility.

At about that time, Eugene Wigner, the great Hungarian-born physicist (and eventual Nobel Prize winner) wrote to the Clinton Laboratories (now ORNL) that "we should have, as the very basis of future work in nuclear physics and chemistry, knowledge of the cross sections of pure stable isotopes. Eventually separated isotopes of the elements may provide invaluable raw material for the production by pile or other irradiation of radioisotopes of value in science, medicine, and industry." Thanks to Wigner's foresight and the efforts of a group of Manhattan Project pioneers, the production of enriched stable isotopes, selected radioactive isotopes, and heavy-element isotopes became a major part of ORNL's mission.

Calutron technology has been used to produce about 250 isotopically-enriched products, though the number in current production has decreased in recent years. These materials are used in many areas of research, but the largest application is in the area of radiopharmaceuticals. For example, calutron-enriched thallium-203 is converted in a cyclotron to thallium-201, which is used in heart imaging. Gallium-67, which is produced from enriched zinc-28, is used in cancer and abscess scanning. Iodine-129, made from tellurium, is used to diagnose thyroid disease. Thus, the calutrons that were built for the purposes of war and that were almost abandoned because they were uneconomical are now playing a major role in detecting and curing disease.

Laser-based Separation Techniques

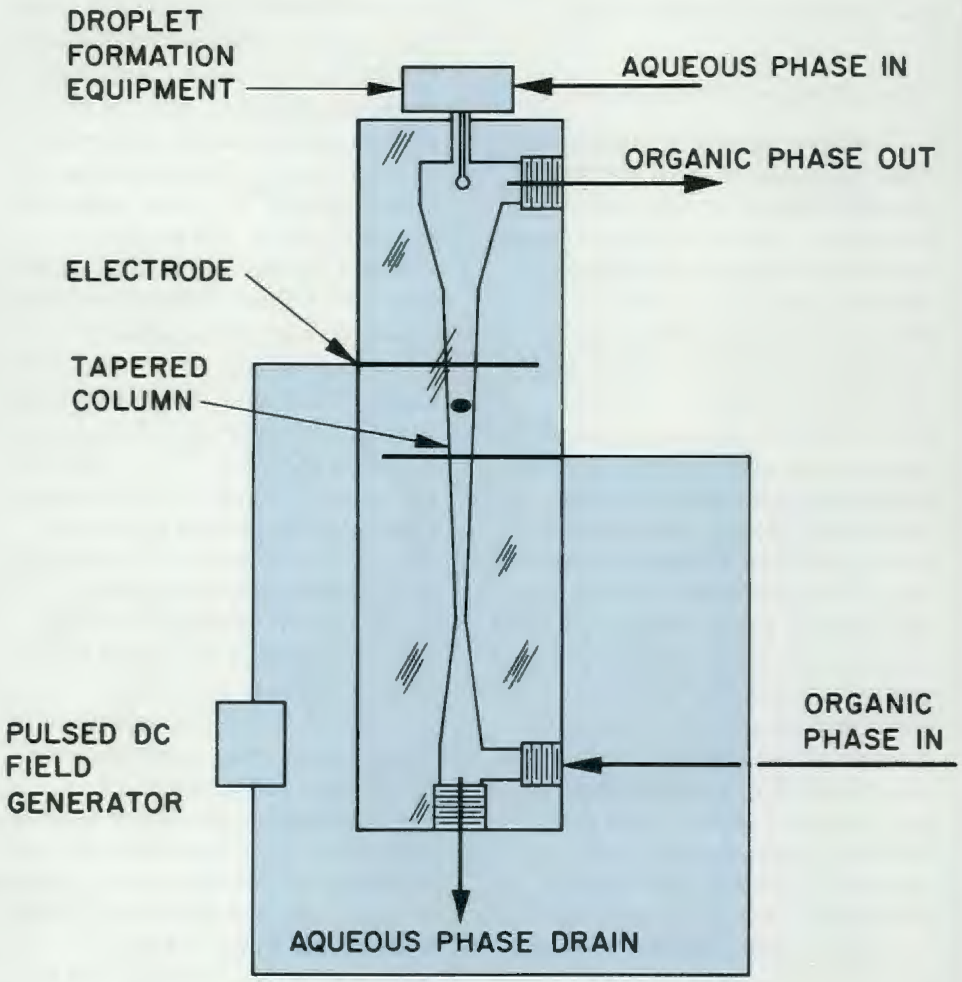
The intense, monochromatic light of the laser beam, which has

Mass Transfer Enhancement In Solvent Extraction Using Electric Fields

Solvent extraction, a separations technique used in industry for product purification, is the process of transferring a substance in solution in one liquid into a second liquid that is immiscible with the first. In ORNL's Chemical Technology Division, Tim Scott, Charlie Byers, and I have developed a system that allows us to examine experimentally the complex physical phenomena involved in mass transfer between fluid phases, with the aim of enhancing mass transfer rates in solvent extraction systems.

The rate of mass transfer between two liquid phases is controlled by the behavior of the liquids at their interface. To enhance transfer rates, most applications of solvent extraction use mechanical mixers to promote intrafacial mixing; in these systems, most of the energy introduced by the mixers is consumed in producing bulk movement of the continuous phase. We hypothesized that if we could concentrate the energy input at the droplet interface by forcing the droplet to oscillate, we might observe an increase in the rate of mass transfer caused by an increase in convection at the interface without expending additional energy on movement of bulk liquids. To test this hypothesis, we have initiated experimental and theoretical studies of droplet oscillation.

Our experimental studies center around a water drop suspended in an organic continuous phase in which the drop is only slightly soluble. We use a special device to suspend a water drop in an upflowing stream of an organic liquid, which fluidizes the drop. A pulsed electric field forces the droplet to oscillate. A video camera continuously records droplet behavior. We can observe the change in droplet volume to determine the amount of mass tranferred into the organic liquid. The video camera and associated equipment is shown in Fig. 4 in the main article.



Oscillating droplets have much higher mass transfer rates than static droplets because of increased convection and a larger surface area. Droplets oscillate naturally at a frequency determined by physical properties and droplet size. The experimental apparatus shown schematically here suspends a water drop in an upflowing stream of an organic liquid. Suspending the drop in this manner allows a video camera to record the droplet behavior continuously. A pulsed electric field can be applied to force the droplet to oscillate. The magnitude and frequency of the electric field can be easily controlled and, thus, a variety of conditions can be studied.

Analysis of the videotape and microcomputer-assisted analysis of droplet shape, volume, and surface area have shown oscillating droplets to have mass transfer rates up to 35% higher than those of static droplets. We are currently examining the effects of field strength and oscillation frequency on mass transfer rates.

Through modeling we hope to develop a better theoretical understanding of the driving forces in mass transfer. Theoretical analysis of the droplet-organic system requires

Bob Wham (left) and Tim Scott of the Chemical Technology Division analyze a videotape of a water drop that has been suspended in an organic liquid and subjected to a high-voltage electrical field. The electric field enhances the rate of mass transfer between the aqueous and organic phases by increasing the convection and surface area of the droplet. The researchers use a microcomputer and a video recorder to selectively digitize droplet shapes, making it possible to calculate the surface area and mass of a single droplet.

information about the hydrodynamics of the system. Mathematical solutions that describe the hydrodynamics of droplet systems usually represent an idealized model of the process that must be verified experimentally. We have found that laser lighting techniques can produce exceptionally good views of flow fields in fluid systems without significantly disturbing the processes. Microscopic particles distributed in the fluid follow stream lines, and images created by the bouncing of the laser beam off the particles are sufficiently intense to be recorded by the video camera. Videotapes of the resulting images yield detailed pictures of the flow pathway that provide quantitative descriptions of velocity profiles around and within the drop. From these observations, we have been able to formulate realistic hydrodynamic models to describe the mixing patterns present.

Future work will provide further improvements in state-of-the-art modeling techniques and will include other solvent-solute systems. Our modeling efforts are developing numerical solutions for mass transfer that account for the complex hydrodynamics of an oscillating spheroid. We are also developing equipment that will examine mass transfer of selected dyes between the droplet and the organic phases under conditions in which the rate of transfer is controlled by concentration gradients of the dye inside the droplet. Laser-induced fluorescence can be monitored to measure the rate of transfer of the dye. Our work examines an important and complex physical phenomenon (mass transfer) and combines theoretical modeling with experimental verification of the theoretical results.—*Robert M. Wham, T. C. Scott, Charles H. Byers, Chemical Techology Division.*

many applications in science and technology, is proving useful in separation science as well. Just as gaseous diffusion replaced electromagnetic separation for the enrichment of uranium, it now appears that a new laser process may replace both technologies in all types of isotope enrichment. In this process, a laser beam is passed through a vapor of atoms or molecules that contain a mixture of isotopes. Despite the great similarity between the properties of the isotopes of a single element, the laser can be so carefully tuned that it ionizes only one isotope, which can then be collected on an electrically charged surface while the un-ionized species pass by. The Atomic Vapor Laser Isotope Separation (AVLIS) method and the Molecular Laser Isotope Separation (MLIS) method have been undergoing development at the Lawrence Livermore National Laboratory, the Los Alamos National Laboratory, and the Oak Ridge Gaseous Diffusion Plant. ORNL researchers have made important contributions to this technology, which promises to make isotope enrichment faster and cheaper than ever before. Joe Tracy and his co-workers in the Operations Division of ORNL are studying the feasibility of using this technology to supplement or replace the calutrons for the production of stable isotopes.

The application of lasers to increase or control the rate of separations is an area that is just beginning to be explored. Mac Toth, Jimmy Bell, and Horace Friedman of the Chemical Technology Division have used a mercury arc lamp (which can produce light that is very intense and nearly monochromatic, though less so than laser light) to alter the chemical behavior of neptunium and uranium in solution and so control their separation using the PUREX solvent extraction process. It is certain that the fundamental research that is being carried out at ORNL will continue to produce new separation techniques that will take advantage of the laser's ability to produce profound chemical changes in carefully selected species.

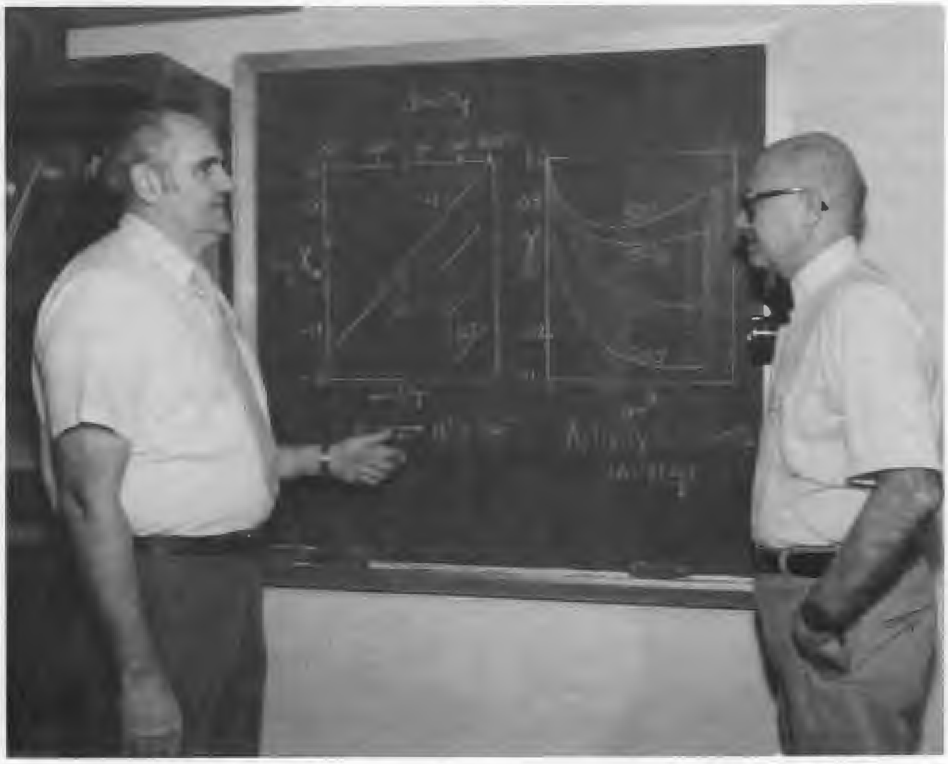
Bioseparations

Bioprocesses—the use of microorganisms (or their constituent parts) to remove organic materials, nitrates, and heavy metals from waste streams—have been and continue to be developed at ORNL. The versatility and high specificity of bioseparation processes make them an important tool in satisfying the increasingly stringent regulations for waste treatment and discharge.

On the other hand, unsolved separation problems are among the chief obstacles to progress in biotechnology. For example, progress in cell biology is hindered by the difficulty of isolating homogeneous, functionally specific population of living cells. The products of a biological fermentation process are often formed in dilute solution in a broth that contains many other, often similar, compounds. A complete, economical separation of the desired products from the undesirable by-products is often very difficult and the lack of such can prevent the commercialization of an otherwise promising new technology. Clearly, separation science will play a significant role in advancing the field of biotechnology, just as the processes developed by biotechnologists will solve separation problems in other fields.

Future Directions

The development of new and innovative methods in separation science and technology has been a major goal of ORNL since the days of World War II. The Laboratory continues to play a leadership role in the field, but where the emphasis was once on the separation of plutonium and uranium in support of the war effort, the focus has shifted to separations problems in the nuclear and fossil fuel cycles and more recently to separations problems in environmental and waste management and in biotechnology. Researchers at ORNL will continue to explore the underlying mechanisms that make separations possible, to develop new separation techniques, to improve old ones, and to extend their use into new areas of application. The results of this research may not always be as dramatic as the mushroom cloud over Alamogordo that ushered in the Atomic Age, but its beneficial effects on the economics and efficiency of energy production, on environmental management, and on human health and safety, may well, in the long run, prove more important. ornl



Robert E. Mesmer is head of the Aqueous, Separations, and Structural Chemistry Section of ORNL's Chemistry Division. He received his Ph.D. degree in physical chemistry in 1961 from the University of California at Berkeley and spent five years with the Inorganic Chemicals Division of Monsanto Company. There he conducted research on inorganic and organic phosphorus compounds before joining ORNL in 1966. His research at ORNL has focused on the thermodynamics of aqueous electrolytes and their reactions at high temperatures, especially with the use of electrochemical cells. He has been group leader in the Chemistry Division since 1974 and section head since 1980. He has authored and co-authored some 70 publications and patents in the areas of solution chemistry and thermodynamics at high temperatures. With C. F. Baes, he is co-author of a book, *Hydrolysis of Cations*, that comprehensively reviews the hydrolysis of metal ions.

William L. Marshall is a research scientist in the Chemistry Division. He received his B.S. degree from Clemson University and a Ph.D. degree in physical-organic chemistry from Ohio State University in 1949. He has spent his entire career at ORNL exploring the nature of water and its solutions at high temperatures and pressures. A group leader (1957–1974), he has authored or co-authored more than 100 publications and has delivered invited plenary lectures at many places throughout the world. He spent 1956–1957 at the University of Amsterdam on a Guggenheim Fellowship, and in 1977 the Georgia Section of the American Chemical Society awarded him the Charles Holmes Herty Gold Medal for "outstanding contributions to chemistry in the southeastern United States." He is a working-group member of the International Association for the Properties of Steam. Motivated earlier by the need to upgrade science education, he helped initiate and co-developed the American Chemical Society's national guidelines for training high school chemistry teachers. Here, Mesmer (left) and Marshall discuss some figures showing how the ion product of water (held at constant density) changes with temperature and how the activity coefficients of a typical salt (NaCl) dissolved in water drop off rapidly with molality of salt, especially at high temperatures.

Research on High-Temperature Water Solutions

By R. E. MESMER and W. L. MARSHALL

Understanding the nature of water and its solutions at high temperatures and pressures has been the goal of a long-standing program at Oak Ridge National Laboratory. This program in the Chemistry Division is at the forefront in basic research on the chemistry of water solutions and has provided information of practical value to designers of energy-related systems—nuclear power stations, geothermal energy facilities, and water desalting

Physical chemists at ORNL apply unique experimental facilities to the study of chemical and thermodynamic properties of many common substances in water at high temperatures and pressures. Their work contributes to the knowledge bases for several energy technologies and for detailed models of geochemical processes.

plants. Results from this program form much of the current basis for chemical and thermodynamic models for: near-field chemistry in nuclear-waste isolation, which is of interest to the U.S. Nuclear Regulatory Commission (NRC) and the Department of Energy (DOE); acidity and water chemistry control in steam generators, which is of interest to the Electric Power Research Institute (EPRI), Westinghouse Electric Corporation, General Electric Company (GE), and other organizations; acidity control in pressurized-water-reactor coolants; solids deposition in desalination facilities and geothermal systems; ore deposition processes; and fission product behavior in reactor accidents. Also, the information provides major input for semitheoretical models being developed here and elsewhere.

Much unique equipment has been developed at ORNL for studies of electrical conductance, electrochemical cell potentials, vapor pressure, heats-of-reaction, and solubilities that are leading to major advances in this field. The effort received a substantial boost in 1975 at ORNL with the successful initiation of an experimental geochemistry program (described in an article in the No. 4, 1984 issue of the *Review*). In that program, geochemists use laboratory studies to define the chemical processes important to hydrothermal geochemistry; more specifically, these studies focus on the transport of materials such as metals, alteration of rock and its porosity, and the detailed compositions of high-temperature brines.

Although scientists have gained a broad understanding of the processes undergone by water itself and by dissolved substances near room temperature, the behavior observed is vastly different at temperatures approaching and exceeding the critical temperature of water (374°C). Above this temperature the liquid and vapor become identical, forming a single fluid. In this region, simple rules, describing the behavior of simple liquids, fail for polar, ionizable, hydrogen-bonding solvents like water. Because of the complex behavior of water and its role as the principal solvent medium in much of modern technology and in natural geochemical transport processes, we need information about the high-temperature behavior of many different solutes in aqueous solution. Since the ions of many elements form a number of different species in aqueous solution, the information required becomes very great.

As a result of the abundance of species that are commonplace for many of the elements in water, very careful examination of these species and their equilibria is essential to a quantitative description that reliably and accurately predicts the stability of chemical phases and their solubilities. The principal experimental problems originate from the reactivity of water with container materials and from the high vapor pressures or containing pressures required to vary the density.

Some limited guidance for predicting the effects of higher temperature is obtained from electrostatic models for the hydration of ions (bonding of a small number of water molecules directly to the ions present). Simple models generally predict that, because the dielectric constant (which reflects the tendency of molecules to align in an electric field) of the water decreases with rising temperature, the hydration heat will rise more and more rapidly as the critical temperature is approached. Also, ions tend to associate, or combine, at high temperatures and low pressures because of the accompanying increase in the electrostatic attraction between ions having opposite charges. These ideas, however, provide only a crude qualitative picture.

Our approaches address principally the following chemical processes: ion association-ionization, hydrolysis, oxidation-reduction, complexation, solubility, and salt effects on all of these. Several approaches may be used to study each reaction type, but the principal methods we use will be described below. Systems for study are generally chosen because of their central role in an important application or for their own special chemical properties.

Ionization Reactions and Electrochemical Cells

Earlier, Bob Mesmer and Fred Sweeton succeeded in devising electrochemical cells capable of high precision at high temperatures and pressures by using hydrogen electrodes in what are called concentration cells. A static facility having duplicate hydrogen electrodes in partially filled compartments permits titration experiments that are essential for unraveling complex equilibria. A flowing cell having duplicate hydrogen electrodes in channels through which two solutions are pumped is available for studies on volatile electrolytes. With such cells, the measured electrical potential reflects the ratio of the concentrations of hydrogen ions (acidity) in the two compartments.

A large array of data sets has been accumulated on ionization constants of acids and bases at temperatures up to 300°C; these data sets provide the most precise information yet reported for any reaction type and form an excellent base for testing theoretical models. Examination of the temperature dependences has led to an important observation. Nearly straight-line plots are obtained for the logarithm of equilibrium constants against the reciprocal temperature when equilibria are written in terms of only cations or only anions—that is, "isocoulombic" reactions. Broad implications from this discovery are likely to exist for other reaction types.

The large body of data on acids, such as phosphoric acid (three acid forms), carbonic acid (two forms), boric acid ($B(OH)_3$), silicic acid ($Si(OH)_4$), bitungstate (HWO_4^-), and bichromate ($HCrO_4^-$), and on bases such as ammonia and some organic amines provides information for acidity control in primary and secondary water systems of light-water nuclear reactors today as well as for estimating acidity in geochemical models of metal transport and deposition (see Fig. 1).

The ionization reaction of water itself has been studied by using these electrochemical cells, which provide the best available information for reactions at temperatures up to 300°C in salt solutions to 5 molal. When combined with results from conductance measurements from this program, we now have a full description of the extent of ionization of water by the reaction, $H_2O \leftrightarrows H^+ + OH^-$, from 0° to 1000°C and at pressures ranging up to several thousand atmospheres.

Electrical Conductance

Salts such as sodium chloride and acids such as sulfuric acid are strong electrolytes (good electrical conductors) at low temperatures. The neutral salt (or acid) dissociates (ionizes) essentially completely in solution to form electrically charged species (ions). Studies by Bill Marshall, Arvin Quist, and others have shown that at supercritical temperatures (above 374°C for pure water), strong electrolytes can associate to form nonconducting dissolved neutral molecules and that this behavior is strongly proportional to pressure (or density) of the fluid. At pressures below about 200 bars (atmospheres) at supercritical temperatures, these salts and acids are like nonconducting organic molecules at 25°C. However, at high pressures (e.g., 4000 bars), the salts again become strong electrolytes and, thus, are strongly dissociated into the ions.

The behavior of these aqueous electrolytes is being explored at ORNL at temperatures up to 800°C (red-hot) and pressures up to 4000 bars. Through the study of the electrical conductance of many electrolytes at several temperatures and pressures and by application of conductance theory, we have arrived at values that describe the quantitative behavior of the extents, or fractions, of ionization. We have discovered several relationships from observing the behaviors at supercritical temperatures and pressures. For example, at a given temperature and pressure, not only are the ionization constants of most simple electrolytes (such as sodium chloride, potassium chloride, hydrogen chloride, and calcium chloride) essentially the same in value, but also the logarithmic plots of their values vs log density yield straight lines over a wide range of density. Also, the slopes for the simple salts have values of approximately 10 at temperatures above 300°C, at least up to 800°C. In addition, at a given constant density, the conductance of one molecular weight of ion divided by the number of its unit electrical charge (the ionic equivalent conductance) is essentially the same for all ions studied (except for hydrogen and hydroxide, the ions of water), and these ionic conductances are found to be 7 to 10 times as great as comparable values at 25°C. When the density is decreased, the corresponding equivalent conductances increase. Extrapolations of these values to zero density yield essentially the same value at this limit for all ions studied. By means of these observed relationships, we can predict behavior at temperatures and pressures greatly exceeding the experimental ranges.

Fig. 1. Don Palmer injects a solution into an electrochemical cell in his experiment on chromium(VI) at 175°C. By observing the change in electrical potential between two hydrogen electrodes as the solution composition is varied widely, he can infer the nature of the species present.

Geochemists have applied this knowledge to understand the manner in which hydrothermal ores are transported and deposited and to locate hydrothermal saline waters. For the latter, electrical conductances are obtained over great distances by inserting electrodes at several different locations within the ground. Knowledge of the nature of species and quantitative extents of ionization has been useful in evaluating and controlling corrosion processes in power-plant steam generators at high temperatures.

By correlating the conductance measurements, we have recently obtained an equation for calculating the electrical conductance of *pure* water when subjected to extremes of temperature and pressure. Pure water has very low conductance values, which are difficult to measure except under moderate conditions of temperature and pressure. The major impediment to a direct measurement of pure water under extreme conditions is that these conditions cause impurities from containment vessels to contaminate the water.

ORNL's current evaluation will allow the calculation of reliable values that can be used to assess the effects of electrolyte impurities, for example, in steam produced in power-plant steam generators. Most importantly, we now have a rather thorough understanding of the conductance and ionization behavior of high-temperature electrolytes at high pressures; such information was not available at the start of this program.

Salt Effects

The effects of the presence of ions on the chemical reactivity of other chemical species are referred to here as salt effects. Activity coefficients, which describe these salt effects, are much misunderstood. Such coefficients, which are an absolutely essential complement to knowledge of speciation in chemistry, are used in representing the chemical reactivity in a real solution compared with that in an ideal solution. The choice of the reference condition is arbitrary, but the magnitude of the resulting activity coefficient is not.

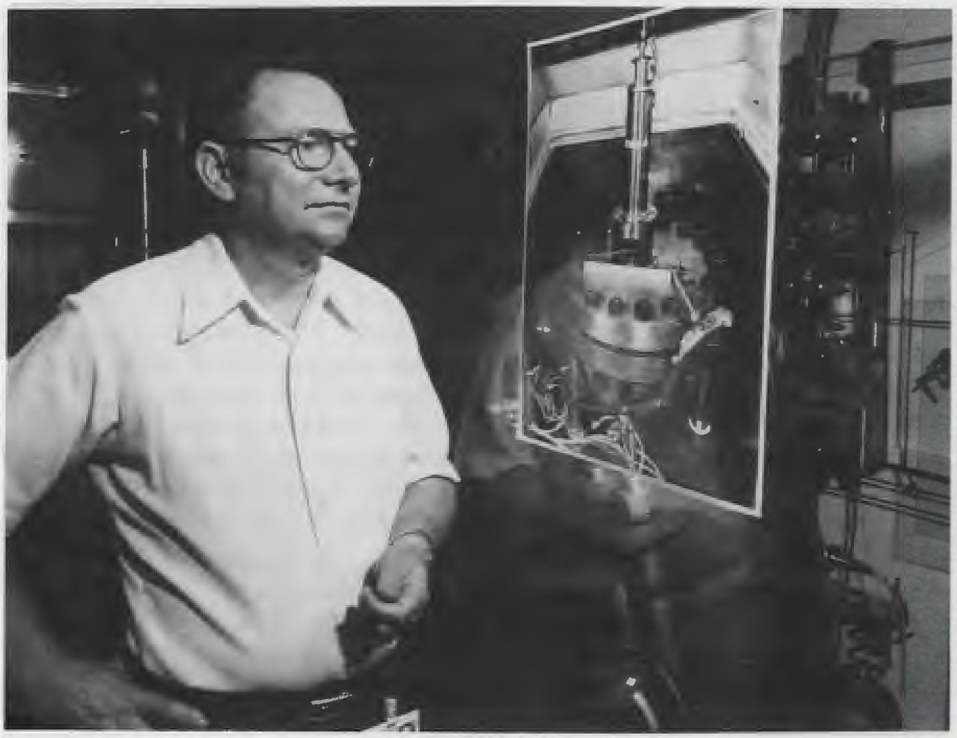


Fig. 2. Howard Holmes points out the features of the 41-cm (16-in.)-diameter isopiestic vessel that operates at temperatures and pressures ranging up to 250°C and 35 bars. Sample pans are manipulated remotely and weighed in place after equilibration in a controlled water-vapor atmosphere. Results provide very precise thermodynamic data on both the solvent and solutes.

At ORNL several approaches are used to obtain this information at high temperatures. Two of the most effective are the isopiestic method (a comparison vapor pressure method) and a flow calorimetric method.

Isopiestic method. Most of the current information on activity coefficients at high temperature has resulted from isopiestic studies at ORNL. The apparatus developed more than 20 years ago at Oak Ridge has been refined for this purpose and operated expertly for more than seven years by Howard Holmes (see Fig. 2).

In this method a number of electrolyte solutions contained in titanium cups are allowed to attain equilibrium in a common vapor phase at a well-controlled temperature. Equilibrium concentrations are determined by weighing the cups in place with an electromagnetic balance that is calibrated frequently using a set of standard masses interspersed with the solution cups. Water is added or removed from the system through a stainless-steel capillary tube. When one of the electrolytes present is a standard (i.e., its vapor pressure is known under the conditions of the experiment), the concentrations of all the electrolytes having this same vapor pressure are thus obtained (see Fig. 3).

Activity coefficients for the electrolytes are calculated from the isopiestic vapor pressures from models suitable for extrapolation to infinite dilution. Such information is now available at temperatures ranging up to 250°C for several important salts—the alkali metal

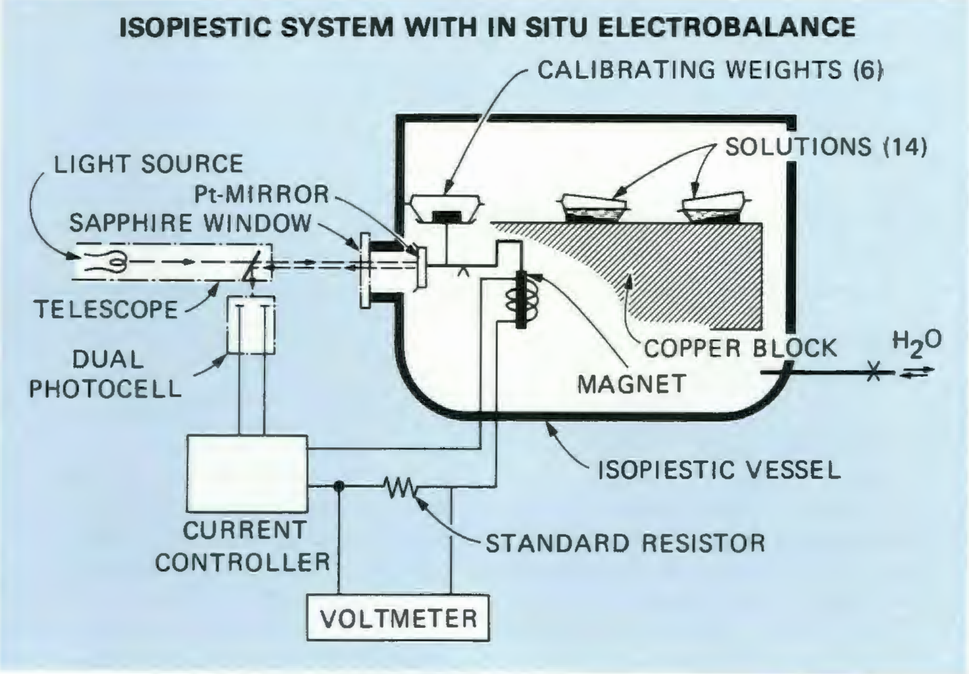


Fig. 3. The isopiestic system (a comparison vapor-pressure apparatus) consists of a balance, a constant temperature block, and a number of sample pans in a well-thermostatted vessel. An in-place torsion balance is operated optically by reflecting a light beam from a mirror on the balance beam. The current through a coil is adjusted to bring the beam to a null position.

(lithium, sodium, potassium, cesium) chlorides and sulfates, as well as several mixtures, and the alkaline earth (magnesium, calcium, strontium, barium) chlorides. For sulfates of magnesium and nickel and chlorides of nickel and cobalt, information has been obtained at temperatures ranging up to about 150°C.

Activity coefficients drop off more and more rapidly with temperature, especially at concentrations below 0.1 molal. This behavior is chiefly the result of increased electrostatic interaction with other charged ions as the dielectric constant of the solvent decreases. Likewise, the hydration characteristics of the ions are reflected in the results because this effect opposes the electrostatic interactions.

Flow calorimetry. A heat flow–solution flow calorimeter invented by Dick Busey and now being applied by Mike Simonson has provided a new and powerful approach to obtaining information complementary to the isopiestic results: heats of mixing and heats of dilution. This information combined with other results also yields activity coefficients. The significant features are described in the accompanying sidebar.

This technique opens up temperature and pressure ranges extending through the critical temperature and pressure of water, 374°C and 220 bars. Currently, our upper limits are 450°C and 500 bars. New evidence has been obtained for association of cations and anions into pairs above 300°C and at pressures near the vapor pressure of water. The results have given Simonson the basis for development of new models for the continuous variation of electrolyte properties from strong (dissociated ions) to weak (associated ions) electrolyte behavior in the range of room temperature up to about 400°C.

Solubilities

Investigations of solubilities of substances in high-temperature water solutions at ORNL are motivated by the lack of the basic solubility information needed for certain developing technologies. These technologies have included the early nuclear power test reactors that operated on aqueous uranyl sulfate solutions, water-desalting plants and geothermal power stations, and nuclear- and fossil-fuel steam power plants. In addition, solubility information is essential to a basic understanding of the transport of minerals in hot waters within the earth's crust and in deep-ocean hot springs. The research of Marshall and his co-workers summarized below has been directed to providing needed information and has led to several discoveries.

In experimental studies performed in sealed capillary glass (fused silica) tubes at temperatures below the supercritical-fluid region, both a liquid solution and a vapor phase are observed. As the temperature rises, more and more of the substances dissolved in the liquid phase transfer into the vapor phase until at the critical temperature, the liquid and vapor phases become identical in all compositions and properties. The single supercritical fluid phase exists above this temperature. A unique restriction at the critical temperature is that the volume of the liquid phase must equal the volume of the vapor phase. Many substances were discovered to be highly soluble in these supercritical-fluid solutions at high temperatures.

Marshall and his co-workers also discovered that, when heated to temperatures of 275 to 350°C, salt solutions of uranyl sulfate (UO_2SO_4), uranyl fluoride (UO_2F_2), disodium phosphate (Na_2HPO_4), and dipotassium phosphate

(K_2HPO_4), all of which dissolve in water at 25°C to form highly soluble, concentrated salt solutions, form two liquid phases. With rising temperature, one of the phases becomes highly concentrated, resembling a molten salt, and the other immiscible phase becomes very dilute.

In other ORNL studies, the effects of many dissolved salts and acids on the critical temperature of pure water (374°C) have shown that the critical temperature of solutions only moderately concentrated (1 to 2 moles per kilogram of water) can be raised to values as high as 500°C compared with the 374°C critical temperature of water itself. This knowledge has been applied to describing the compositional nature of the hot waters in the deep ocean springs, which commonly exist at temperatures of 200 to 450°C and at pressures up to several hundred atmospheres.

At ORNL the solubility of amorphous silicon dioxide (quartz is a crystalline form of silicon dioxide) has been studied at temperatures up to 350°C in many different salt solutions. The results of these studies and correlations with basic chemical principles were used in designing the steam generator of the first successful geothermal power plant [Union Oil of California (UNOCAL)] in the Imperial Valley, California.

In the purification, or desalting, of water by boiling at high temperatures, prevention of calcium sulfate scale on the boiler surfaces is essential for efficient, economical operations. The results of ORNL studies of the solubilities of calcium sulfate in high-temperature aqueous salt solutions, including sea water and brackish waters, together with the application of semitheoretical equations to describe this solubility behavior, have been applied throughout the world in the design of water desalting plants.

One important problem in the operation of power-plant steam generators is the potential precipitation of a common salt, sodium sulfate, within crevices of tubing walls. Such precipitation can reduce heat transfer and enhance corrosion, thus decreasing the efficient operation of the plant. In a basic investigation sponsored by EPRI, ORNL performed a detailed experimental study on the high-temperature solubility of sodium sulfate in salt and acid solutions that are common in natural waters. Although steam generator water is highly purified, parts-per-billion impurities often are present, and

New Calorimeter for Heats of Mixing Fluids

In 1979 Dick Busey invented a novel way to adapt a commercial calorimeter for use in precisely measuring the change in heat content of fluids during mixing at increasingly high temperatures and pressures. He and Mike Simonson have demonstrated the technique in experiments on dilution of several salt solutions with water (heats of dilution) at temperatures ranging up to 400°C. The system, which has been applied to sodium and calcium chlorides, hydrochloric acid, and sodium hydroxide solutions, has provided a wealth of new precise information (see figures).

Two fluids delivered through platinum capillary tubing are mixed at a point inside the heat-sensing chamber of the calorimeter. The exceptional sensitivity of the calorimeter (3 microwatts) permits measurements on very dilute solutions and on very small volumes (thus eliminating the need for the massive vessels previously used for such studies at high temperatures and pressures) and provides accurate data never before obtained.

Key insights into the behavior of aqueous solutions of electrolytes at temperatures near 300°C and beyond can be gained from their dilution heats as a function of temperature and concentration. At temperatures below about 300°C, the slopes of plots of

Mike Simonson operates the heat flow–solution flow calorimeter. He observes heats produced by mixing solutions in a special heat exchanger placed in a Calvet calorimeter in a system that operates at temperatures and pressures ranging up to 400°C and 400 bars.

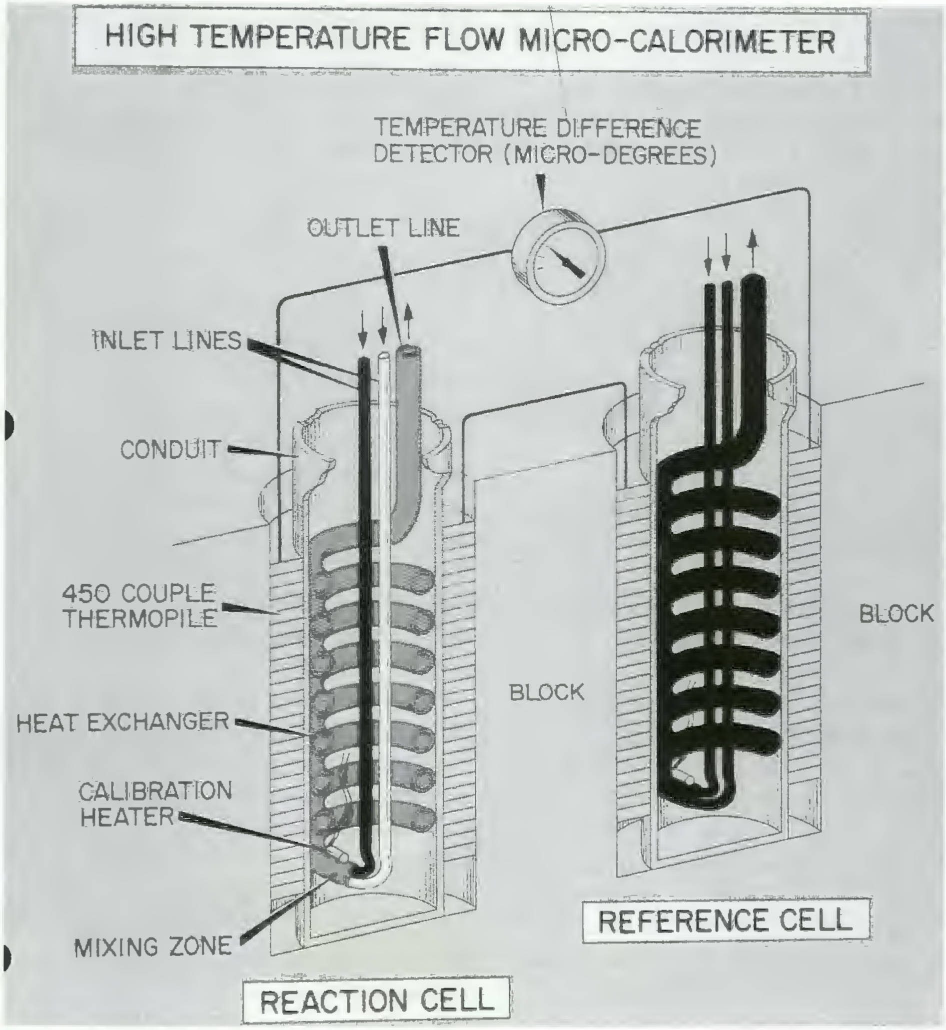
when concentrated by boiling in crevices they can precipitate sodium sulfate. ORNL's model, which was developed from the experimental results, used semitheoretical equations to express the temperature, composition, vapor pressure, and boiling point for these solutions under all conditions relevant to power-plant operations.

Another problem in nuclear power plants has been the buildup of corrosion products around steam generator tubes and their containment plates. This phenomenon called "denting" compresses the tubes. In other parts of the steam generator containment vessel, rapid corrosion, or "wasting," occurs. In ORNL's basic studies of alkali phosphate salts in water solution, two coexisting liquid phases were discovered. Earlier, the cause of wasting was attributed to the use of sodium phosphates as corrosion

dilution heats as a function of (square root) final molality typically correspond closely to the theoretical Debye-Hückel limiting law at low concentrations and then depart gradually with increasing concentration. Such behavior has been successfully described by models of strong electrolytes that include some empirical parameters to take account of short-range interactions that are poorly understood.

The ORNL calorimeter allows precise dilution heat data to be obtained at higher temperatures (up to and beyond the critical temperature of water, 374°C) and down to lower final diluted concentrations (into the millimolal range) than have previously been possible. New results in this high-temperature, low-concentration range show slopes that considerably exceed those predicted by the theory for hydrochloric acid (HCl), calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), and, to a lesser extent, sodium chloride (NaCl). Such behavior cannot be rationalized by strong electrolyte models and suggests that endothermic ion association has begun to occur. That is, as the dielectric constant of water decreases with increasing temperature, these familiar solutes no longer behave as fully dissociated strong electrolytes.

Hydrochloric acid has been used as the test case to develop an extended ion-interaction model that explicitly includes the formation of associated species and their interactions with other solute species. Earlier ORNL conductivity data (obtained by Bill Marshall and his co-workers) in the supercritical region were used to assign an association constant and its temperature dependence. The final model leads to very good fits of the heat of dilution data in a temperature range from 25 to 374°C over the concentration range 0.008 to 2 molal; this model is consistent with all other available thermodynamic data. Development of such comprehensive models to represent aqueous electrolyte behavior at high temperatures has relevance to energy applications as diverse as steam generation systems, waste disposal, and geothermal energy.



These two heat exchangers are made from platinum-20% rhodium capillary tubing and are inserted into duplicate ports with 450 junction thermopiles in the calorimeter. A mixing reaction is carried out on the left, and solvent is pumped through the right side as a reference.

inhibitors, a belief reinforced by the discovery of the existence of concentrated and corrosive, immiscible phases at 290 to 300°C. The ORNL studies showed that potassium phosphates also produced second liquid phases but only at temperatures too high for formation to occur in existing steam generators. Therefore, Marshall suggested that potassium phosphates be used for possible corrosion control instead of the sodium phosphates used previously at lower temperatures.

Redox, Hydrolysis, and Complexing

Our program dealing with redox, hydrolysis, and complexing relates to the identity of species present under selected conditions. Knowledge of all these processes at high temperatures is limited, but we are making good progress. The first, the redox state, is established by the activity of hydrogen (or oxygen) with which the solution is in equilibrium; for example, iodine may exist as $I^-(1-)$, $I_2(0)$, or $IO_3^-(5+)$.

The first study in this program of a redox equilibrium in solution was conducted by Don Palmer and Dick Ramette (Carleton College) on the stability or disproportionation of I_2 in water as this relates to the assessment of ^{131}I release in light-water reactor accidents such as that at Three Mile Island. An electrochemical method was used that splits the reaction to produce IO_3^- and I^- into its two redox partners, the oxidizing half with I_2 and IO_3^- and the reducing half with I_2 and I^-. This cell, whose potential indicates the equilibrium distribution of all the species, has produced very precise results at temperatures up to 210°C, and the information is being used in models to assess the behavior of iodine in accident scenarios. Information on other redox systems is badly needed to describe the complex chemistry of the elements in the middle of the periodic table.

An important aspect of the chemistry of metal ions in solution is the possibility of hydroxy complexes formed by reaction with water itself (hydrolysis). Such reactions at 25°C were surveyed comprehensively in a book by Charles Baes and Mesmer called *Hydrolysis of Cations*. In a few cases, experimental studies have been made at ORNL up to high temperatures using concentration cells (e.g., studies of hydroxy species of ions of magnesium, aluminum, uranyl, thorium, and the acids and bases mentioned under "Ionization Reactions"). A special need exists for more information, especially in dilute solutions because of the very low solubility of hydroxides and oxides. In one notable study, Sweeton derived information on the hydrolysis of Fe^{2+} from solubility studies on magnetite (Fe_3O_4) at temperatures ranging up to 300°C. The results are widely used for analysis of corrosion of ferrous metals in power-plant systems. It is apparent now that monomeric species become more predominant at high temperatures and that the greater importance of the hydrolysis reactions that produce these species results from the large positive heat for the first hydrolysis step. In addition, our lack of knowledge of complexing behavior (forming species between metal ions and neutral or anionic species) is another barrier to a full description of the chemistry of metals at high temperature. At ORNL, Palmer and Ed Drummond have succeeded in developing approaches to studying complexing of Fe^{2+} with acetate using the solubility of magnetite on the one hand and an electrochemical approach on the other. The increasing strength of the complexes at high temperatures is probably typical of many other cases, and this result has important implications for the transport of metals in geochemical environments and in steam generators.

Outlook

Many realms of high-temperature water chemistry research remain untouched. The chemistry of the middle part of the periodic table (the transition elements) and the heavier elements is still largely unknown. Unraveling the chemistry of these elements will require, in addition to our present capabilities, the development of new techniques and much careful experimentation involving solubilities, Raman scattering and absorption spectroscopic identification of species, and new reversible electrode systems. Neutron scattering could now be applied for unambiguous determination of hydration behavior as well as to provide new information on pairing of ions at high temperatures and pressures. Also, new experimental information on densities and compressibilities of solutions is needed to understand the increasingly large pressure effects at high temperatures.

This program should continue to yield new scientific insights as a result of our ability to take chemical processes through the extremes of temperature and pressure. Also, new results will provide a knowledge base needed for the development of new, more efficient energy technologies and waste-handling systems. New concepts in power plants, for example, envision operating temperatures upwards of 600°C, conditions which we are only now beginning to understand

A. C. Buchanan III (left) is group leader of the Organic Chemistry and Chemistry of Fossil Fuels group in ORNL's Chemistry Division. Born and raised in Abingdon, Virginia, he received his Ph.D. degree in chemistry from the University of Wisconsin at Madison in 1978. Immediately thereafter he joined the Molten Salt Catalysis group in ORNL's Chemistry Division, where he conducted research on organic-reaction chemistry and mechanisms in molten salt media. In 1984 he assumed his current position. His research interests include the characterization and reaction chemistry of organic reactive intermediates (free radicals, radical ions, and carbenium ions) and the application of techniques such as nuclear magnetic resonance spectroscopy and electron spin resonance spectroscopy to problems in physical organic chemistry.

Marvin L. Poutsma is director of ORNL's Chemistry Division. A native of western Michigan, he received his Ph.D. degree in organic chemistry from the University of Illinois in Urbana in 1962. He joined the Corporate Research Laboratory of Union Carbide Corporation in Tarrytown, New York, where he conducted research in physical organic chemistry and heterogeneous catalysis. After a one-year stint as a visitor at ORNL in 1975–1976, he joined the Chemistry Division in 1978, where he applied this background to coal research. Poutsma was appointed group leader in 1979, section head in 1980, and division director in 1984. He has held several offices in the New York Section of the American Chemical Society and the Section of Chemical Science of the New York Academy of Sciences. He has served on the editorial advisory board of the *Journal of Organic Chemistry* and *Energy and Fuels*. He has chaired Gordon Research Conferences in Free Radical Reactions and in Hydrocarbon Chemistry. He has contributed several chapters to the monographs, *Free-Radical Chemistry* and *Zeolites, Chemistry and Catalysts*.

Organic Chemistry of Coal

By A. C. BUCHANAN III and MARVIN L. POUTSMA

The energy crisis of the early 1970s revived interest in developing processes for converting abundant U.S. coal resources to liquid transportation fuels. This, in turn, led to renewed emphasis on fundamental research into the chemical structure and reactivity of coal. Because coal originated in living matter, Oak Ridge National Laboratory's organic chemists, headed by Clair Collins, turned their attention to this unusual organic natural product.

Before facing the new challenge of coal, Collins, Ben Benjamin, and Vernon Raaen had established their reputations in physical organic chemistry, the subdiscipline concerned with the quantitative relationships between structure and reactivity of organic compounds—not the typical background for studying natural products. Yet it proved very valuable not only in formulating questions about the reactivity of coal based on its structure (to the degree it was known) but also in using coal reactivity as a probe to study coal structure. In addition, these scientists brought a penchant for quantitation to what was largely a qualitative, empirical field.

Collins and his group had pioneered the use of carbon-14 as a

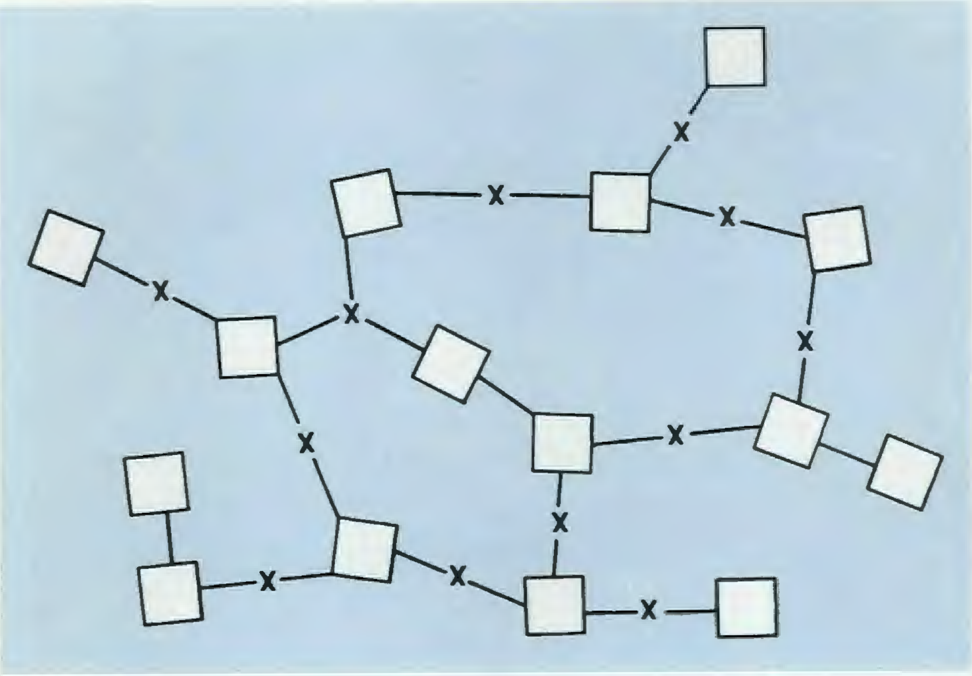


Fig. 1. The organic structure of coal can be visualized as a cross-linked macromolecular network composed of a variety of aromatic clusters and their derivatives (squares) connected by a variety of linkages (X) such as alkyl and ether groups.

Research at ORNL on the quantitative relationships between structure and reactivity of organic constituents in coal is contributing to a growing body of knowledge about coal chemistry. Improved instruments and better insight on the part of researchers are aiding the understanding of the many complexities. The information derived from these fundamental studies should provide the framework for the development of novel processes for the efficient use of coal as a source of liquid fuels and chemicals.

radioactive tracer in structure-reactivity studies. This tool was quickly used in coal studies with considerable success. Procedures developed for ^{14}C labeling were equally applicable to the stable but naturally rare ^{13}C. Because ^{13}C is the only carbon isotope detectable by nuclear magnetic resonance (NMR) spectroscopy, an instrumental technique in which the group had also established expertise, the roots of another important approach to studying coal were in place. Hence, the personnel and tools were available for a timely, energy-relevant, and fundamental study of the structure and reactivity of coal.

Not only were appropriate tools needed but also the right conceptual approach. A piece of coal is not a typical organic natural product and is hardly as aesthetically pleasing or as intellectually manageable as a newly isolated protein or nucleic acid. To a chemist, coal is distressingly heterogeneous at every level of examination. The most casual observer can distinguish a piece of anthracite ("hard coal") originating in an underground mine in Pennsylvania from a piece of subbituminous coal (which is geologically much younger) out of a strip mine in Wyoming. Even for a specified "rank" (related to the degree of geologic maturation), the unaided eye can detect a banded structure in the organic portion of coals (indicative of its sedimentary origin), along with inclusions of inorganic mineral matter. A microscope reveals further heterogeneity in the form of intimately intermixed units called macerals, which are derived from different plant structures: woody tissue, leaf cuticles, spores, and even algae. Finally, at the molecular level within any given maceral, it is now clear that coal must be viewed as a microporous cross-linked macromolecular network (see Fig. 1). Unfortunately, in contrast with most polymers, the coal "polymer" has no simple set of "monomers" joined in a specific sequence. There are no coal "molecules," each having the same arrangement of atoms, in the sense that there are unique molecules of hemoglobin or polystyrene. Rather, the structure of coal, in terms of the kinds and subtle variations of structural building blocks present, must be determined statistically: how many of each there are on average; how they are connected together on average; and how these building blocks and connecting links vary with maceral and rank.

Thus equipped, the organic chemists set out to resolve questions of coal structure and reactivity quantitatively at the molecular level. The most powerful state-of-the-art spectroscopic tools for determining a typical organic structure are largely inappropriate for coal because of its unusual properties. As normally practiced, NMR spectroscopy requires some solubility; coal, a cross-linked macromolecule, is insoluble. Conventional mass

ORNL researchers (left to right) A. C. Buchanan, Emily Douglas, and Ben Benjamin use high-resolution gas chromatography combined with mass spectrometry to analyze the complex product mixtures generated from transalkylation reactions on coal and from studies of thermal reactions of coal model compounds.

spectroscopy requires at least slight volatility; coal is nonvolatile. X-ray crystallography requires that the sample be crystalline; coal is amorphous. The more classical methods for structure determination involve chemical transformations and degradations whose occurrence is diagnostic of structure. In this case, we were lucky— coal is chemically quite reactive so that carefully applied chemical reactions can yield quantitative structural results.

The ORNL program in fundamental coal chemistry has evolved to the point where it now has three interrelated themes. First, structurally diagnostic reactions are designed and used to quantify specific structural features of coals. Interpretation of results requires continual supplementation using analogous studies with model compounds which highlight the particular structural unit in question. Second, special NMR techniques applicable to amorphous solids are applied to coals and especially to chemically modified and isotopically labeled coals. Third, the thermal reactivity of coal is studied with particularly heavy emphasis on the use of model compounds. Each of these themes is described below.

Transalkylation Probes Aliphatic Structures in Coal

Saturated aliphatic hydrocarbon chains (each carbon is attached to four other atoms) in coal play a key role in binding together the aromatic clusters (ring systems of which benzene is the simplest example) into a cross-linked network. In addition, they occur as substituents on the aromatic rings and as part of hydroaromatic rings. Various chemical reactions have been used to attempt to identify and quantify these aliphatic groups by excising them from the coal as identifiable soluble molecules. Special oxidation procedures to produce carboxylic acid derivatives (R-COOH) have been the most popular, but they continue to be plagued by undesirable secondary reactions that can confuse the results.

In 1983 Benjamin became intrigued by the potential of a conceptually simple nonoxidative approach—transalkylation. In the presence of acid catalysts, alkyl groups can be transferred between aromatic rings. As applied to coal, the goal was to excise an alkyl substituent (R) from the insoluble coal and transfer it to an aromatic acceptor (ArH) to form a soluble identifiable product (ArR). In practice, reaction conditions must be designed to be vigorous enough to liberate and transfer as many aliphatic groups as possible, yet mild enough to minimize isomerization or fragmentation of these groups. In addition, improved procedures are required to analyze the very complex mixture of soluble products (ArR) formed. From a study of several coals and numerous model compounds, Benjamin developed a procedure that uses trifluoromethanesulfonic acid (CF_3SO_3H) as the catalyst and toluene ($C_6H_5CH_3$) as the acceptor of the aliphatic groups removed from the coal network (see Fig. 2). The key technique used to analyze the complex mixture of toluene derivatives formed is high-resolution capillary-column gas

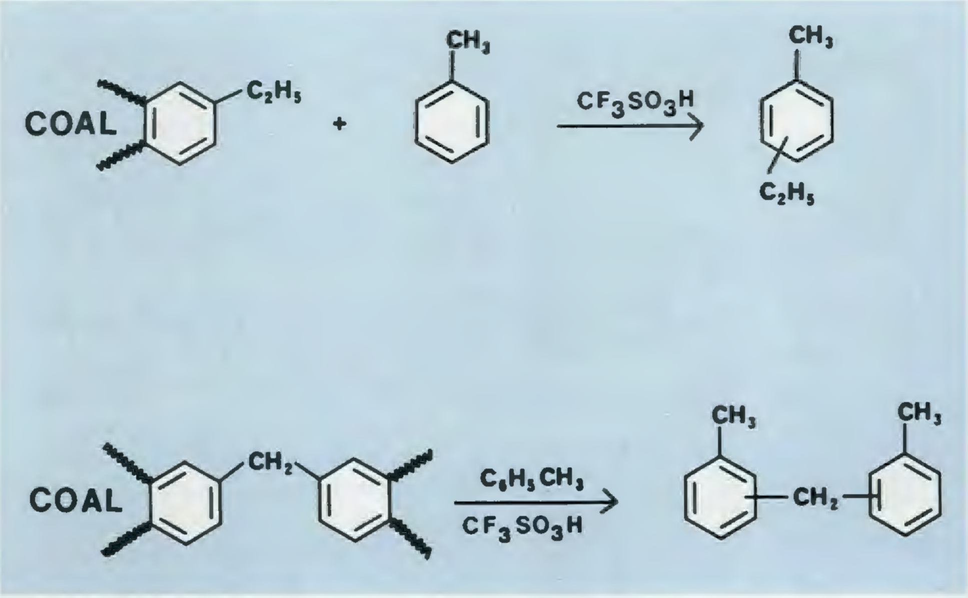


Fig. 2. Transalkylation method carves aliphatic substituents (e.g., -C_2H_5) and connecting groups (e.g., -CH_2-) out of the insoluble coal and transfers them to toluene to form soluble derivatives for GC-MS analysis.

chromatography combined with mass spectrometry detection (GC-MS).

By applying this methodology to nine coals varying in rank from lignite to anthracite, Benjamin could identify some 45 separate toluene derivatives in varying abundance. Although some of these proved to be common to all coals, the detailed composition of the aliphatic structures thus diagnosed depended on the nature of the coal. They fall into three main classes. The first type is the expected alkyl side-chains, exemplified by the ethyl (-C_2H_5) group, that range in some coals up to 20 carbons in length. These side chains proved to be more prevalent in the higher-rank bituminous coals than in the lower-rank subbituminous coals and lignites. The second type is connecting groups between two aromatic moieties as exemplified by the methylene (-CH_2-) and dimethylene (-CH_2CH_2-) groups. The -CH_2- group is the most abundant aliphatic structure observed in all coals, ranging from 0.5 to 1.0 groups per 100 coal carbons. We were also surprised to find several branched connecting groups (-CHR-, where R is another alkyl group). These structures had not previously been recognized as important connecting groups in coal. The third type is cross-linking structures that connect three aromatic moieties as exemplified by the methine ($\equiv$CH) and 1,1,2-ethylidyne (=$CHCH_2$-) groups. In contrast to the alkyl side chains, these cross-linking groups proved to be more abundant in the lower-rank members of the set of coals studied. For example, the methine group reaches the surprisingly high concentration of 0.38 groups per 100 coal carbons in a North Dakota lignite compared with only 0.0076 per 100 coal carbons in a Pittsburgh seam bituminous coal. The identification of these aliphatic cross-linking groups provides new evidence supporting the network structure of coal. Furthermore, this improved knowledge of aromatic-alkyl linkage points in coal will be valuable because these are potentially reactive sites for improved methods of coal depolymerization.

Carbanion Chemistry Probes Benzylic Carbon Sites in Coal

Another reaction that initially appeared promising for structural studies was the breaking of C-C bonds in the aliphatic structure of coal when it is treated with sodium-potassium (Na-K) alloy in polyether solvents. Extensive research with coal and model compounds by Collins, Benjamin, Rife Chambers, and Ed Hagaman of the Chemistry Division indicated the formation of anions centered at carbons adjacent to an aromatic ring, so-called "benzylic carbanions" ($ArCH_2CH_2Ar + 2K \rightarrow 2ArCH_2^- + 2K^+$). When this chemistry did not ultimately prove as selective as hoped in diagnosing coal structure, Chambers decided to explore related carbanion chemistry with the aim of categorizing the C-H bonds at benzylic centers according to their acidity. His approach has its roots in physical organic chemistry principles that allow the correlation of acidity of C-H bonds (as measured by their pK_a values, where pK_a is a negative logarithmic scale analogous to pH) with their immediate structural environment. Hence, a determination of the distribution of acidic C-H bonds in coal could provide information on their chemical environment.

Chambers' methodology is based on the fact that the position of the proton-transfer equilibrium

$$AH + B^- \leftrightharpoons A^- + BH$$

is determined by the relative acidities (pK_a values) of AH and BH. For a distribution of benzylic C-H sites in coal (AH$\equiv$ coal-H), addition of even a large excess of a soluble carbanion base ($B^- \equiv R_3C^-$) will only deprotonate those coal-H sites having an acidity greater than (lower pK_a) or comparable to that of the conjugate acid (R_3CH) of the probe base. He found that the number of coal carbanion sites produced by this deprotonation can be counted by derivatizing them by methylation with ^{14}C-labeled methyl groups:

$$A^- + {}^{14}CH_3I \rightarrow A{-}{}^{14}CH_3 + I^- .$$

Radioassay of this coal product coupled with elemental analysis gives a quantitative measure of the number of C-H bonds deprotonated by any given probe base. A series of probe carbanions of known base strength can then be used to quantitatively categorize benzylic C-H sites in coal according to acidity and to translate this information into the probable structural subunits responsible.

This methodology has been applied first to an Illinois No. 6 bituminous coal. The results clearly show that this coal does contain a distribution of acidic C-H sites, a substantial number having an acidity greater than or equal to that of 9,10-dihydroanthracene ($pK_a < 31$). However, a most surprising discovery is the presence of an unexpectedly large number (0.7 per 100 coal carbons) of much more acidic (pK_a of 18 to 23) sites that must be associated with five-membered cyclopentadiene-type ring substructures as exemplified by fluorene (see Fig. 3) and its analogs. Structures having such five-membered rings had not previously been considered to be prevalent in coal. If we take fluorene ($C_{13}H_{10}$) itself as the smallest such unit, then at least 9% (0.7 × 13) of the carbons in this coal must be present in five-membered-ring configurations. Investigation in progress on other coals using this diagnostic technique will allow us to further assess the general importance of these five-membered rings in coal structure. Moreover, great potential exists for exploiting this selective carbanion chemistry to graft new structural probes at specific sites in a coal. For example, Chambers and Hagaman are currently investigating the introduction of phosphorus-containing substituents at selected benzylic sites in coal in connection with the ^{1}H-^{31}P-^{13}C double cross-polarization NMR studies described in the next section. The ability to perform such chemical reactions at fluorene-type sites but not at dihydroanthracene-type sites, for example, represents a new breed of chemistry on coal of remarkable specificity.

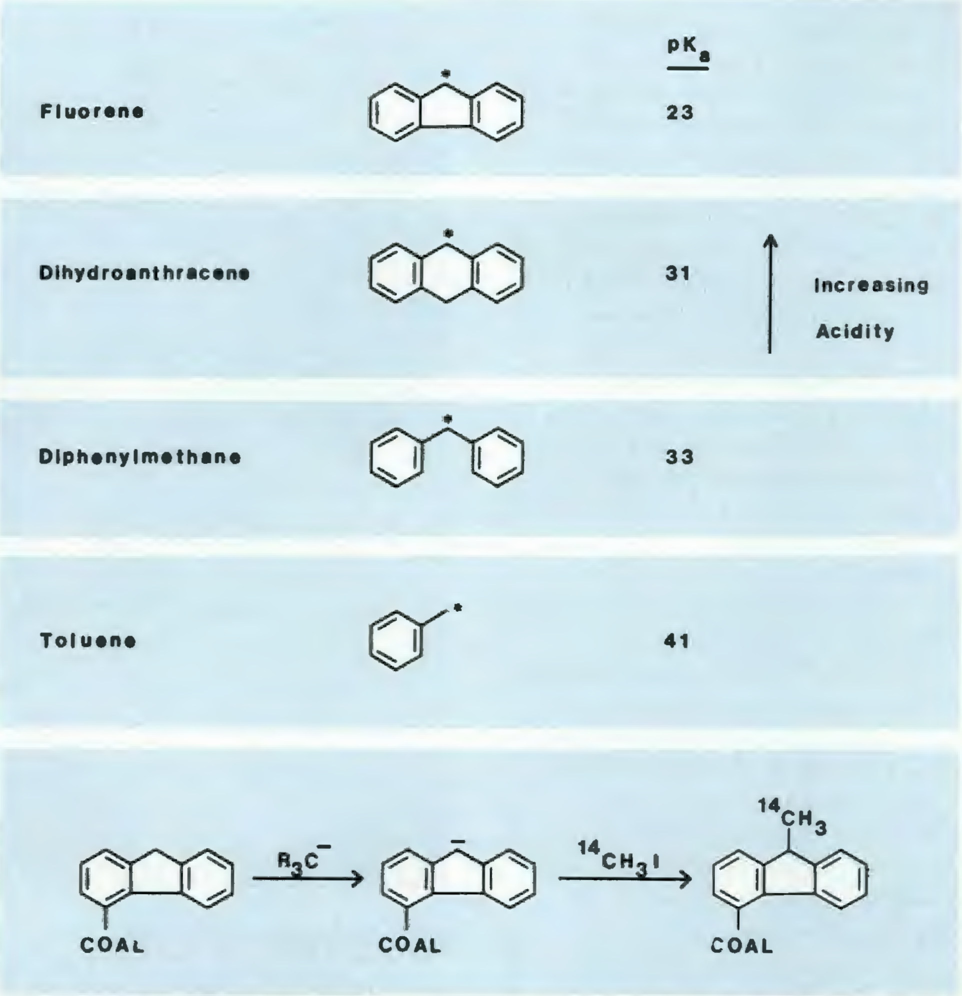


Fig. 3. Acidities of benzylic C-H bonds (*) as measured by pK_a values are very sensitive to their structural environment. Carbanions of differing base strengths are used to probe the benzylic C-H structures in coal. Trapping benzylic carbanions produced in the coal with ^{14}C-labeled methyl groups allows quantitation of the reaction and categorization of these structures according to their acidity.

High-Resolution Solid-State ^{13}C-NMR Studies of Coal

Atomic nuclei possessing a nuclear spin (such as ^{1}H or ^{13}C) will, in the presence of a strong magnetic field, absorb certain frequencies of applied radio-frequency electromagnetic energy. The discovery that the nuclear magnetic resonance (NMR) frequency for a given nucleus depends on its chemical environment led to the explosive development of NMR spectroscopy as a structural probe of liquids and solutions, particularly in the field of organic chemistry.

High-resolution ^{13}C-NMR in solids became a viable structural tool for chemists beginning in the mid 1970s with the development of cross-polarization (transfer of magnetization from ^1H to ^{13}C nuclei)–magic angle spinning (rotation of a sample rapidly about an axis that makes an angle of 54.7° with the applied magnetic field). Use of these special CP/MAS approaches, in combination with high-power ^1H decoupling, removes much of the peak broadening that occurs in solids as a result of anisotropic spin interactions (^1H-^{13}C dipolar coupling and chemical shift anisotropy). This leads to ^{13}C-NMR spectra of discrete organic solids that approach solution ^{13}C-NMR spectra in resolution and sensitivity.

ORNL researchers (left to right) Rife Chambers, Lloyd Brown, Ed Hagaman, and Madge Woody use CP/MAS-^{13}C-nuclear magnetic resonance spectroscopy of ^{13}C,^{14}C doubly labeled coals in combination with ^{14}C-radioassay to investigate structural changes that occur in selective chemical modifications of coal.

Unfortunately this high spectral resolution is not realized in CP/MAS-^{13}C-NMR spectra of coals. The primary complicating feature is the heterogeneous nature of coal that results in the occurrence of carbon nuclei in many slightly different chemical environments. Hence, the overlapping of many closely spaced peaks led to the initial observation of only two extremely broad bands in coals, one each for the aromatic and aliphatic carbons. Until quite recently, this measurement of percentage aromaticity was the major application of CP/MAS-^{13}C-NMR to coal. However, the potential of this nondestructive technique for elucidating details of the structure of coal and chemically modified coals continued to stimulate research by several groups aimed at gaining more specific structural information.

Hagaman's initial research at ORNL, beginning in 1976, was also aimed at developing techniques that could draw more structural information out of the broad aromatic and aliphatic carbon NMR bands. Using various resolution enhancement methods, he separated the aromatic band into contributions from aromatic carbons directly bonded to oxygen, to hydrogen, and to carbon atoms only (quaternary carbons). The aliphatic band was separated into contributions from aliphatic carbons that are oxygen substituted, quaternary, methyl (R-CH_3), and methine (R_3CH) plus methylene (R_2CH_2). These methods thus provide a much more detailed description of major carbon types in coal that reflects their immediate bonding environment.

A major concern in the application of CP/MAS ^{13}C-NMR to coal or coal derivatives has been its quantitative accuracy. The one-to-one correspondence between numbers of nuclei present and signal intensity that characterizes NMR studies of liquids is not necessarily true for coal, primarily because of two characteristics: its low H/C ratio (some carbons may be isolated from protons and incapable of the ^1H-to-^{13}C magnetization transfer required for cross polarization) and its paramagnetism ($\sim 10^{18}$ to 10^{19} unpaired electrons/g that could make a fraction of the carbon invisible by electron-nuclear dipolar interactions). Opinion has been divided as to the existence and significance of this quantitation problem.

Hagaman and Chambers recently devised two complementary CP/MAS-^{13}C-NMR experiments that answer this important question. In the first approach, a pure diamagnetic solid organic compound is blended with

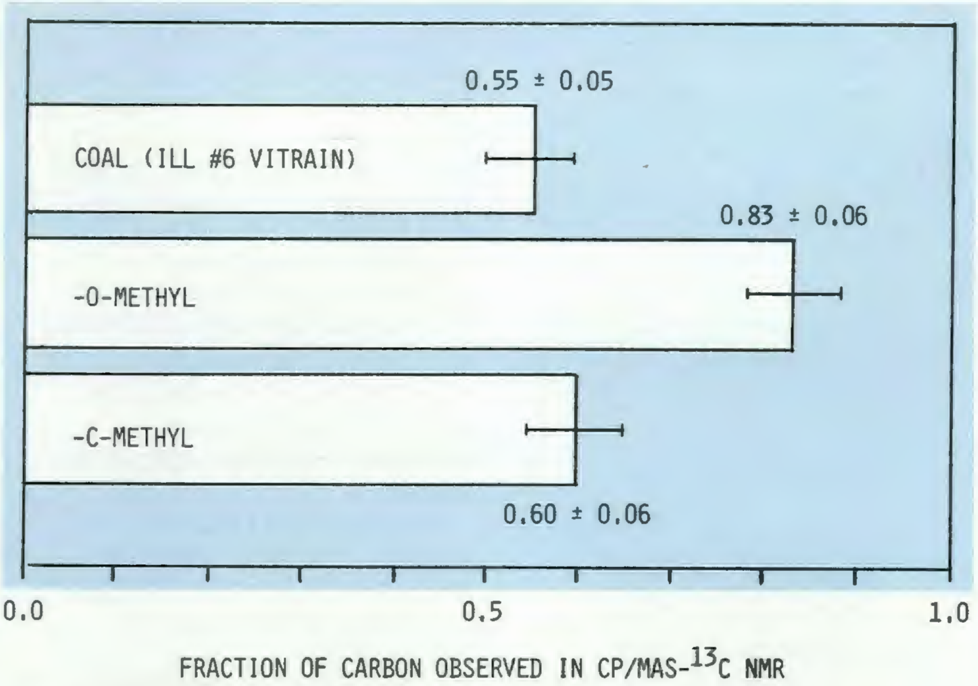


Fig. 4. Assay developed at ORNL uses glycine as internal standard to determine the fraction of native coal carbon observed. The different NMR responses for methyl groups chemically introduced at specific oxygen and carbon sites in the coal are determined from ^{14}C,^{13}C-double labeling experiments.

the coal, and its spectrum is used as the reference against which the coal spectrum is quantitatively compared. Such a standard reference compound must have several demanding characteristics: a minimum number of carbon signals, one of which is completely resolved from the coal spectrum; nuclear relaxation time constants that permit quantitative detection of its signals under conditions appropriate for coal analysis; and absence of reactivity with coal. Hagaman and Chambers have found glycine ($H_2NCH_2CO_2H$) to be a suitable internal standard (see Fig. 4). Recent results show that only 55% of the carbons in an Illinois No. 6 bituminous coal are detected by the CP/MAS-^{13}C-NMR experiment. Studies of a lignite (60% of the carbon detected) and an anthracite (44% of the carbon detected) indicate the generality of this phenomenon of "invisible" carbon, and suggest a possible correlation with coal rank.

In the second approach, ^{13}C, ^{14}C-doubly labeled methyl groups (60 to 90% ^{13}C and tracer-level ^{14}C) are selectively introduced into the Illinois No. 6 coal by chemical reactions. In one derivative, the labeled methyl groups were bound to phenolic oxygen sites in the coal, and in a second derivative, they were bound to benzylic carbon sites by the carbanion chemistry described above. The absolute number of introduced methyl groups, as determined by ^{14}C-radioassay, then serves as the calibration point for assessing the NMR response of the introduced ^{13}C methyl carbons. The sum of these complementary experiments demonstrates that (1) native coal carbon, (2) introduced O-methyl carbon, and (3) introduced C-methyl carbon are not only each substantially underestimated in the NMR spectrum but, furthermore, are each detected with a different sensitivity (Fig. 4). Our current hypothesis is that this unobservable carbon fraction is related to the unpaired electron density present in coal. These important developments will now allow coal researchers to optimize the quantitative value of the NMR technique and to avoid erroneous conclusions on coal structure based solely on integrated intensity data from CP/MAS-^{13}C-NMR spectra.

Hagaman and Chambers are also investigating a new NMR methodology involving a ^{1}H-X-^{13}C double cross-polarization (DCP) experiment in which abundant proton magnetization is first transferred to probe nucleus X and then subsequently from X to ^{13}C. Because of the $1/r^6$ ($r = X - {}^{13}C$ internuclear separation distance) dependence of the $X - {}^{13}C$ dipolar interaction, this technique will highlight those carbons closest to the site of introduction of X. The probe nucleus under current investigation, ^{31}P, is being selectively added to the coal primarily at benzylic carbon sites as described earlier. The substantial spectrometer modifications needed have been completed to the extent that the feasibility of the ^{1}H-^{31}P-^{13}C DCP/MAS-NMR approach has been demonstrated for a series of organophosphorus model compounds. An example of the spectral simplification that is achievable is shown for the compound, di-*ortho*-anisyl phosphine oxide (see Fig. 5). In the DCP spectrum, only carbon nuclei that are one and two bonds removed from the phosphorus nucleus (3-Å radius) are observed. Hence, we may now be able to identify the reactive carbon sites in the modified coal and also obtain information on their immediate chemical environment. The combination of state-of-the-art ^{13}C-NMR methodologies for solids and selective chemical reactions continues to provide a most

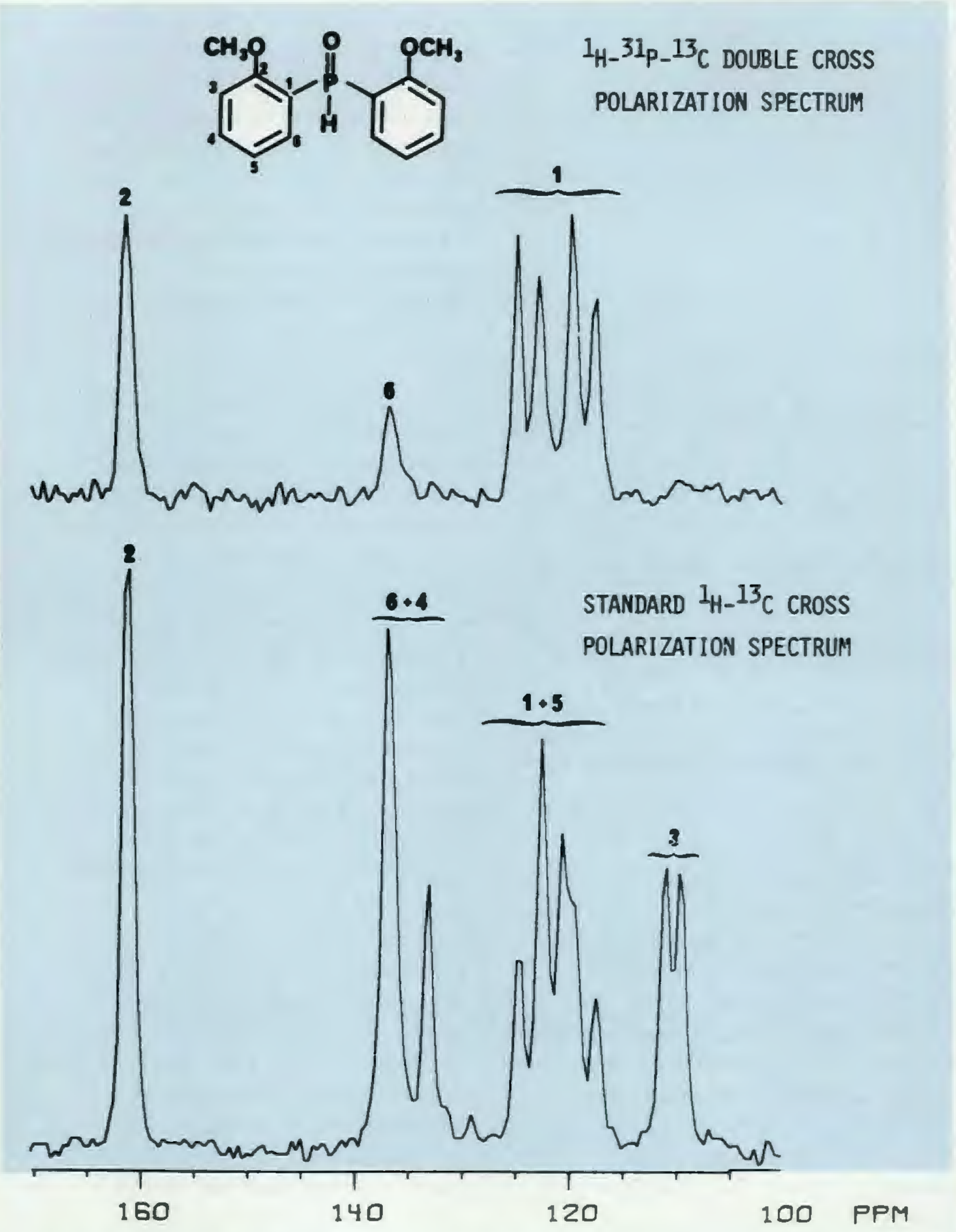


Fig. 5. ***^{1}H-^{31}P-^{13}C double cross-polarization NMR technique probes carbon nuclei that are within about a 3-Å radius of the phosphorus nucleus.***

powerful approach to the study of coal structure and reactivity.

Modeling the Thermal Reactivity of Coal

At about 400°C, chemical bonds in the framework of coal begin to break. Heating of coal underlies the technologically important production of metallurgical coke or, in the presence of hydrogen, liquids and gases that may in the future serve as petroleum substitutes. Thermal breaking of bonds forms "free radicals" that have only three electron-pair bonds to carbon and one unpaired electron. These species tend to react rapidly to reestablish the fourth electron-pair bond. Because of the structural complexity and heterogeneity of coal, unraveling the molecular details of free-radical bond-breaking and bond-making reactions from data derived only from coal is virtually impossible. Therefore, about 10 years ago the ORNL group explored the thermal lability (tendency to break down when heated) of over 50 model compounds that individually represented most of the then-suspected key structural features in coal. This seminal survey stimulated much more intensive research by several groups on intriguing individual examples that emerged.

At ORNL, Marv Poutsma focused on aliphatic linkages of varying length between aromatic clusters in coal. These can be modeled by the α,ω-diphenylalkanes, $Ph(CH_2)_nPh$, which consist of prototypical aromatic phenyl (Ph) groups separated by n methylene groups. Known thermochemistry of free radicals predicts a large (226 kJ mol^{-1}) variation in C-C bond dissociation energies as n varies in the range 0 to 3 (Table 1). The half-lives for bond rupture at 400°C estimated from these predictions vary by over 17 orders of magnitude (Table 1) and suggest that only 2-carbon linkages would be labile enough to be of any relevance for coal decomposition. For $n = 0$ to 2, experimental data and prediction showed satisfactory agreement (Table 1), but for $n = 3$, decomposition occurred some 4 orders of magnitude faster than predicted. These results have shown that 3-carbon linkages can also be significant cleavage sites during coal decomposition.

Detailed kinetic and isotopic labeling studies by Poutsma demonstrated that the serious disagreement between prediction and experiment when $n = 3$ results from incursion of a radical chain process. 1,2-diphenylethane ($n = 2$) decomposes by elementary steps (1) through (3) in which the rate is controlled by bond breaking step (1). In contrast, although the corresponding step (4) for 1,3-diphenylpropane ($n = 3$) indeed occurs much less frequently, it induces the decomposition of a very large number of additional molecules by the repeating sequence of chain-propagating steps (5) and (6). This chain is occasionally terminated by radical-radical coupling in step (7). Once this chain pathway was unraveled, it became understandable kinetically why corresponding pathways were not available for $n < 3$.

Table 1. Thermal Lability of Carbon-Carbon Bonds in Certain Coal Model Compounds

Bond being broken	Bond energy (kJ mol^{-1})	Half-life at 400°C (h)	
		Predicted	Observed
Ph-Ph	485	9×10^{18}	Stable
$PhCH_2$-Ph	372	2×10^{10}	Stable
$PhCH_2$-CH_2Ph	259	26	10
$PhCH_2$-CH_2CH_2Ph	301	5×10^{4}	1

Primary Thermal Decomposition Pathway for 1,2-Diphenylethane

$$PhCH_2CH_2Ph \rightarrow 2\,PhCH_2\cdot \qquad (1)$$

$$2\,PhCH_2\cdot + 2\,PhCH_2CH_2Ph \rightarrow 2\,PhCH_3 + 2\,Ph\dot{C}HCH_2Ph \qquad (2)$$

$$2\,Ph\dot{C}HCH_2Ph \rightarrow PhCH_2CHPhCHPhCH_2Ph \qquad (3)$$

$$3\,PhCH_2CH_2Ph \rightarrow 2\,PhCH_3 + PhCH_2CHPhCHPhCH_2Ph \qquad (Sum)$$

Decomposition Pathway for 1,3-Diphenylpropane

$$PhCH_2CH_2CH_2Ph \rightarrow PhCH_2\cdot + \cdot CH_2CH_2Ph \qquad (4)$$

$$PhCH_2\cdot + PhCH_2CH_2CH_2Ph \rightarrow PhCH_3 + Ph\dot{C}HCH_2CH_2Ph \qquad (5)$$

$$Ph\dot{C}HCH_2CH_2Ph \rightarrow PhCH = CH_2 + PhCH_2\cdot \qquad (6)$$

$$PhCH_2CH_2CH_2Ph \rightarrow PhCH_3 + PhCH = CH_2 \qquad (Sum)$$

$$2\,PhCH_2\cdot \rightarrow PhCH_2CH_2Ph \qquad (7)$$

Most recently our attention has expanded beyond model compounds per se to address one of several complex factors involved in making the extrapolation from liquid or gaseous model compounds to solid coal. Even though the reactive radicals live only a fraction of a millisecond, that still allows them time in liquids to diffuse considerable distances between their generation and consumption. In contrast, in the early stages of coal decomposition, radicals formed by breaking a bond within the cross-linked framework will not be free to diffuse because they will still be attached to the framework at other points (see Fig. 6). Research was originated by Poutsma; A. C. Buchanan is examining how such restrictions on mobility might influence radical chemistry. Our approach is to attach a model compound to an inert solid surface by use of a strong chemical bond. Thus immobilized, the compound's thermal reactivity can then be compared with that in the liquid and gaseous states.

The same series of α,ω-diphenylalkanes has been successfully immobilized on high-surface area silica by covalent bonding through the para position of one aromatic ring. Remarkable changes from liquid-state thermolysis behavior have been found so far for the case where $n = 2$. As noted above, 90% of liquid bibenzyl is converted to toluene and a dehydrodimer by steps (1) through (3). The remaining 10% undergoes a carbon skeleton rearrangement through steps (8) and (9), which constitute another repeating chain sequence, albeit in this case an inefficient one. The ratio of dehydrodimerization to rearrangement is determined by the fate of the intermediate $Ph\dot{C}HCH_2Ph$ radical. Mostly it couples in step (3), which represents chain termination, and only occasionally enters into propagating sequence (8) and (9). In the surface-immobilized condition, the ratio of the analogous reactions

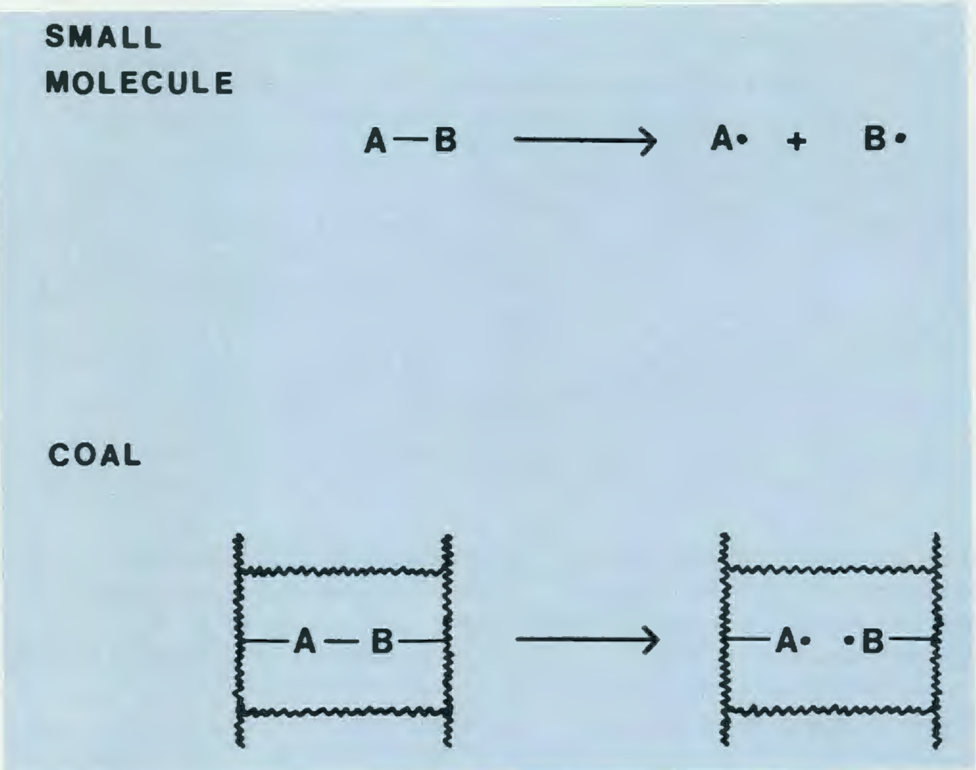


Fig. 6. The thermal breaking of A-B bond in a small molecule produces radicals that are free to diffuse before reacting. However, the breaking of A-B bond in a cross-linked network like coal produces radicals that are immobilized.

is completely reversed; radical coupling is negligible, whereas rearrangement consumes 70% of the starting material. This dramatic increase in the rearrangement chain length results directly from immobilization of the $Ph\dot{C}HCH_2Ph$ radical. No longer free to diffuse, it cannot easily encounter one of its twins in a bimolecular terminating process, but it can still undergo step (8), which is unimolecular. A second surprise for this immobilized 1,2-diphenylethane is that about 10% forms phenanthrene derivatives, which had been barely detectable in the liquid phase. The same underlying generality that chain lengths are increased because of the diffusional restrictions to radical-radical termination accounts for this cyclization process.

Radical Chain Rearrangement Pathway for 1,2-Diphenylethane

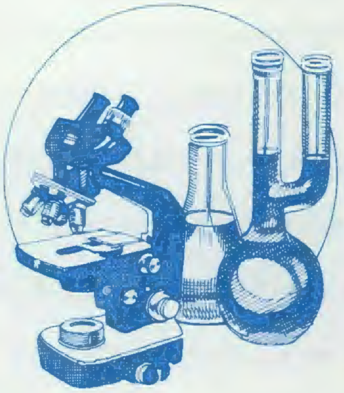
$$Ph\dot{C}HCH_2Ph \rightarrow Ph_2CH{-}CH_2\cdot \qquad (8)$$

$$Ph_2CHCH_2\cdot + PhCH_2CH_2Ph \rightarrow Ph_2CHCH_3 + Ph\dot{C}HCH_2Ph \qquad (9)$$

$$PhCH_2CH_2Ph \rightarrow Ph_2CHCH_3 \qquad (\text{Sum})$$

These alterations in chemical reactivity accompanying restricted diffusion are relevant to interpreting and manipulating the thermal decomposition of coal. For example, both rearrangement and cyclization are undesirable for ultimate depolymerization and should be avoided to maximize coal liquefaction. A good means to this end would be to ensure that good hydrogen atom donors are present within the coal matrix at all times during decomposition.

Our research at ORNL on the quantitative relationships between structure and reactivity of organic constituents in coal is contributing to a growing body of knowledge on coal chemistry. Substantial challenges remain ahead because of the extreme complexity of this material and the associated difficulties with its study. Fortunately, improved instrumentation coupled with better insight on the part of researchers is permitting even more sophisticated approaches to probing coal structure and reactivity. The information derived from these fundamental studies should ultimately provide the framework for the development of novel processes for the efficient utilization of coal as a source of liquid fuels and chemicals.



Michelle Buchanan is leader of the Organic Spectroscopy group in ORNL's Analytical Chemistry Division, where she has worked since 1978. Born in Independence, Missouri, she received her B.S. degree from the University of Kansas and her Ph.D. degree in analytical chemistry from the University of Wisconsin. In 1985 she received a Martin Marietta Energy Systems publication award. In 1986 she and Marc Wise received an I-R 100 award from *Research & Development* magazine for the development of a multimode ionization detector. She serves on the editorial board of *Biomedical and Environmental Mass Spectrometry* and is editor of a book on Fourier transform mass spectrometry. Here, Buchanan and Wise review data from ORNL's Fourier transform mass spectrometer (see sidebar on page 193).

David Donohue has been on the staff of the Analytical Chemistry Division since 1974. He received his B.S. and M.S. degrees from the University of Virginia and his Ph.D. degree from the University of Tennessee. His main research interest is mass spectrometry, especially isotopic analysis and, most recently, the development of resonance ionization mass spectrometry. Donohue spent two years (1979–1981) on assignment with the International Atomic Energy Agency (IAEA) in Vienna, Austria, and is now there again on another two-year assignment managing the analytical mass spectrometry laboratory for IAEA safeguards. Here, Donohue is at the controls of one of ORNL's many mass spectrometers.

Analytical Challenges in Mass Spectrometry Research

By MICHELLE BUCHANAN and DAVID DONOHUE

The name mass spectrometer conjures up a vision of massive magnets and vacuum plumbing attached to several relay racks full of power supplies. Invented by physicist F. W. Aston at Cambridge University in 1919, the mass spectrometer has developed into one of the most powerful and sophisticated tools available to the analytical chemist today. From house-sized calutrons to miniature instruments on the surface of Mars, the types and capabilities of mass spectrometers cover an impressive range. Research performed at Oak Ridge National Laboratory over the past 40 years has helped shape the field of mass spectrometry significantly. Some of the future advances in this field are likely to occur in the Organic Chemistry and Analytical Spectroscopy sections of ORNL's Analytical Chemistry Division.

The beginning of analytical mass spectrometry at ORNL extends back to the Manhattan Project. Electromagnetic separators, dubbed "calutrons" by their developer, E. O. Lawrence of the University of California at Berkeley, used the basic principles of mass spectrometry to separate uranium-235 from ^{238}U, making a product highly enriched in the fissile isotope. The large calutrons at the Oak Ridge Y-12 Plant produced the uranium used in the atomic bomb dropped on Hiroshima, Japan. Smaller mass spectrometers were built to measure the purity of the ^{235}U product.

How does a mass spectrometer work? A material is ionized by one of several means. The ions are then extracted from the ionization region and accelerated and collimated into a beam. Because ions of each element have their own characteristic mass and charge, they are deflected by magnetic fields into individual paths through the spectrometer before detection. As a result of this magnetic sorting process, the constituents of a material can be identified and quantified (see Fig. 1).

The early isotope ratio mass spectrometers were based on a design by A. O. C. Nier of the University of Minnesota. Nier's device used a single magnetic sector to deflect the ions through an angle of 60° and a radius of 15 cm (6 in.). In 1943 A. E. (Gus) Cameron, one of Nier's students, came to Oak Ridge to set up instruments based on the Nier design. Cameron was head of the Mass and Emission Spectrometry Section of ORNL's Analytical Chemistry Division until he retired in 1971. His list of achievements included contributions to the fields of mass spectrometry and the determination of the precise isotopic abundance of the elements. Under his guidance, mass spectrometry research at ORNL expanded to include the analysis of organic as well as inorganic materials, the development of high-sensitivity, pulse-counting mass spectrometers (which actually count the ions as they reach the detector), and the challenging task of measuring the higher actinide elements, such as berkelium, einsteinium, and fermium. Joel Carter, who succeeded Gus as head of this section in 1971, has maintained and strengthened ORNL's tradition of excellence in mass spectrometry.

Research performed at ORNL over the past 40 years has helped shape the field of mass spectrometry. Recently, ORNL has made advances in the development of and/or application of resonance ionization mass spectrometry, organic secondary ion mass spectrometry, MS/MS, gas chromatography/mass spectrometry combined with chemical ionization processes, resin-bead isotope ratio mass spectrometry, and Fourier transform mass spectrometry. The future looks bright as plans are made for building a new Mass Spectrometry Laboratory at ORNL.

Today, in keeping with this tradition, we are constantly expanding our horizons by designing new instruments and searching for new ways to solve problems with mass spectrometers. Our main facilities, still located at Y-12, house every major type of mass spectrometer, from small, portable quadrupole instruments to the most sophisticated state-of-the-art research instruments. We use energetic electrons, ions, and laser beams to ionize samples and are even studying positrons as a potential ionization method. Surface analysis at the part-per-million level is routine with our ion microprobe mass analyzers. We are solving the tough problems of identifying components in organic mixtures by using two new techniques, mass spectrometry/mass spectrometry (MS/MS) and Fourier transform mass spectrometry, or FTMS, both of which are described in this article (also see sidebar on page 193). In short, ORNL is at the forefront in all aspects of mass spectrometry, which is one of the fastest growing fields in modern analytical chemistry.

Basic research in mass spectrometry at ORNL

	Acronym	Task
Resonance ionization	RIMS	Explore spectroscopy of rare earth and actinide elements; develop ability to ionize all isotopes uniformly for one element in a mixture
Resonance ionization/ secondary ionization	RIMS/ SIMS	Develop methods for ultratrace elemental analysis
Inorganics/actinides		Refine and expand application of isotope dilution measurements
Organic secondary ionization	SIMS	Elucidate mechanism of SIM ion emission; develop methods for analysis of intractables
Mass spectrometry/mass spectrometry	MS/MS	Develop new MS/MS instrumentation for the exploration of gas phase ion chemistry
Fourier Transform	FTMS	Investigate gas phase reactions for the structural identification of organics; develop techniques for the analysis of high molecular weight and polar compounds

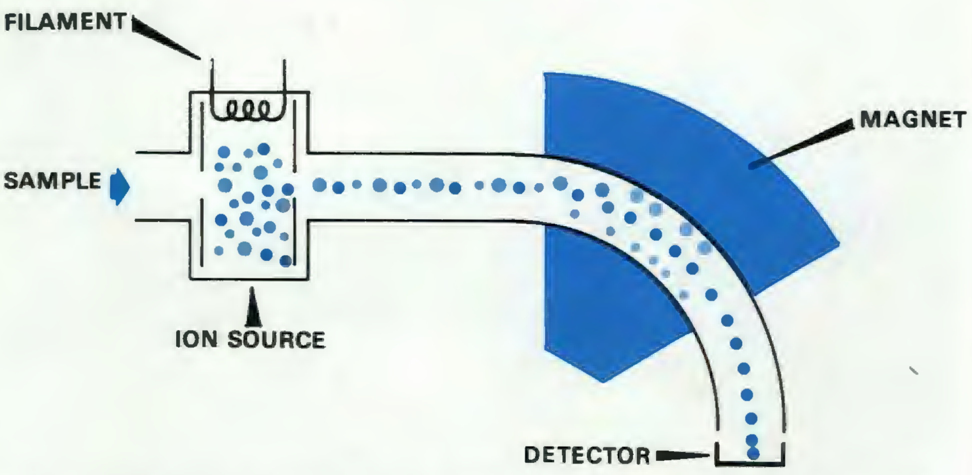
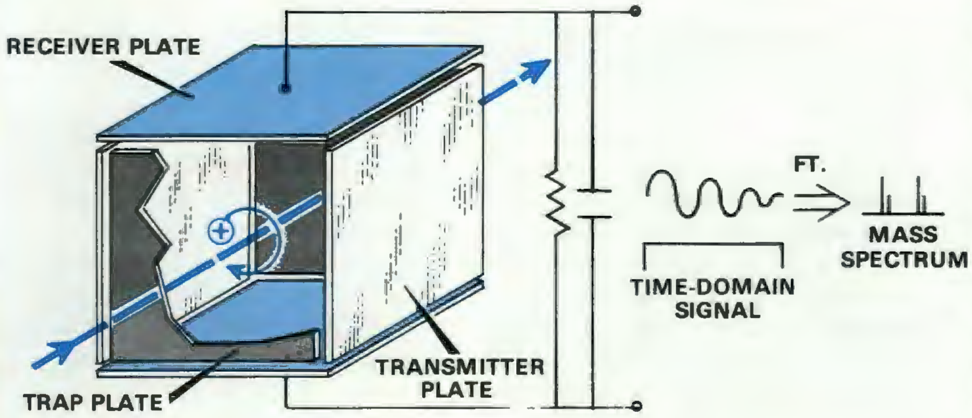


Fig. 1. As the atoms are ionized, they are deflected through the magnet into individual paths and detected one mass-to-charge ratio at a time.

Resonance Ionization Mass Spectrometry

The recent development of resonance ionization mass spectrometry (RIMS) in the Analytical Chemistry Division originated with a suggestion by division member Jack Young that we try coupling a dye laser to an isotope ratio mass spectrometer (see Fig. 2). He had collaborated with the Photophysics Group in the Health and Safety Research Division, which performed the now-famous "single-atom detection" experiment that demonstrated the unique power and elegance of laser-induced resonance ionization spectroscopy (RIS).



Fourier Transform Mass Spectrometry Comes to ORNL

A new generation of mass spectrometer, a Fourier transform mass spectrometer (FTMS), was installed at ORNL in late 1985. This instrument is based on the principles of ion cyclotron resonance and represents a radical change from the design of conventional mass spectrometers. It has no slits, ion lenses, flight tubes, high-voltage power supplies, or electron multiplier tubes. Instead, it consists simply of a 5-cm (2-in.) cubic cell within a 3-tesla superconducting magnet. Ions formed within the cell move in circular paths perpendicular to the magnetic field axis. A fast sweep of radiofrequency waves is used to excite the ions into a coherent motion, which induces image currents on the top and bottom plates of the cell. These currents are amplified, digitized, and converted from a time-domain signal to a frequency-domain signal using a fast Fourier transform algorithm.

Each ion has its own cyclotron frequency in the cell, which is inversely proportional to the ion's mass. Because frequencies can be so accurately measured, the mass of an ion can be precisely determined. Mass resolution exceeding 10^6 has been obtained on ORNL's new FTMS. In addition, the atomic mass range of the instrument exceeds 5,000 amu, allowing accurate mass measurements to be obtained on species having high molecular weights, such as polymers and biological molecules.

The computer-controlled instrument is unique because it can be operated in a number of modes simply by changing a few operating parameters on a computer keyboard. This versatility allows the FTMS itself to do a variety of experiments that previously were possible only by using several individual mass spectrometers, such as double focusing, quadrupole, and tandem (MS/MS) mass spectrometers. ORNL researchers plan to make extensive use of the FTMS's ability to perform chemical experiments on ions trapped within the FTMS. These ions, which can be trapped for hundreds of seconds, can be reacted with other ions, molecules, and photons. The results of these reactions can be used to study basic physical and chemical properties of gas-phase ions.

ORNL analytical chemists are particularly interested in using these reactions to probe the structure of molecules. The versatility of the FTMS can be used to reveal more detailed structural information than heretofore possible with conventional mass spectrometers.

In RIS, a dye laser is tuned to the exact energy required to promote a valence electron in atoms of a given element to an allowed excited level. These excited atoms can become ions by the absorption of additional energy, which induces each excited electron to leave its atom, making it a positively charged ion. The use of resonantly tuned laser light ensures that the atoms of only one element or only one particular isotope are ionized, even though atoms of other elements are 10^{17} times more abundant. This kind of selectivity makes resonance ionization a uniquely powerful new tool for isotope ratio mass spectrometry because it eliminates the possibility of isobaric interferences, which can occur in conventional instruments when two or more isotopes of different elements have the same mass.

The successful marriage of resonance ionization with analytical mass spectrometry was accomplished in 1982 by Dave Donohue, Dave Smith, and Young, all of the Analytical Spectroscopy Section. For the past four years, they have refined the technique of RIMS into a useful analytical method for measuring isotope ratios of uranium, plutonium, and neodymium. In addition, because RIMS is a powerful spectroscopic method, they plan to use it to make the first measurements of the optical spectrum of fermium (Fm, or element 100), the highest actinide available in sufficient quantities (up to 1 ng) for analysis. In this undertaking the researchers will make use of the inherent selectivity of resonance ionization, as well as the isotopic information provided by the mass spectrometer, to unambiguously measure the absorption spectrum of Fm—that is, the range of wavelengths of light that it will absorb. This task would be nearly impossible to accomplish by conventional emission or absorption spectroscopy.

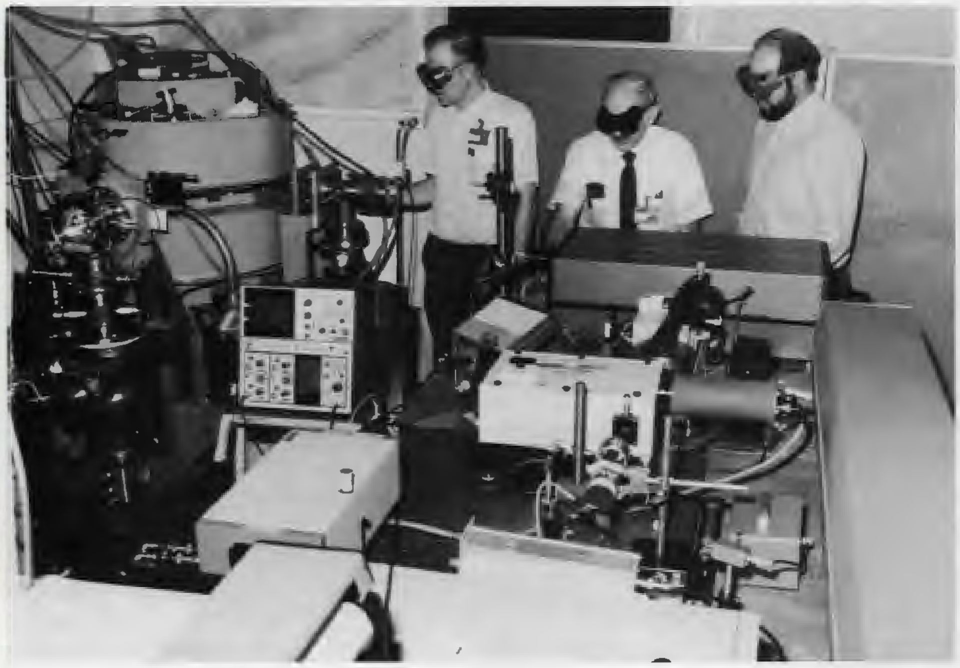


Fig. 2. Dave Smith (left), Jack Young, and Bob Shaw (all in laser goggles) align a laser beam used in a RIMS experiment.

Elemental selectivity is also important in measuring the isotopes of less exotic elements, such as uranium and plutonium (Pu), for nuclear accountability (see sidebar on resin beads and safeguards) or environmental analyses. Both U and Pu exhibit isobaric overlap at mass 238, whereas Pu at mass 241 will always show an interference from its decay daughter americium-241. RIMS has been used to measure these elements essentially free of interference, thus eliminating the biases seen with the conventional thermal ionization method. A precision of within 0.5% has been achieved, but the ORNL chemists are striving to reach the 0.1% precision level to make RIMS competitive with high-performance thermal ionization methods following chemical separation of these elements. Current research is aimed at finding the best laser system for RIMS; the copper vapor laser designed for atomic vapor laser isotope separation (AVLIS, the technology being developed for uranium enrichment) is a strong contender.

The RIMS group is also looking into the resonance ionization process in more detail to understand and use it better. Resonance ionization photoelectron spectroscopy (RIPES) has emerged as a way of unraveling the complicated ionization pathways of the rare-earth elements. In this method, photons from a dye laser are used to ionize atoms of the element under study. However, rather than the ions, the electrons remaining on each atom are analyzed to determine the amount of excess energy absorbed by the atom. This excess energy, which is the difference between the cumulative photon energy and the energy required to ionize the atom, indicates the atomic energy level at which the resonance ionization process started. This information can be coupled with other pieces of the puzzle to reveal the details of the ionization ladder, or RIMS spectrum.

Organic SIMS

The phenomenon of secondary ion emission caused by bombarding a material surface with energetic

Fig. 3. Chris Leibman (left) and Pete Todd work on the SIMS instrument that was designed and built at ORNL for studies of organic materials.

Fig. 4. Doug Goeringer (left) and Warner Christie adjust the optics of the RIMS/SIMS instrument.

ions or atoms has been known for many years. It forms the basis for secondary ionization mass spectrometry (SIMS), which is used to study both the inorganic and organic constituents of sample surfaces. In SIMS, the secondary ions produced when a surface is bombarded with ions are detected and quantified in a mass spectrometer, thus providing information such as the concentrations and distribution of impurities in an alloy. However, a detailed understanding of how secondary ions are formed by ion bombardment is lacking, a situation that Peter Todd of the Analytical Spectroscopy Section hopes to change. He has been working in the field of organic SIMS for a number of years and has constructed a uniquely powerful instrument for carrying out fundamental studies of the physics and chemistry of secondary ion emission. His design for an ion bombardment source produces 10 to 100 times more intense ion beams than those in other laboratories. Such a source would give him a clear advantage in performing studies of a fundamental nature (see Fig. 3).

Other workers in the field have tried to construct theories of secondary ion formation that are consistent with experimental results in the literature. Todd, in collaboration with Gary Groenewold and Chris Leibman, has approached the problem by designing simple but powerful experiments based on known physicochemical laws. In the most useful series of experiments, a known amount of analyte (substance to be analyzed) is admitted in the form of a gas, which is adsorbed on the surface of a liquid matrix such as glycerol and is then sputtered off in the form of ions following ion bombardment. Most organic SIMS experiments use a prepared solution of an involatile analyte in glycerol, but this combination leads to ambiguities in the interpretation of results. Evaporation of glycerol from the matrix in this case enhances the analyte signal, thus preventing a true measure of the analyte's concentration. Introducing the analyte as a gas gives a more accurate measure of its concentration because the sample molecules diffuse into the matrix at a rate that can be calculated using known diffusion coefficients.

This novel approach was suggested by work that Todd and Groenewold, then a postdoctoral researcher from the University of Nebraska, performed for the Department of Defense. The object was to detect chemical warfare agents at very low concentrations in air. Using organophosphorus simulants (molecules similar to nerve gas but less deadly), they found that the choice of a liquid matrix was crucial. The usual matrix, glycerol, was not chemically suited to these molecules and resulted in poor sensitivity. However, by using polyphosphoric acid as the matrix, detection limits were improved 400-fold—that is, as little as 10^{-13} g of dimethyl methyl phosphonate could be detected. This study, while useful to the Army, was even more valuable in

Isotope Ratio Mass Spectrometry Aids Safeguards Program

Beads about the size of sugar grains will soon be used on a large scale to determine whether plutonium and uranium have been diverted illegally from nuclear facilities for making nuclear weapons. Amazingly, the amount of plutonium picked up by each bead is so small and its radioactivity so slight that the bead can be legally mailed to a laboratory for analysis.

The technique of using these resin beads, combined with highly sensitive mass spectrometry equipment to measure the proportions of elements adsorbed onto the beads, was developed at ORNL in 1975 to help the international safeguards program. The technique has already saved the safeguards program several thousand dollars and promises to save it millions of dollars when it goes into widespread use, probably in 1988.

In 1976 a high-sensitivity isotope ratio mass spectrometer designed and built at ORNL was delivered to the International Atomic Energy Agency (IEAE) in Vienna, Austria, which administers the safeguards program. Since then, the ORNL instrument has been used to measure thousands of samples of uranium (U) and plutonium (Pu) from around the world to verify compliance with the Nuclear Nonproliferation Treaty. The samples, which come primarily from nuclear fuel fabrication and reprocessing facilities in the Federal Republic of Germany, France, and Japan, are collected by the IAEA's inspectors and sent to Seibersdorf, Austria, where the Safeguards Analytical Laboratory (SAL) performs a variety of chemical and physical measurements. For example, SAL measures the ratio of uranium to plutonium on each bead; if the elements are not found in a specific ratio, tampering may be suspected.

The ORNL mass spectrometer was designed by Dave Smith and Warner Christie of the Analytical Chemistry Division. It includes a high-sensitivity pulse counting system like one they had built previously at the Laboratory. Such a system can count individual ions, providing the sensitivity needed to measure the small samples collected on tiny beads.

The high sensitivity of the instrument (1 ng U and 0.1 ng of Pu are typical sample sizes), combined with the resin-bead loading technique developed at ORNL under the direction of Ray Walker, allows the analysis of highly radioactive spent fuel samples from reprocessing plants. The IAEA places high priority on such measurements because of the large amounts of fissile U and Pu at these facilities. The timeliness of reporting these measurements is considerably improved by using resin beads because they can be shipped air mail with little or no red tape. The bead technique also saves money because conventional techniques require 1000 to 10,000 times as much sample, which is expensive to ship as a result of the need for heavy shielding. In fact, the resin-bead method is so convenient that it is being adapted for use in commercial mass spectrometers.

The ORNL instrument has been a workhorse for SAL, performing several thousand analyses per year with less than 5% downtime—a record that few commercial instruments can match. It will soon be the key to making the international safeguards program more effective and economical.

Ray Walker (left) and Joel Carter discuss the resin-bead loading technique developed at ORNL to help the international safeguards program.

understanding the mechanisms of secondary ion formation, Todd's primary interest.

SIMS can also be combined with RIMS. ORNL researchers are now developing methods of using RIMS/SIMS for ultratrace elemental analysis (see Fig. 4).

MS/MS: A Powerful Tool

Mass spectrometry/mass spectrometry (MS/MS), a technique developed in the mid-1960s, uses mass spectrometers in sequence to isolate and obtain information on ions in the gas phase. The first mass spectrometer is used to select ions of one mass (parent ions) from a mixture of ions formed in the ionization source. These isolated parent ions are collided at high pressure with a target gas to form fragment ions (daughter ions), which are then sorted and detected in the second mass spectrometer, yielding the mass spectrum of the parent ion.

The MS/MS technique is particularly well suited for the analysis of a target compound in a complex mixture because the first analyzer acts as a separation device, minimizing the need for extensive sample preparation. For example, MS/MS has been employed to determine the concentration and distribution of cocaine in whole tissues of the coca plant by taking small samples of the plant and analyzing them directly for characteristic daughter ions. In addition to its use in chemical analysis, MS/MS is also a powerful tool for studying basic principles of gas-phase ion chemistry, such as the determination of proton affinities and the elucidation of fragmentation pathways.

At ORNL, research in MS/MS has focused on the development of new instrumentation with the goal of expanding the types of information that these new MS/MS instruments can obtain for both chemical analysis and fundamental properties of ions. One approach has been the development of instruments in which different types of mass analyzers are combined. Four types of analyzers are commonly used: magnetic (B) and electrostatic (E), which are high-energy (kilo electron volts) analyzers, and quadrupole (Q) and time-of-flight (T), which are low-energy (tens of electron volts) analyzers. Essentially any combination of two or more of these analyzers can be used for MS/MS.

The first MS/MS instrument developed at ORNL was designed by Dave Russell in 1979. This instrument used three analyzers, EBE, and had the capability of separating parent ions at high resolution in the first stage (EB) of this instrument. In 1984, Doug Goeringer and Gary Glish developed an MS/MS instrument based on a QT configuration. Although this instrument has limited mass resolution, it was designed to be a rugged, low-cost instrument that is ideally suited for the detection of selected compounds in complex mixtures.

Recently Glish along with Scott McLuckey, E. H. McBay, and L. K. Bertram, have developed a versatile new MS/MS instrument based on a QEB configuration (see Fig. 5). The foundation for this instrument was a commercial high-resolution double focusing instrument (EB), which was modified by interfacing a quadrupole mass analyzer to the front end. The instrument has three collision regions in which an ion can be reacted to undergo a change in either mass or charge. In addition, these collisions can be performed using either high or low energies. The QEB configuration allows all of the MS/MS experiments that are typically conducted with a number of separate MS/MS instruments to be performed on this one instrument. In addition to the formation of daughter ions, the third collision region makes it possible to observe the formation of granddaughter ions, or MS/MS/MS. This instrument was selected by *Science Digest* as one of the 100 top U.S. innovations in 1985.

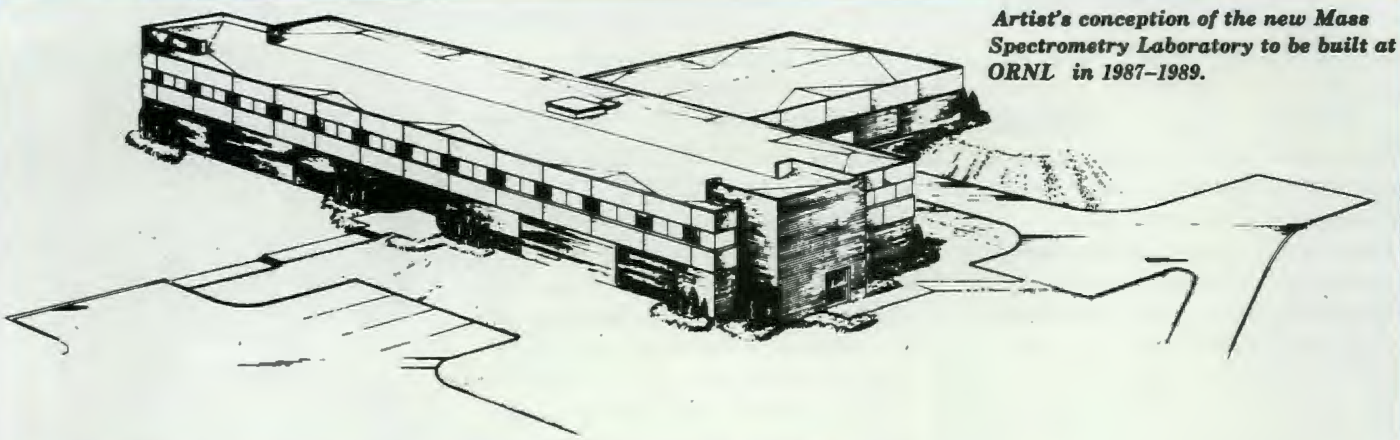
Numerous variations of MS/MS and MS/MS/MS experiments are possible on this versatile instrument, and new experiments are continually being devised. One area in which Glish and McLuckey are particularly interested is the use of low-energy, ion-molecule association reactions as a possible means for screening mixtures for various classes of compounds.

Molecular Structure and Chemical Ionization

Combined gas chromatography/mass spectrometry (GC/MS) is perhaps the most widely used tool for the analysis of organics in complex mixtures because of its ability to separate the components of the mixture prior to mass spectral analysis. Yet conventional GC/MS, which employs electron impact ionization (i.e., bombarding molecules with electrons to produce ions), is often limited in its ability to identify organics unambiguously. This limitation in particular applies to isomeric compounds that have the same elemental composition but a different arrangement of elements. The development of methods for the unambiguous identification of organics in complex mixtures is the goal of researchers in the Organic Spectroscopy group. Their studies focus in particular on the identification of compounds that exhibit biological activity, such as carcinogenicity, mutagenicity, or teratogenicity. In many cases, isomeric structure can profoundly affect the biological activity of a compound. Thus, it is imperative to determine the exact structure of a compound to help assess the potential health risks of a complex mixture.

Fig. 5. Gary Glish (left) and Scott McLuckey tune the QEB instrument used for MS/MS studies.

Several years ago, Michelle Buchanan, head of the Organic



Artist's conception of the new Mass Spectrometry Laboratory to be built at ORNL in 1987–1989.

New Mass Spectrometry Laboratory Proposed for ORNL

Since its beginnings in the 1940s, the Analytical Chemistry Division's work in the area of mass spectrometry has grown in reputation and scope; today ORNL is recognized for having one of the world's foremost broad-based analytical mass spectrometry laboratories. Currently, most of the large ORNL spectrometers are located at the Y-12 plant in facilities that date back to the 1940s and are quite unsuitable for modern mass spectrometry. In addition, being located in a high-security area of the Y-12 plant allows researchers limited access to facilities that have been described as a "national resource." This limited access has severely restricted interactions and collaborations not only with scientists in other divisions of ORNL but also with colleagues in industry and academia.

Now, after 15 years of planning, the mass spectrometry researchers will soon be joining the rest of the Analytical Chemistry Division at ORNL. A new Mass Spectrometry Laboratory (MSL) will be built just south of Building 4500-S; it will house laboratories, offices, and supporting facilities. When completed, the MSL will contain the most comprehensive collection of mass spectrometers in the United States.

Analytical chemists at the ORNL facilities at Y-12 are excited about the prospect of moving to a new facility and are looking forward to the broader collaborations with both ORNL researchers and scientists from around the world that this move will make possible. Construction of the laboratory, which is meant to be a user-friendly collaborative research center, will be started in 1987, and completion is expected in mid 1989.

Spectroscopy group, began investigating chemical ionization (CI) processes as a means of probing the structure of organics with mass spectrometry. Unlike conventional electron impact ionization, CI uses ions (rather than electrons) to react with neutral analyte molecules to form analyte ions by a number of gas-phase reactions. For example, CI processes employing proton-exchange reactions have been developed at ORNL to distinguish among various types of aromatic amines (aromatic organic compounds containing nitrogen), including primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) amines, where n is the number of substituent groups, R, attached directly to the nitrogen atom.

In this technique ammonium ions are used as the CI reagent to transfer a proton to the amines, forming protonated molecular ions. When deuterated ammonia is used as the CI reagent, gas-phase exchange of any hydrogens attached to the nitrogen atom occurs as well, allowing the three types of amines to be distinguished readily. This technique allows primary aromatic amines, which are primary contributors to the mutagenic activity of many coal-derived liquids, to be distinguished from isomeric tertiary aromatic amines, which are much less mutagenic.

By judicious choice of a CI reagent, chemists can also design these gas-phase reactions to be very selective. Ammonia has a very high gas-phase proton affinity and will transfer a proton only to compounds having higher proton affinities. In general, only aromatic amines meet this requirement; thus, a complex mixture containing trace amounts of amines can be analyzed by ammonia CI directly without interference from other non-nitrogen-containing compounds. This attribute eliminates the need for prior isolation of the amines from the sample matrix. A similar approach has been developed to identify isomeric oxygen-substituted aromatics, including phenols, aromatic ethers, and aromatic alcohols, using methanol as the CI reagent.

Fig. 6. Buchanan (left), Ira Rubin, and Gerry Olerich discuss chemical ionization spectra of polycyclic aromatic hydrocarbons.

More recently Buchanan, Gerry Olerich, and Ira Rubin (see Fig. 6) have studied negative-ion chemical ionization processes for the identification of isomeric polycyclic aromatic hydrocarbons (PAH). In these studies, methane is ionized to produce electrons having nearly thermal energy. PAHs having sufficiently high electron affinities can capture these electrons to form molecular anions, whereas other PAHs having lower electron affinities do not ionize. Using this negative-ion CI technique, the ORNL researchers have distinguished among a number of PAHs. For example, benzo(*a*)pyrene, a potent carcinogen, forms molecular anions under these conditions, whereas its relatively benign isomer, benzo(*e*)pyrene, does not ionize and is not, therefore, observed in the resulting mass spectrum. The selectivity and sensitivity of gas-phase reactions hold great promise for obtaining detailed structural information on organic compounds. The research in this group includes not only ion-molecule reactions, as in the CI processes, but also photon-molecule reactions.

Future of Mass Spectrometry

Mass spectrometry research at ORNL has a long and noteworthy history. According to W. D. Shults, director of the Analytical Chemistry Division, "We are now seeing big payoffs from the basic research we've already done. The cost of the technology is coming down, and the power of the technique is going up. We are already seeing mass spectrometry applied to problems in ways we never thought possible or affordable. Because recent advances have made mass spectrometry technology more sensitive and versatile, it is one of the most widely used techniques in analytical chemistry today."

The future of mass spectrometry at ORNL looks bright, as well. The addition of the Fourier transform mass spectrometry (FTMS) to ORNL's mass spectrometry capabilities opens up completely new areas of research. Says Shults, "We are privileged to have the first FTMS in the Department of Energy community. Because this instrument represents the next generation of mass spectrometers, we are excited about having it at ORNL."

Other new areas of MS research are also opening up. Current studies being conducted on sputtering techniques to get molecules into the gas phase represent a new and particularly exciting area of research, especially with respect to ultratrace analysis. Another area of great potential is the marriage of mass spectrometry to optical techniques, such as photoionization and photodissociation, for increases in selectivity as well as the ability to obtain structural information.

Perhaps the most exciting event in the future of mass spectrometry at ORNL is the plan to build a new mass spectrometry laboratory at the X-10 site (see sidebar on page 198). "Our current mass spectrometry facilities have been called a national resource," says Shults. "The new Mass Spectrometry Laboratory will unlock this resource so it can be used by students, professors, and other visitors in ways that have not been possible in the past." ornl

Joe McGrory has been leader of the Nuclear Theory Group in ORNL's Physics Division since 1977. After earning a Ph.D. degree in physics from Vanderbilt University in 1963, he came to ORNL. In the Nuclear Theory Group his research has focused on nuclear structure theory in terms of the nuclear shell model. McGrory served two years with ORNL's Program Planning and Analysis Office and in 1983–1984 was program officer for theoretical nuclear physics in the Division of High Energy and Nuclear Physics of the U.S. Department of Energy. He is an associate editor for nuclear physics of *Physical Review Letters*. Here, McGrory (second from right) and his fellow theorists take a break in the picnic area near the Physics Division offices. The other theorists are, from left, C. Y. Wong, Dick Becker, Mike Strayer, Ray Satchler, Baha Balantekin, and Georg Leander. Missing from the picture are ORNL theorists Chris Bottcher and Tom Davies.

Nuclear Physics Theory at ORNL

By JOSEPH McGRORY

Nuclear physics has been the subject of intense study for almost all of the 20th century. Modern nuclear physics, as we know it now, began about the time of the discovery of nuclear fission in the late 1930s. These studies have provided many valuable insights about the beauty and symmetry of nature, and technological spinoffs from the research have been enormously beneficial to modern society. However, the atomic nucleus has such a complicated structure that much remains to be learned.

Heavy-ion nuclear physics, which is central to the work of ORNL's Physics Division, has grown rapidly over the past 15 years largely because heavy-ion beams allow physicists to attain regions of the nuclear topography that were unreachable when only light-ion beams, such as protons and alpha particles, were available. Using heavy-ion projectiles such as carbon-12, neon-20, nickel-58, lead-208, or uranium-238, we can form nuclei at high temperatures that have masses far beyond those that occur naturally, we can produce nuclei that spin at frequencies so high that centrifugal and Coriolis force effects become strong enough to change radically the shapes of the nuclei, or we can form composite systems having charge $Z >$ 137 (i.e., they have more than 137 protons in the combined nuclei) that produce electromagnetic fields so strong that the usual perturbative quantum electrodynamic theories may break down. All of these topics are of great interest in heavy-ion physics.

Progress in these areas depends heavily on an active iteration between experimental and theoretical physicists. As new experimental data are analyzed and understood, theorists must modify the current models to account for the new data and allow further predictions for new measurements. The Theory Group in the Physics Division is involved in research that touches on all the areas of heavy-ion physics mentioned above. In this brief review, I will focus on

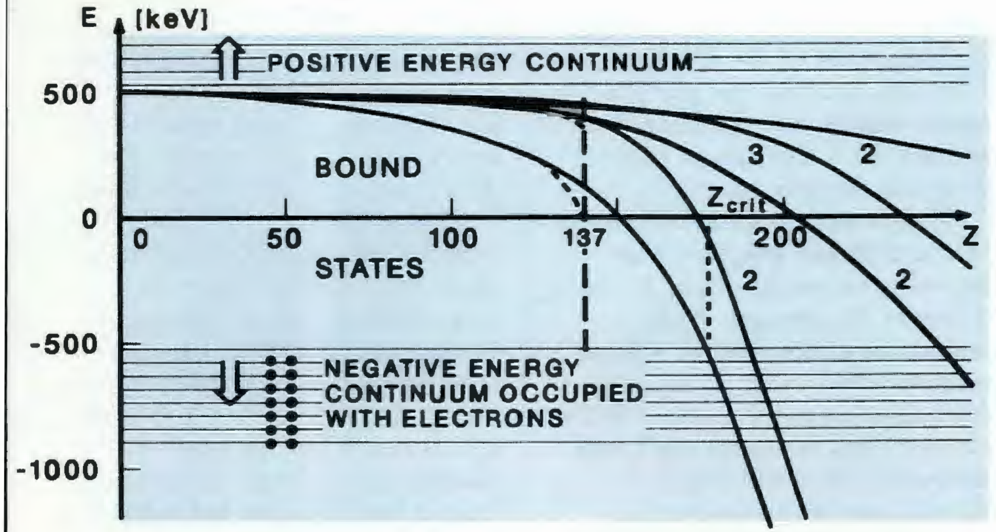


Fig. 1. Plot of allowed energy states of a single electron in the electric field of a point charge, Z, as a function of Z. The curved lines plot the allowed energies of bound "positive-energy" states. In normal circumstances, all the negative-energy continuum states are filled with electrons. At Z_{CRIT} the lowest bound positive-energy electron state becomes degenerate with negative-energy continuum states.

a few projects of particular interest that are improving our current level of understanding of nuclear phenomena.

Positron Puzzle

The first topic is the positron mystery in heavy-ion physics. To explain the mystery, I must first provide a little history. One of the crowning achievements of 20th-century physics was the development by P.A.M. Dirac of Cambridge University of a fully relativistic quantum-mechanical model of the behavior of a single electron (e^-) in an electric field. This model, which leads to the so-called Dirac equation, predicts a set of states for electrons having specific discrete values of energy, angular momentum, and several other quantum labels. The theory also postulates the existence of a mirror set of states, called negative energy states (see Fig. 1). According to the theory, *all* negative-energy states in nature are filled with electrons, but evidence that these states exist can be obtained only if one of the electrons in a negative-energy state is absent. This "hole" in a negative-energy state behaves as if it were a positively charged electron, or positron (e^+).

Soon after the existence of these positrons was predicted, they were observed experimentally. The Dirac model can be applied to systems in which the electric field is generated by nuclei having relatively small electrical charges, $Z\alpha << 1$, where α is the fine-structure constant ($\alpha = 1/137$). An extension of the theory predicts that some strange things might happen if Z were significantly larger than 137 (a value set by the fine-structure constant of quantum electrodynamics). Unfortunately, no naturally existing nuclei have atomic numbers >100, so that no tests of any of this behavior have been possible. But Walter Greiner of Frankfurt University (a regular consultant to the Physics Division for some years) realized that very strong fields could be formed during heavy-ion collisions. For instance, during the collision of two uranium nuclei (each having $Z = 92$), the two nuclei are close together long enough to form a system having 184 protons. This di-nuclear system is still much smaller than typical electron orbits, so the electrons act as if the di-nuclear system is a point charge of 184. Greiner had predicted that for these large Z' values, the lowest allowed normal electron level is lowered in energy until it becomes degenerate with, or has the same energy as, the negative-energy states, as indicated in Fig. 1. If no electron were present in this normal electron state, Greiner theorized that an electron in the negative energy state might spontaneously make a transition to the degenerate positive-energy state, resulting in the emission of a positron. He referred to this spontaneous positron emission as a sparking of the charge vacuum in strong fields.

The Theory Group in ORNL's Physics Division is involved in research that touches on many areas of heavy-ion physics. The group has developed models to help predict the shape and structure of the nucleus during high spin and other conditions attainable when heavy nuclei collide violently in an accelerator. Two groups of ORNL theorists have had an impact recently with their explanations of the origin of fixed-energy positrons in heavy-ion reactions. One group proposes that the positron is evidence for the decay of a new elementary particle.

Several years ago, physicists at ORNL and elsewhere were excited about observations of positrons produced at fixed energies during two-uranium-ion collisions because the experimental results were in agreement with the Frankfurt predictions. Two other predictions of the Frankfurt group, however, seem to have missed the mark. According to theory, the measured energy of the spontaneously produced positron should vary by a factor proportional to Z^{20}, where Z is the combined charge of the colliding ions. By using different ions (e.g., uranium and thorium or californium) to vary the total charge, experimenters expected to see a strong Z-dependence. The theory also predicts no positron production when $Z < 173$. To make a long story short, experimental results contradict both predictions. The energies of the positrons are constant, no matter what the total charge of the colliding systems, and positrons seem to be produced by systems in which $Z < 173$. Herein lies the positron puzzle.

New Particle Proposed: The Short-Lived Axion

Where do the fixed-energy positrons in heavy-ion reactions come from? This question has been debated vigorously over the last year or so. Two possible explanations have been proposed by ORNL nuclear theorists. Baha Balantekin, Chris Bottcher, and Mike Strayer have considered the possibility that the positron is evidence for the decay of a new elementary particle, which they often refer to as a short-lived axion. (For the paper they published on this subject, they received a 1986 Publications Award from Martin Marietta Energy Systems, Inc., which also honored Balantekin as Author of the Year.)

According to the ORNL theory, the new particle carries no net electric charge. When the particle decays by producing an electron-positron pair, limits on the mass of the new particle and the lifetime for this e^+-e^- decay branch can be extracted from the measured energies of the positrons and from the geometries of the detector. From this analysis, the particle model implies that the mass of the particle is 1.6 MeV (about three times the electron mass).

If such a particle exists, it could have a profound effect on other physical phenomena. First, it would influence the strength of the interaction of the electron with a magnetic field—that is, the anomalous magnetic moment of the electron. This interaction is known accurately. By combining information on this interaction strength and on the measured cross sections for producing the positrons in heavy-ion reactions, it follows that the lifetime of the new particle would be $\sim 10^{-13}$ s. Second, the existence of such a particle would have a cosmological consequence: it would measurably affect the rate at which energy is lost from red-giant stars. The measured energy losses of red giants are quite compatible with the existence of this new particle. In fact, no known data in nature have been found to be inconsistent with the existence of the particle. Several tests have been proposed to support or disprove the existence of this particle, to prove the theory right or wrong. First, because the theory holds that the particle decays into an electron-positron pair, one approach is to turn the reaction around and try to form the new particle by scattering positrons from electrons at an appropriate energy. Several groups are conducting such experiments, including one first led by Karl Erb (formerly a member of the Physics Division who is now with the National Science Foundation). Secondly, if the particle hypothesis is correct, experimenters should be able to observe the coincident production of electrons and positrons at the same energy in heavy-ion reactions. The coincidence experiments are very difficult because the probability that the pairs can be observed is very small. However, evidence that such coincidences had been observed was recently obtained by a group from Yale University. The data analysis is still being refined.

Cheuk-Yin Wong of ORNL explains the origin of positrons in terms of a composite particle rather than the short-lived axion. In the summer of 1985, he was reading a collection of the papers of his thesis advisor, John A. Wheeler, who is one of the "fathers" of nuclear fission theory. He noticed that in 1946 Wheeler had calculated the properties of the three-body system, which consists of two electrons and a positron $(e^+, e^-, e^-) \equiv P_s^-$ and its charge-conjugate partner $(e^+, e^+, e^-) \equiv P_s^+$. Wheeler predicted that the two systems could be self-bound. The most probable mode of disintegration of the systems was by the emission of two photons,

$$P_s^+ \rightarrow e^+ + \gamma + \gamma$$
$$P_s^- \rightarrow e^- + \gamma + \gamma$$

However, a one-photon decay mode is allowed:

$$P_s^+ \rightarrow e^+ + \gamma$$
$$P_s^- \rightarrow e^- + \gamma$$

The negatively charged P_s^- system was observed experimentally three years ago, lending credence to Wheeler's calculations. If P_s^- exists, then P_s^+ certainly exists as a slightly bound three-body system. Wong studied the properties of the one-photon decay mode of P_s^+. The energy of the e^+ in this decay mode is calculated to be 340.66 keV, in excellent agreement with the measured energy, 336 ± 10 keV, of some of the positrons observed in the heavy-ion reactions. This coincidence is striking.

Wong's hypothesis can be tested. It should be possible to observe electrons at the same energy as the positrons. In the one-photon decay mode, the photon has a discrete energy of 681.3 keV, so that gamma rays having this energy should be detectable. In Wong's picture, no coincident production of electrons and positrons should occur. If no alternative explanation of the coincidences reported by the Yale group is found, Wong's picture is in trouble.

Another problem with Wong's concept is that the predicted decay probability is too small. To initiate the two-photon decay mode, one electron and one positron must be very close to the same point in space. The probability for this spatial coincidence is inversely proportional to the volume of the three-body cluster (i.e., $\alpha\ 1/R^3$), where R is the cluster radius. For one-photon decay to occur, all three particles must be spatially coincident. This probability is inversely proportional to the volume squared (i.e., $\alpha\ 1/R^6$). Because Wheeler's bound clusters are very large, ~10^5 fermis ($10^5 \times 10^{-13}$ cm), the relative decay branch to the one-photon system is probably too small to allow observation of this branch. However, the analysis does suggest an explanation.

In a nucleus having a large positive charge, the radius of the closest electron orbit is relatively small compared with atoms having a low atomic number because the electrons are bound more tightly as the attractive force increases. For the nuclear molecular system U + U (Z = 184), the orbital radius of the innermost electron is on the order of 10^2 fermis—that is, it is three orders of magnitude smaller than is the case for the loosely bound $P_s{}^+$ system. This reduced orbital radius increases the relative probability for decay of three bound leptons (electrons and positrons) by the one-photon branch. Unbound systems of $P_s{}^+$ may be formed around the Z ≃ 184 nuclear molecular system during heavy-ion collisions and then decay by $P_s{}^+ \rightarrow e^+ + \gamma$. The strong field binds the three leptons in a configuration that is much smaller than $P_s{}^+$ or $P_s{}^-$; thus, the relative branch to the one-photon decay mode is greatly enhanced.

While studying the physics of electrons and positrons in strong electromagnetic fields, Wong and Dick Becker considered effects in electron-positron systems that arise from magnetic interactions. Consider an electron fixed in space and spinning in one direction; around this electron moves a positron. Between these two particles is a magnetic force. By solving a two-particle version of the Dirac equation, Wong and Becker have found a resonant "superpositronium" state. In this resonance state, the mean separation of the electron and positron is ~23 fm. The two-body breakup of the resonance leads to a positron and an electron produced in coincidence at an energy of ~279 keV. This energy is also in good agreement with the energy of one of the positron groups produced during the heavy-ion collision.

The physics of strong electromagnetic fields formed during heavy-ion collisions has been studied intensively for a decade and remains one of the more widely discussed topics in heavy-ion physics. Central to all the considerations is the very concept of what constitutes a "vacuum." As the electromagnetic field becomes stronger, the basic nature of the vacuum is altered. Thus, understanding how vacuums change with field strength is crucial to the solution of the positron puzzle. Although none of the previously mentioned models definitely resolves the positron puzzle, these speculations by the ORNL theorists have played a central role in the consideration of the problem in the last year.

Many-Body Problem

The justification of nuclear physics research as fundamental basic research continues to be rooted in the quantum-mechanical many-body character of the nucleus. It is now possible to obtain exact descriptions of systems that have two or three particles but only two-body forces [i.e., a given particle is subjected to the same force exerted by a second particle despite the presence of a third (or more) spectator particle(s).] For more than three particles, various approximations must be made. Physicists continue to develop more nearly accurate solutions of the many-body problem.

The nucleus is the best laboratory in nature for testing the various quantum-mechanical many-body models. The number of neutrons and protons in known nuclei is no more than 200 to 300, small enough that all the nucleons could conceivably be treated explicitly. (By contrast, in solid state and chemical physics, the number of particles is on the order of 10^{23} or more; thus, a truly microscopic many-body theory is impractical for these fields.) Because the nuclear force between neutrons and protons is so strong compared with the electromagnetic force in atomic physics, a rich diversity of reactions occurs between nuclei, providing a wide variety of tests of the many-body theories.

The starting point of any quantum-mechanical microscopic or many-body model of the nucleus is the famous Schrödinger equation (see Eqs. 1 and 2 shown in box on page 204), where $T(r_i)$ is the kinetic energy of particle i and $V(r_1,r_2)$ is the potential energy of the interaction between two particles at positions r_i and r_j, i and j stand for any one of the N particles (neutrons or protons) that make up the nuclear system, and $\psi(r_1 \ldots r_N)$ is the wave function that describes the nuclear system (it contains all the information we can know on how the nucleus behaves). To describe the scattering of two nuclei, it is common to assume that many essential features of the scattering can be found, not as two many-particle composites, but by treating each of the nuclei as two single "particles" whose behavior is described by the two-body Hamiltonian equation (see Eq. 3 in box), where T_1 and T_2 are the total kinetic energies of the two nuclei and $V_N(\bar{R}_{12})$ is the potential energy of interaction when the two nuclei are separated by $\bar{R}_{12} = R - R_2$. In this way, the many-body equation has been reduced to a two-body problem. A typical procedure is to measure properties of the scattering of two nuclei. The nuclear potential $V_N(\bar{R}_{12})$ is expressed in terms of a set of free parameters. The parameters are chosen to fit the measured data. Then models are developed to express the parameters of Eq. 3 in terms of the ingredients of the microscopic Hamiltonian Eq. 1. The nuclear potential serves as a testing ground of the models for solving Eq. 1.

What is the nuclear potential? Because nuclear forces are very strong, a number of events can occur when two nuclei collide in an accelerator. Consider two oxygen nuclei, each of which has 8 protons and 8 neutrons. When one oxygen ion is scattered from another, many "reactions" can happen. One possible event is elastic scattering, in which both oxygen ions "bounce" off each other without exchanging energy and thus remain in their lowest-energy, or ground, state. The ions can inelastically scatter—that is, transfer or exchange energy upon contact, causing one or both nuclei to end up in excited states upon separation. Another possible nuclear event is a one-particle transfer—in the case of oxygen, a neutron moves from one ion to the other, resulting in the transformation of the two ^{16}O nuclei into an ^{17}O ion and an ^{15}O ion. If a one-proton transfer occurs between the oxygen ions, the final products are a fluorine-17 ion and a nitrogen-15 ion. In the case of a multiple-particle exchange, the final products could be, at one extreme, a single neutron or proton, or, at the other, a totally fused system—sulfur-32. Thus, the behavior of many systems must be described in terms of the nuclear potential in Eq. 2 (see box).

The common approach is to assume that the nucleus-nucleus interaction is complex and that it depends on the relative energy E of the scattering systems (see Eq. 4 in box), where $V_N^R(r,E)$ (called V^R below) is the real nuclear potential, $W_N^I(r,E)$ (called W^I below) is the imaginary part of the potential, and $V_c(r)$ is the potential energy from the Coulomb (electrostatic) interaction between the charged particles in the two nuclei. The assumption is that V^R describes elastic scattering and all other processes (reaction channels) are described by the imaginary (absorptive) potential W^I. Elastic scattering is the dominant process in most low-energy scattering reactions. Often V^R and W^I are given phenomenological shapes. One commonly used form is the so-called Woods-Saxon potential (see Eq. 5 in box), where c, r_0, and a are energy dependent parameters.
An important question is the energy dependence of the nuclear potential. For instance, in ^{16}O the first excited state has an energy level of ~6 MeV. Thus, if the projectile energy is less than 6 MeV, no inelastic scattering can occur; the contribution of inelastic scattering processes to W^I for $E <$ 6 MeV is therefore 0. As the projectile energy is stepped up, an increasing number of reactions can occur between the two ions; thus, the W^I has an energy dependence. Similar arguments can be made for energy dependence of W^I from particle transfer reactions. On the other hand, the general belief has been that no significant energy dependence exists in the real part of the nuclear potential. However, experimental evidence clearly shows that significant energy dependence exists in the real nuclear potential. This behavior is commonly referred to as the "threshold anomaly."

Sub-Barrier Fusion: Another Nuclear Puzzle

Another puzzle in low-energy nuclear scattering involves so-called sub-barrier fusion. A number of experiments have measured the probability that two nuclei will stick together, or fuse, when one nucleus impinges on another. This "fusion cross section" has been a topic of great experimental interest at ORNL's Holifield Heavy-Ion Research Facility. The puzzle occurs at very low energies. The Coulomb force $V_c(r)$ in Eq. 4 is a long-range repulsive force, whereas the nuclear force is strong, attractive, but

EQUATIONS

$$H\,\Psi(r_1,r_2 \ldots r_N,t) = -ih\frac{\partial\psi(r_1 \ldots r_N,t)}{dt} \ , \tag{1}$$

$$H(r_1,\ldots r_N) = \sum_{i=1}^{N} T(r_i) + \sum_{i=1}^{N}\sum_{j=1}^{i-1} V(r_i,r_j) \ . \tag{2}$$

$$H(R_1,R_2) = T_1 + T_2 + \mathrm{V_N(R_{12})} \tag{3}$$

$$V_N(r,E) = V_N^R(r,E) + iW_N^I(r,E) + V_c(r) \ , \tag{4}$$

short-ranged. Therefore, the nuclei must have enough kinetic energy to break through the repulsive force of the Coulomb interaction (i.e., to overcome the Coulomb barrier) to respond to the attractive nuclear force by sticking together. The probability for fusion near the Coulomb barrier depends sensitively on a delicate balance between the Coulomb force and nuclear force. The experiments on fusion cross sections near the Coulomb barrier have shown that the fusion cross section is much larger than would be expected from our assumptions about the nuclear potential. But because of the existence of the Coulomb barrier, our knowledge of the nuclear potentials at low energy is very incomplete.

In the last year, Ray Satchler of the Physics Division, working with Claude Mahaux at Liege (Belgium), has developed a tool that has been used to resolve the energy-dependence anomaly and will be of tremendous help in sorting out the Coulomb barrier anomalies. The method makes use of so-called dispersion relations. Dispersion relations involve complex functions. The nuclear potential is a complex function (i.e., it is expressed as a complex function of r and E, in which V^{R}_{N} and W^{I}_{N} are the real and imaginary parts of the function). Under certain conditions, it is possible to express V^{R}_{N} in terms of W^{I}_{N} and vice versa, as is shown below. The first conditions are quite reminiscent of the "smooth and well-behaved" function, conditions taught in introductory calculus. The other condition is causality, which can be very roughly stated as follows: "The effects of a given event cannot be sensed until after the event occurs." This very logical assumption, however, has surprising implications. For the nuclear potential described above, the relation takes a (simplified) form (see Eq. 9 in box). The relation expresses the value of the real potential at one fixed energy E as an integral over the value of the imaginary potential at all energies, that is, if we know the imaginary part of the potential at all energies, we know the energy dependence of the real potential at all energies. By making some simple but quite reasonable assumptions about the imaginary potential, Satchler and his co-workers learned some very interesting information about the low-energy part of the real potential.

The imaginary potential was assumed to consist of two linear segments. As argued above, $W^{I}(r,E)$ starts out at zero at low energies and increases with increasing energy as more channels become accessible. The imaginary potential reaches a maximum, and then is assumed to be constant over the high-energy range (see Fig. 2). The curve in Fig. 2 for the real potential $V^{R}_{N(r)}$ is calculated by using this simple form of $W^{I}_{N(r)}$ in the dispersion relation (Eq. 6). The dots are a summary of all measured values of the potentials. So far, we have precise information about the heavy-ion nuclear potential only at a narrow range of values of r around the point where the two ions barely touch. The potentials are plotted in Fig. 2 at this radius.

The shape of the real potential curve calculated from the dispersion relation is independent of the shape of the imaginary potential at high energies. The width of the peak in the real potential is determined by the slope of the first, increasing segment of the imaginary potential. The important fact here is that, from the dispersion relation, the inevitable increase of the imaginary potential as the projectile energy increases must be reflected in a rather strong energy dependence of the real potential in the same energy region. The real potential cannot be energy independent at low energies. Causality says the "threshold anomaly" must exist.

The predicted behavior of the nuclear potential has important implications for the sub-barrier fusion anomaly. In the example shown in Fig. 2, the Coulomb barrier is indicated by a vertical arrow. The increase in the real potential strength near this barrier leads to a predicted fusion cross section at the Coulomb barrier, which is 50 times the cross section predicted from an energy-independent extrapolation of the potential from those extracted from measurements at energies above the barrier. This prediction is in qualitative agreement with the measurement of enhanced fusion cross sections at the Coulomb barrier. It should also be pointed out that recent measurements of the real potential at low energies support the predicted decrease in the real potential below the barrier shown in Fig. 2.

This development, based on very simple and plausible premises, has

EQUATIONS, cont.

$$V^{R}_{N}(r,E) = \frac{C(E)}{1 - e^{\frac{-r - r_0(E)}{a(E)}}} \,, \tag{5}$$

$$V(r,E) = V_0(r) = \frac{P}{\pi}\int_0^{\infty}\frac{W(r,E')}{E' - E}\,dE' \,, \tag{6}$$

dual virtues: it provides a pedagogically clear insight into previously puzzling experimental facts and it serves as a useful tool for extrapolating potentials to an energy domain where they are needed but may not be directly obtainable experimentally.

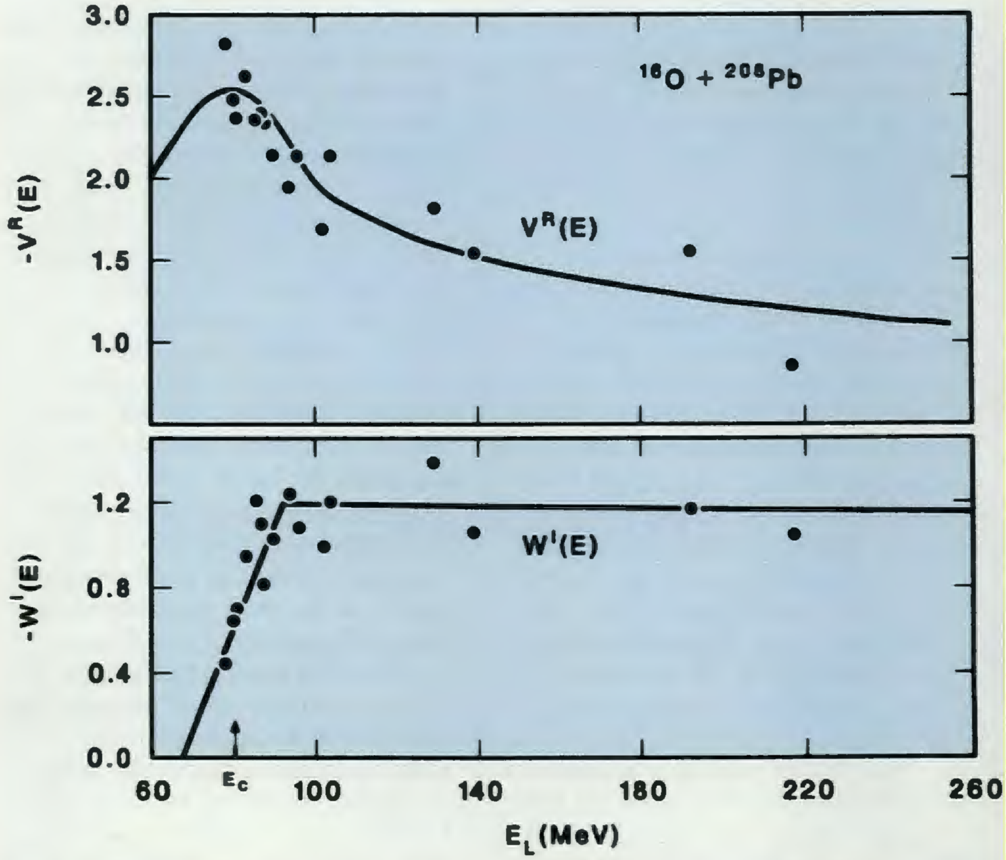


Fig. 2. Real, $V^R(E)$, and imaginary, $W^I(E)$, parts of the nucleus-nucleus potential for the interaction between ^{16}O and ^{208}Pb. The data are values extracted from experiments. The solid line for $W^I(E)$ is the assumed imaginary potential, and the solid curve for the real potential, $V^R(E)$ is calculated from the assumed $W^I(E)$ by the dispersion relation. E_c is the energy to overcome the Coulomb barrier.

Microscopic Models of Nucleus-Nucleus Scattering

Satchler's work on the nuclear potential deals with the phenomenological potential, where the potential parameters were chosen to fit experimental scattering data on nucleus-nucleus scatterings. As previously stated, the next step is to calculate these potentials starting from microscopic models of the nucleus, where the explicit degrees of freedom are the neutrons and protons interacting through *effective* two-body forces. [Particle physics has moved to study sub-nucleon degrees of freedom—that is, they assume that the nucleons are made up of even smaller entities (quarks and gluons) and that the nucleons can be described in terms of quantum chromodynamics (QCD). Attempts are being made to calculate the nucleon-nucleon force from QCD, but we are a long way from having a quantitative model of the nucleus in terms of quarks and gluons. Thus, the three-body (quark) nucleon of particle physics is the elementary single particle of nuclear physics. The effective nucleon-nucleon force attempts to describe processes that at a more microscopic level involve quark and gluon exchanges. For most purposes in today's nuclear physics, this description is certainly a good approximation.]

Much effort has been expended to develop microscopic models of nucleus-nucleus scattering. The basic tool most generally used in microscopic nuclear physics is the Hartree-Fock approximation. What is the Hartree-Fock theory? The starting point is again the Schrödinger equation for a many-particle quantum-mechanical system which involves only two-body interactions (see Eq. 1 in box). If we are concerned only with the properties of low-lying bound states of nuclei and of only one nucleus (i.e., center-of-mass motion is irrelevant), the time-dependent Eq. 1 can be reduced to a time-independent eigenvalue equation (Eq. 7 in the box). That is, we must

EQUATIONS, cont.

$$H\psi_i = E\psi_i \ , \tag{7}$$

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + \sum_{i=1}^{N} \sum_{j=1}^{i-1} V(r_i,r_j) \ , \tag{8}$$

$$h = \sum_i \frac{P_i^2}{2m_i} + u(r_i) \ . \tag{9}$$

find the eigenfunctions ψ of the Hamiltonian H of the system, with energy eigenvalues E, where H is given in Eq. 8 (see box) and N is the number of particles in the system. This equation, however, is not soluble exactly if $N > 3$. The Hartree-Fock approximation replaces the complete Hamiltonian H by an approximate Hamiltonian h as in Eq. 9 (see box). That is, it replaces the two-body potential $V(r_i,r_j)$ by the approximate one-body potential $u(r_i)$, where $u(r_i)$ represents the average interaction that the particle labeled i undergoes in response to forces exerted by all the other particles in the system; for obvious reasons, $u(r_i)$ is called the mean field. The approximation replaces a system of mutually coupled particles by a system in which each particle moves as an independent particle in a common central potential; thus, $u(r_i)$ is not a phenomenological one-body potential. It is calculated from the wave functions for the individual particles and the nucleon-nucleon potential. Thus, $u(r_i)$ depends on $\psi_i(r)$. But $\psi_i(r)$ are the solutions of the one-body Eq. 9—that is, $\psi_i(r)$ depends on $u(r_i)$. The Hartree-Fock theory treats this circular reasoning self-consistently by an iterative procedure. Start with a guess for $u(r_i)$ and calculate the corresponding $\psi(r)$. Then calculate a new $u(r)$ by averaging the nucleon-nucleon potential $V(r_i,r_j)$ over the $\psi(r)$. Keep going until there is no change from one step to the next.

The Hartree-Fock approximation was developed for atomic physics, where it made intuitive sense. The electrons in an atom are always affected by the strong central charge field of the nucleus, which acts to stabilize the electronic motion. To this nuclear charge field, the average effects of all the other electrons on a given electron are added. The Coulomb force between charged particles is long-ranged and smooth, so the averaging procedure sums up smooth behavior. The nucleus, however, has no strong nuclear field analogous to the electric charge at the center of an atom; furthermore, the nuclear force is short-ranged and much more complex than the Coulomb. The relevance of mean field theories to nuclear physics was first suggested by the success of one mean-field theory, the nuclear shell model, in describing observed nuclear structure. It is now known that the nuclear force is essentially smoothed out by the Pauli principle, which states that two identical particles cannot be at the same place at the same time. If a nuclear system has numerous particles, this Pauli blocking suppresses many fluctuations induced by mutual scatterings; as a result, the nucleon-nucleon scattering is not very violent.

For many years ORNL's Theory Group has been a world leader in investigating nuclear properties in terms of the Hartree-Fock approximation. The Hartree-Fock equations are solved numerically. Because the procedures are computer intensive, the availability of excellent computing facilities at ORNL has given the group a distinct advantage.

The early history of nuclear Hartree-Fock calculations involved the examination of static nuclear properties—masses, shapes, and density distribution of nuclei. These shapes and densities could be used to analyze various types of nuclear reactions, particularly electron scattering. At ORNL, Dick Becker and Tom Davies were extremely active in this field in the late 1960s and early 1970s. Their investigations showed that once a "realistic" force between two nucleons was determined from nucleon-nucleon scattering experiments, these static properties of nuclei could be calculated quite accurately using the Hartree-Fock approximation. With the onset of studies of heavy-ion reactions, it was suggested that the best microscopic theory for such reactions would be a time-dependent version of the Hartree-Fock theory. Here two nuclei start at some separation distance r at an initial relative velocity v. The nuclei are each assumed to be described initially by a static Hartree-Fock solution. As the two nucleons approach each other, they "feel" an average interaction caused by nucleons in both the target and projectile nuclei (analogous to the mean-field interaction discussed above for a single nucleus). The mean-field changes as a function of time during the collision. Because two nuclei are involved and because the mean field is calculated as a function of time during the collision, these calculations are much more complex and time consuming than are the static Hartree-Fock calculations.

A major effort in the nuclear theory program in recent years has been to develop efficient algorithms to carry out the time-dependent calculations on a computer. These efforts have been led by Tom Davies, Mike Strayer, and Chris Bottcher. The time-dependent Hartree-Fock (TDHF) equations are solved by various numerical methods such as finite difference or finite element techniques. These involve finding solutions to the equations at a number of discrete, closely spaced, points instead of over continuous space. A number of factors determine the size of the calculations. The most obvious factors are the number of spatial dimensions and the number of points at which the solutions are obtained. Much effort has been made to define the smallest useful space for a given physical calculation.

Another factor that influences the size of the TDHF calculation is the type of interaction potential that is used. The function that describes the nucleon in a given nucleus can be expressed in terms of the position and momentum vectors of the nucleon, the nucleon's electric charge, and the nucleon spin (i.e., the nucleon can be thought of as spinning around an axis through its center, and the force on the nucleon depends on the direction of the rotation.) Angular momentum can describe the nucleon function equally as well as linear momentum. Thus, a nucleon function can be specified by its position, angular momentum, nuclear spin, and charge. The nucleon-nucleon force then depends on (1) the distance between the two particles, (2) their relative angular momentum, (3) their total nucleon spin, and (4) their total charge. The relative angular momentum and total spin are vector quantities, and the relative orientation of these two vectors influences the nucleon-nucleon force. The force that depends on this relative orientation is called the spin-orbit force. The inclusion of this force in Hartree-Fock theory leads to a very complex set of coupled differential equations. However, for many macroscopic quantities in heavy-ion reactions, this force is not believed important. Thus, in most TDHF calculations, the spin-orbit force is ignored.

To date, the vast majority of TDHF calculations have been 2D calculations in which symmetry about the line joining the two nuclear centers is assumed and in which the spin-orbit force is ignored. The calculations have been highly successful in describing many of the gross properties of heavy-ion scattering. The angular distributions of the scattered ions are well described. In low-energy heavy-ion collisions, one of the surprising experimental discoveries is that the so-called deep-inelastic cross section is very large. In a deep-inelastic collision, almost all of the kinetic energy contained in an accelerated ion is converted into heat after that ion collides with the target ion. The kinetic energy of relative motion between the two ions following the collision is essentially equal to the energy of Coulomb repulsion of two touching charged spheres, where the charges are the charges on the two ions. This strong damping of the projectile kinetic energy in heavy-ion collisions is reproduced quite accurately by the TDHF calculations.

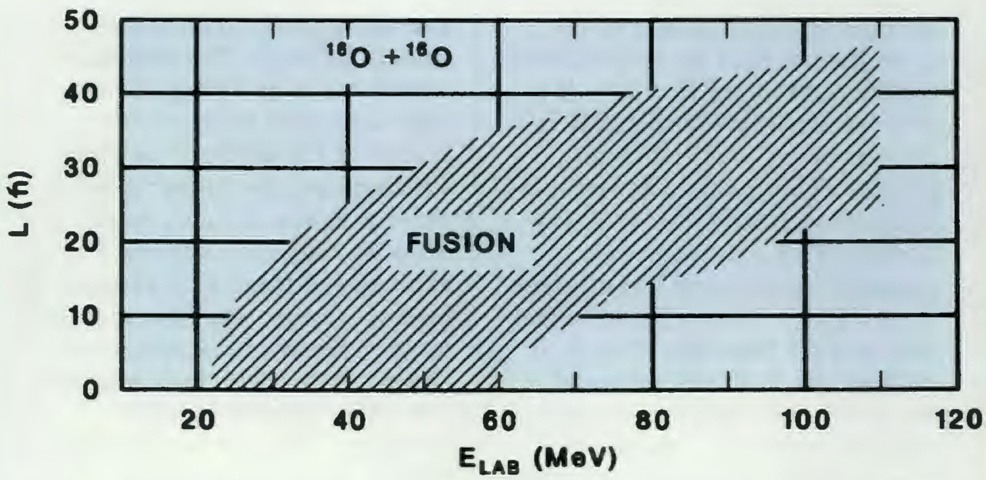


Fig. 3. Typical calculated map of fusion for the ^{16}O + ^{16}O system. E$_{LAB}$ is the incident energy of an ^{16}O ion, and L(ħ) is the angular momentum of the incident particle, which is proportional to the impact parameter. The shaded area represents that region where fusion is calculated to occur. For an impact parameter of zero (L(ħ) = 0), the ^{16}O ions fuse for projectile energies between 20 and 60 MeV.

The Fusion of Nuclei

One major problem faced by those performing TDHF calculations has to do with calculating the probability for the fusion of two heavy ions—that is, determining how often the ions stick together when they collide. If the incident ion has a large enough impact parameter, it would simply pass the nucleus so far away that it would be unaffected by the nuclear potential—the force that can produce fusion. (The impact parameter is the distance of closest approach between two colliding objects when no deflecting forces are present. If two nuclei would collide head-on in the absence of any interactions, the impact parameter is zero.) For central, head-on collisions, it is reasonable to expect fusion to occur at all energies up to a very high energy. TDHF calculations, however, indicate that the nuclei stop fusing at a much lower than expected projectile energy (referred to as the TDHF "fusion-window anomaly" and illustrated in Fig. 3). There is experimental evidence for fusion up to 70–80 MeV for zero impact parameters. Many experimental searches were made to find evidence for this predicted fusion window, but none has been successful. This theory-experiment disagreement casts doubt on the validity of TDHF theory when applied to fusion.

In the past year, Strayer and his collaborators at ORNL have apparently found the source of the discrepancy. They have carried out the first realistic calculations of the scattering of two ^{16}O ions in which the effect of the spin-orbit force is included in the calculations. The inclusion of the spin-orbit force had a dramatic effect on the fusion window. With spin orbit, fusion of nuclei involved in central collisions is now predicted to occur up to very high projectile energies (up to 80 MeV for ^{16}O + ^{16}O at zero-impact parameters). All disagreements with

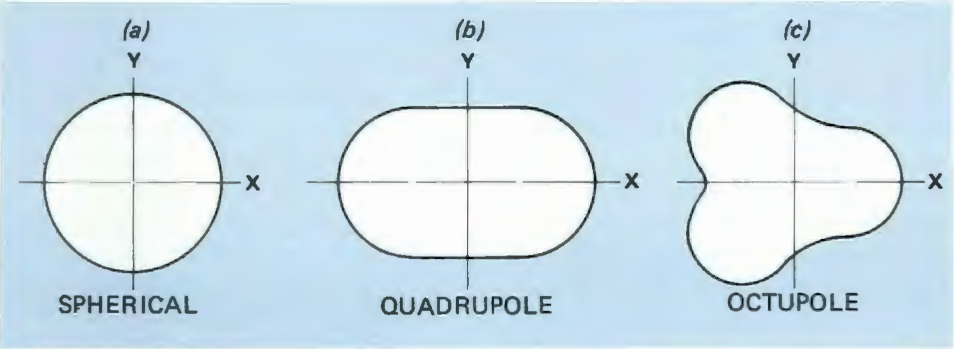


Fig. 4. Possible shapes of nuclei in the intrinsic frame of reference: (a) and (b) are symmetric under reflection along the x axis but (c) is not.

experiment are now resolved. The inclusion of spin-orbit forces effectively increases the available degrees of freedom for absorption of energy from the motion of the incident projectile; this energy damping leads to fusion. The spin-orbit force is velocity dependent, so for very low energies it has no effect, but it becomes stronger as the energy increases.

With the apparent resolution of the fusion-window problem, the TDHF theory is now well established as a good first-order theory for low-energy, heavy-ion collisions. The algorithms developed by Bottcher, Davies, and Strayer have a wide range of applicability. Bottcher has made much use of the same general approach to study ionization processes in ion-atom collisions. Strayer and Bottcher have also developed numerical solutions of the time-dependent Dirac relativistic equation. They can now generate nonperturbative relativistic quantum-mechanical solutions for the motion of an electron in the field of two colliding ions. Such solutions are a central ingredient of the study of the production of positrons in strong fields (see beginning of this article).

Shapes of Nuclei

Most of this article has dealt with the interactions between two nuclei. Much of nuclear physics research deals with nuclear structure and the properties of individual nuclei—size, shape, density, surface thickness, etc. One particularly intensive area of research deals with the identification of the discrete states in which a nucleus can exist for a small but finite length of time. These "excited" states are labeled by their total energy relative to the ground state and by the symmetry properties that the wave functions describing these states possess under certain transformations—for instance, how the function changes when the nucleus is rotated around various axes of the nucleus. A very simple measurable symmetry property of the nucleus is its behavior under a reflection of the axes of the defining coordinate system. In Fig. 4 shapes that have reflection symmetry—a sphere and a prolate quadrupole shape—are shown. Also shown is an octupole shape, which is not reflection symmetric along the x-axis. All the nuclear wave functions should have total reflection symmetry to within a sign; that is, if $\psi(r)$ is a wave function describing a certain nuclear state, then either $\psi(-r) = \psi(r)$ or $\psi(-r) = -\psi(r)$. The nuclear state has a parity label π of $+1$ or -1, depending on whether the phase changes under reflection. If parity is a good quantum number, then nuclei cannot have electric dipole moments, and, in fact, no such moment has ever been observed. This symmetry exists in the laboratory. Often it is useful to study the nucleus in a frame of reference that is fixed to the nucleus. In this body-fixed frame, asymmetries can be found that cannot exist in the laboratory frame. This technique can be useful provided that the symmetries are removed when the results are re-expressed into the laboratory frame. For example, in the intrinsic frame, the nucleus may have the shape of a football. The transformation of this description to the laboratory frame amounts to averaging the properties of this football over all its possible orientations, so that the nucleus appears spherical in the laboratory, as it must. A massive body of data tells us that many nuclei have quadrupole (football) shapes.

In recent years, physicists have shown much interest in the possibility that nuclei can have octupole (pear) shapes. If the nucleus in the intrinsic frame has an octupole shape, then in the intrinsic frame an electric dipole moment is no longer forbidden. A consequence of an intrinsic octupole shape is that strong electric dipole (E1) transitions might occur in the nucleus. Over the past several years increasing evidence suggests that certain nuclei have octupole shapes and that some of these nuclei have very strong electric dipole transitions. In several anomalous cases, however, octupole deformations were predicted and/or observed even though E1 transitions were highly inhibited. This anomaly cast doubt on the validity of the intrinsic octupole shape description of these nuclei. Georg Leander of the UNISOR program at ORNL has played a leading role in the last few years in the study of the role of octupole deformations in nuclei. He has resolved this apparent dipole anomaly in the course of this work.

Leander's first step was to map out the size of the octupole deformation in heavy nuclei. Recently amassed evidence indicates that mean-field calculations (see preceding) provide quantitatively accurate pictures of the classical shapes of nuclei. The classical shape includes all those nuclear effects occurring as all the nucleons move coherently—rotate in the same direction or vibrate collectively. At the same time, however, the nucleons retain an individual identity and sometimes move independently in a way that influences the collective behavior. These "shell effects" cannot be described by a classical picture; they are quantum mechanical in origin. The proper treatment of these quantum-mechanical shell effects was developed by the famous Russian nuclear theorist V. I. Strutinsky. By proper treatment of Strutinsky shell effects, we can now understand asymmetric fission. Leander and co-workers have used these same Strutinsky procedures to study the dipole anomaly. The major ingredients are (1) calculation of the "classical" octupole shapes and (2) the development of a theory to calculate the effects of the quantum-mechanical shell effects on dipole transitions. When these two calculations are combined, the model is able to account for the dipole anomaly. The anomaly arose as a result of an interference effect between the classical mean-field behavior and the quantum-mechanical shell effects. In some cases, the classical and quantum effects were added together, and in other cases, the two contributions cancelled each other. In all known cases, when weak transitions are observed, a cancellation results, and in cases of enhanced transitions, the two contributions add together. The study of octupole effects has also been extended to phenomena involving odd-mass nuclei and nuclei at very high rotational frequencies or angular momenta. The work has greatly extended our knowledge of exotic deformations in nuclei and has increased our understanding of the macroscopic structure of nuclear motion.

This brief article discusses only a few of the topics under investigation within the Theory Group. We are also looking for effects stemming from relativity in nuclear physics, trying to understand how effectively one nucleus can stop another nucleus when they collide at velocities very close to the speed of light, and studying the structure of nuclei at high temperatures. These topics should remain at the forefront of nuclear physics over the next five to ten years. Our theoretical research remains coupled closely to and should influence the evolution of the experimental program in the Physics Division. ornl

McGrory (second from right) and his fellow theorists chuckle at a box of detergent with the same name as a nuclear particle proposed by several ORNL theorists.

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Macroscopic Nuclear Physics

By FRANK PLASIL

Atomic nuclei are fascinating objects of investigation. Aside from the many practical reasons for our interest in their properties, they present unique challenges to nuclear physicists. One of the reasons for the uniqueness of atomic nuclei is that their size and makeup make them behave, at times, like classical objects and, at other times, like quantum mechanical ones.

Consider a uranium nucleus consisting of 92 protons and 146 neutrons—238 nucleons in all. It can exist essentially indefinitely and is found in nature. Now, add a neutron to it. This nucleus, ^{239}U, is radioactive and has a half-life of 23.5 min. This effect is clearly not a consequence of the bulk of the system (239 vs 238 nucleons) but rather of the special combination of the numbers of neutrons and protons. However, physicists are also greatly interested in the nature of nuclear matter and in the little-known "bulk," or "gross," properties of nuclei. These properties include, for example, nuclear compressibility, the ability of nuclei to dissipate energy (friction), as well as their ability to withstand high temperatures (excitation energy) and high amounts of rotational energy (angular momentum). Thus, there are two broad categories of nuclear studies: microscopic, emphasizing properties that depend sensitively on the exact number of neutrons and protons in the nucleus, and macroscopic, emphasizing those properties of nuclei that do not depend on their precise makeup. This second category of nuclear studies is the subject of this article.

Collisions between nuclei, which occur with the help of accelerators, are one of the primary means by which macroscopic nuclear properties can be investigated. One of the best places in the world to undertake such studies is the

ORNL physicists who study nuclear reactions have demonstrated that any nucleus can fission if bombarded with heavy ions having sufficient energy, that a new model more accurately predicts fission barriers of all rotating nuclei, and that light nuclei can orbit around each other during collisions before going their separate ways. They also have designed and built two calorimeters for use in an international experiment at CERN aimed at creating a new state of nuclear matter—the quark-gluon plasma.

accelerator complex of the Holifield Heavy-Ion Research Facility (HHIRF) of the Physics Division at Oak Ridge National Laboratory. The only purpose of HHIRF is to provide a wide variety of beams of energetic (up to 25 MeV per nucleon) nuclei, or heavy ions, for basic nuclear research. A large fraction of the work at HHIRF, somewhere between one-third and one-half, can be considered to be macroscopic in nature. Considering the scale of the research effort (about 20 ORNL research staff members are engaged full-time in HHIRF research, publishing between 40 and 50 papers per year in journals and conference proceedings), it is not possible to cover the work adequately in the limited space available here. Instead, I have selected an example of recently completed work, one of work in progress, and one out of our plans for the future.

The completed work deals with heavy-ion-induced fission and has been at the center of my research interests since my graduate student days. The ongoing work is the research of Dan Shapira and his collaborators, who are conducting a fascinating study of nuclei that orbit around each other as they collide. Finally, a glimpse into the future is provided by our preparations for a collaborative experiment to be carried out at CERN (the European Laboratory for Particle Physics), at energies nearly 10,000 times as high as those achievable at our own HHIRF. The ORNL *Review* also has previously covered the intriguing hunt for pions emitted at energies below the threshold (see the account by Glenn Young in the No. 4, 1985 issue).

Fission? Any Nucleus Can!

When we think of fission, we think of the heaviest nuclei, such as uranium. When such nuclei split into two lighter nuclei (e.g., silver and rhodium), they release some neutrons and considerable energy. But do silver nuclei, or even lighter nuclei, also fission? These questions are answered in the latest chapter of the heavy-ion-induced-fission story, which has recently been concluded at ORNL. The earliest chapter in this story, however, goes back about 20 years.

Nucleons inside a nucleus are held together by the short-range nuclear force. The constituent protons, however, repel each other by the Coulomb repulsion between like charges. Although the nature of the nuclear force is very complex, for all except the very lightest nuclei, it can be approximated, in the average macroscopic sense, by a surface tension. This concept forms the basis of the liquid-drop model, in which nuclei are represented by uniformly charged drops having a surface tension, the cohesive nature of which wins out over the disruptive Coulomb force. The liquid-drop model was first worked out in detail by Niels Bohr in 1936 and was later used to explain the fission process (discovered in 1939). In this model, it is possible to calculate not only stable, spherical ground states of nuclei, but also highly deformed shapes of unstable equilibrium, known as saddle-point shapes. A nucleus at the saddle point, if given a slight push in one direction, will wind up back in its ground state. If pushed slightly in the opposite direction, it will fission. The difference in energy between the saddle and the ground state is the fission barrier. The saddle-point shapes (see Fig. 1) of the heaviest nuclei look like stubby cigars and of the lightest nuclei, like hourglasses.

If we add another disruptive force to the nucleus—the centrifugal force (expressed in terms of rotational energy)—the rotating-liquid-drop model now has two disruptive energies (the Coulomb energy and the rotational energy) in equilibrium with the cohesive surface energy. The opportunity to work on this theoretical problem was presented to me by my mentor, W. J. Swiatecki of the Lawrence Berkeley Laboratory (LBL), while I was a student at the University of California at Berkeley. It quickly became apparent to us that any nucleus will become unstable enough to fission if given enough disruptive rotational energy and that such rotational energies are easily achievable with modern heavy-ion accelerators. This instability with regard to fission places an absolute limit on the amount of rotational energy a nucleus can support and has widespread consequences for heavy-ion-induced reactions.

Several years later, after I came to ORNL in the early 1970s and after the calculations had been completed, I found an opportunity to chase down some of the specific predictions of the rotating-liquid-drop model. First, we wanted to see if it is indeed possible to induce fission in relatively light nuclei,

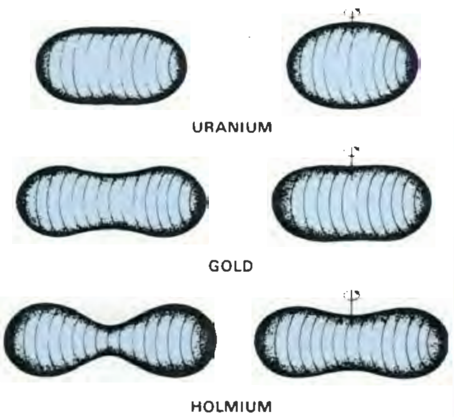


Fig. 1. Examples of saddle-point shapes of nuclei calculated with the rotating-liquid-drop model. The saddle point is a point of unstable equilibrium from which a nucleus may proceed by either fissioning or returning to its ground state. The shapes on the left side correspond to nonrotating nuclei. The rotating nuclei on the right side are shown for rotational energies that are close to the upper limit for each particular nucleus. For even greater rotational energies, no saddle-point shapes exist.

such as silver. Second, we wanted to see if the rotating-liquid-drop theory was valid in a quantitative sense.

To accomplish our first goal, Bob Ferguson, Frances (Tony) Pleasonton, and I bombarded a silver target with the newly available neon projectiles from the Oak Ridge Isochronous Cyclotron (ORIC). It was expected that after a neon nucleus collides with a silver nucleus, the two nuclei coalesce to form a rotating, excited, compound nucleus of lanthanum. If this compound nucleus is endowed with sufficient rotational energy, it may be unstable enough to fission. Our first measurements were confusing, to say the least. We did not know about all the different reaction products that had energies similar to those of the fission fragments and that overshadowed the small fission yield for which we were looking. The effect that came to the rescue was that fission fragments are always produced in pairs and that, in the moving frame of the system, these fragments always have equal—and opposite—momenta. Thus, by measuring coincident pairs, we found the needle in the haystack—neon-induced fission of silver.

Following our measurements, interest in heavy-ion-induced fission of relatively light systems (mass range from $A \simeq 100$ to $\simeq 150$) had picked up, and by the time we were ready to test the quantitative aspects of the liquid-drop theory, several other groups were involved in similar studies. One of the strongest efforts was that of Marshall Blann and his co-workers at the University of Rochester. Marshall and I shared the common interest of putting our studies on a more quantitative basis. But, before we could proceed, we had to take an additional theoretical step—incorporate the rotating-liquid-drop fission barriers into the appropriate nuclear reaction theory.

As previously mentioned, the fission barrier is a sensitive function of the rotational energy. However, the amount of rotational energy imparted to the compound nucleus depends on the impact parameter, which is a measure of the off-center aspect of the collision. Obviously, no rotational energy (angular momentum) is involved in a head-on collision. The fission barrier, and hence the stability against fission, thus depends on the impact parameter. In any given bombardment, many impact parameters are involved, and as a result, some of the compound nuclei formed are expected to fission, whereas others will lose their excitation energy by "evaporating" nucleons, resulting in so-called evaporation residues, or fusion products.

This competition between fission, on the one hand, and deexcitation by particle emission, on the other, had to be calculated as a function of the rotational energies (impact parameters) involved in the nuclear reactions of interest. To make these calculations, Blann and I developed a computer code called ALICE, which, until its replacement by more accurate approaches, was widely used by the heavy-ion physics community.

At this point, the stage was set for a quantitative test of the rotating-liquid-drop model. The investigations were pursued independently by Blann and his group and by us. Blann published his results first. He concluded that his data could best be described in terms of fission barriers that were much lower (in one case 50% lower) than those given by the liquid-drop model! To us, something appeared to be seriously wrong with the theory. In due course, we confirmed Blann's findings that the fission barriers are lower than those predicted by the rotating-liquid-drop model, although the discrepancy between our data and the theory appeared to be much smaller than that of Blann. There followed a period during which we tried to nail down the exact magnitude of this discrepancy. This seemed important at the time, and often led to strained exchanges between us and our old friend and colleague Blann.

The final resolution of the dilemma came about almost accidentally, as a result of one of those scientific exchanges that often turn out to be much more valuable than could be foreseen. In 1982 Arnie Sierk of Los Alamos National Laboratory came to ORNL to spend a year on such an informal exchange. He is an associate of J. R. Nix, who, like me, is a former student of Swiatecki. The rotating-liquid-drop model, including its limitations and approximations, was very familiar to Sierk. We discussed the status of our experiments with him and pointed out that heavy-ion-induced fission measurements indicate that fission barriers are, on the average, 20% lower than those of the rotating-liquid-drop model. This result came as no surprise to Sierk, who has worked extensively on nuclear masses and who was aware of the pitfalls of the oversimplified liquid-drop model. His point was that, although it may be reasonable to consider a balance between the repulsive Coulomb and rotational forces, on the one hand, and a cohesive nuclear force, on the other, it is too simple to consider nuclei to be uniformly charged objects having sharp surfaces. The nuclear surface is diffuse (i.e., the density of the nucleus decreases gradually at its surface), and the effects of the finite (short) range of the nuclear force should be considered. Sierk agreed to incorporate these important effects into a new version of the liquid-drop model, which we called the "rotating-finite-range model."

The results of this new approach were very gratifying. Without adjusting any parameters, the consistency between the data and the theory was immediately apparent. If such agreement between theory and experiment were to hold up, physicists would have a reliable means to predict fission barriers for all nuclei at all rotational energies, as well as a tool with which to predict the course of many heavy-ion reactions and an indication of the absolute stability limits of rotating nuclei. Following Sierk's calculations, we studied many systems with our colleagues at Los Alamos National Laboratory, in experiments carried out at ORNL and Brookhaven National Laboratory (BNL). An example of the results [the fission of the erbium compound nucleus (^{158}Er) formed in four different reactions] is shown in Fig. 2. The rotating-finite-range model stood up very well, both under our tests and those of other groups, and is now replacing the rotating-liquid-drop model in most applications.

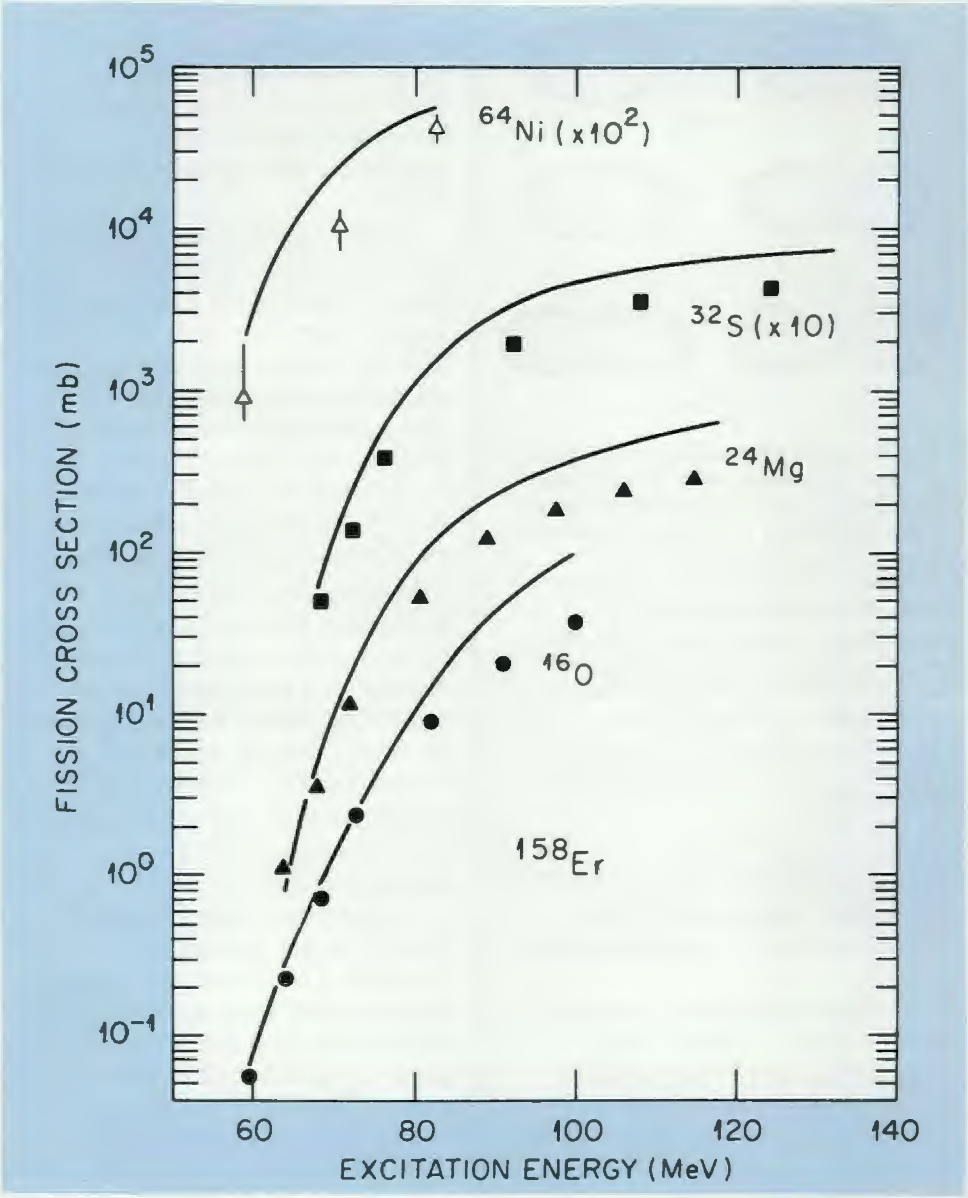


Fig. 2. Fission excitation functions (cross section vs excitation energy plots) for a number of different reactions leading to the same fissioning compound nucleus ^{158}Er. The different projectiles, ranging from oxygen to nickel, are indicated next to the excitation functions. The solid curves are calculated using the rotating-finite-range model. No parameters were adjusted in the calculations. The data were obtained by an ORNL–Los Alamos National Laboratory collaboration.

Nuclear Orbiting

When nuclei collide with each other, the range of reactions that take place is very broad. The types of reactions can be characterized, roughly, by the impact parameter. At large impact parameters, the nuclei may just be deflected in each other's Coulomb field, perhaps exciting each other in the process (Coulomb excitation). They may not lose any energy (elastic scattering), or they may lose a little energy (inelastic scattering). If the target and the projectile exchange one or two protons and/or neutrons, physicists observe nuclear-transfer reactions (quasi-elastic scattering). As the impact parameter decreases, the collisions become harder. The amount of energy lost in the collision (damping) and the number of nucleons transferred back and forth between target and projectile increase. These reactions are called deeply inelastic or strongly damped collisions. Finally, for the smallest impact parameters, fusion may take place, leading to the compound nuclei previously discussed in conjunction with heavy-ion-induced fission. In the region of impact parameters appropriate to both fusion and to deeply inelastic collisions, conditions sometimes occur to make "nuclear orbiting" possible.

The idea of nuclear orbiting was first postulated by Janusz Wilczynski of the Institute of Nuclear Research in Warsaw, Poland, thirteen years ago. He used it to explain the observation that, in deeply inelastic collisions, at certain angles, two groups of reaction products result. One group involves a much higher degree of energy damping than the other. Because the degree of energy damping depends on the reaction time, Wilczynski conjectured that the events having a small energy loss involve higher impact parameters and a direct deflection to the observed angle, whereas events having the larger energy loss occur at somewhat smaller impact parameters. He surmised that these latter events are the result of projectile nuclei that start out on one side of a target nucleus, clutch or stick to it long enough to swing to the other side of it, and then reseparate, having lost considerably more kinetic energy in the process. It is obvious that, for the clutching conditions to occur for a significant length of time, the three relevant forces (the nuclear cohesive force and the Coulomb and centrifugal repulsive forces) have to be, once again, nearly balanced.

Dan Shapira and his colleagues in the Physics Division did not set out to investigate Wilczynski's postulate when they started their studies in 1979. Over the years, however, the group has made extensive contributions to the study of nuclear orbiting, especially in light nuclei, and has placed orbiting into its proper context in the hierarchy of nuclear reactions. Shapira's original motivation was to understand puzzling features of elastic scattering—reactions between nuclei that resemble the deflections of colliding billiard balls and involve essentially no energy loss. As in the case of my fission studies, when Shapira came to ORNL from Yale University, he already had this problem in mind.

When relatively light nuclei such as oxygen and silicon interact with each other, the elastic yield is enhanced beyond expected values at backward angles, and this enhancement is accompanied by fluctuations. In 1979, when the ORNL studies were initiated by Shapira, many competing explanations were offered for these phenomena: Regge poles, resonances, parity-dependent potentials, diffraction, particle exchange, etc. Orbiting, thought to apply only to the deeply inelastic scattering of much heavier nuclei, was a long-shot contender. The ORNL team set out to investigate these questions: Is this backward enhancement a general phenomenon? Does it apply to inelastic (harder) collisions?

In 1979, Shapira, Jim Ford, Jorge Gomez del Campo, Bob Stokstad, and Los Alamos colleague Ralph DeVries set out to bombard a carbon target with neon projectiles. Their findings set the stage for the next seven years of research. They found that (1) the collisions give a large yield of targetlike products in the backward direction, (2) these reactions involve full energy damping (maximum loss of incoming kinetic energy), (3) this damping does not depend on the angle of observation, and (4) the yield is isotropic in the center-of-mass reference frame, again indicating that the angle of observation is not an important variable. Only two explanations can account for all of the observed results. The first is the familiar formation of a compound nucleus followed by its statistical decay. The second is orbiting, whereby two nuclei clutch and form a dinuclear complex, the complex rotates (one or more revolutions) while the identities of the original nuclei are maintained, and, finally, the two nuclei reseparate. Although both alternatives were discussed by Shapira and his colleagues in their 1979 article in the prestigious journal *Physical Review Letters*, the authors favored the orbiting hypothesis based, to a large extent, on quantitative theoretical arguments. Statistical fission was ruled out because the observed cross section was much too large to be consistent with the expectations based on the type of calculations described in my earlier discussion of the fission work.

In the years that followed, several other systems were studied by Shapira and his co-workers, as well as by other groups. A consistent picture of orbiting in light systems began to emerge. The occurrence of orbiting, under appropriate circumstances, indicates that special mechanisms are at work to maintain the dinuclear complex at a point of unstable equilibrium—one in which the cohesive nuclear force is very nearly balanced by the repulsive Coulomb and centrifugal forces. The required conditions change with the circumstances. For example, nuclear quasi molecules are formed when light nuclei interact with each other near the Coulomb barrier. In such reactions, plots of cross section vs scattering angle show the peaks characteristic of resonant behavior attributed to their vibrational and rotational properties. At the higher energies encountered in deeply inelastic collisions, the required conditions are reached by means of the conversion of a very large fraction of the kinetic energy associated with the approach of the colliding nuclei into the internal energy of excitation (heat) of the reaction products and by the analogous conversion of a portion of the incident orbital angular momentum to internal angular momentum, or spin. The relatively long-lived clutching, or sticking, condition studied by the Oak Ridge group is, thus, one of an important class of reactions. A pictorial representation of the orbiting of light nuclei is shown in Fig. 3.

One key finding of Shapira and his colleagues involves the question of the dependence of the kinetic energy of the orbiting products on the bombarding energy. At first, a linear dependence was found. Since the initial kinetic energy is fully damped (i.e., converted into the excitation energy of the fragments), the observed final kinetic energy of the separating fragments is made up of only two components: the potential energy (Coulomb repulsion) and the rotational energy stored in the rotating dinuclear complex. Because the Coulomb repulsion does not depend on the bombarding energy, only the rotational energy is responsible for the linear dependence.

With the further increase of bombarding energy, a curious observation was made: beyond a certain point, the final kinetic energy increased no further. A saturation plateau was reached. The data depicting this situation are shown in Fig. 4 for carbon and silicon nuclei and for oxygen and magnesium nuclei (the $^{12}C + ^{28}Si$ and $^{16}O + ^{24}Mg$ systems). Because the increase in observed kinetic energy has been shown to be linked directly to angular momentum, it became clear that the observed saturation implies that, at some bombarding energy, a value of orbital angular momentum is reached, beyond which the formation of a dinuclear complex is not allowed as a result of centrifugal repulsion. The next step was to estimate this value of limiting angular momentum with reference to various theoretical and semi-empirical nuclear potentials. This work led to the key finding that the limiting value of angular momentum is the same within the accuracy of the measurements as that which limits fusion.

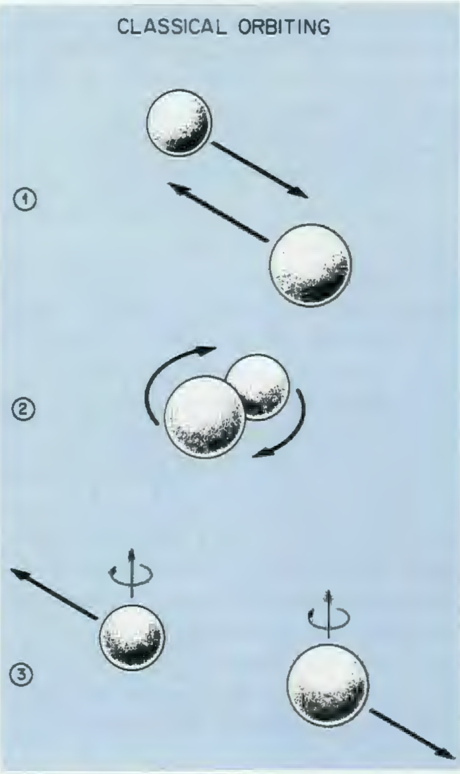


Fig. 3. A pictorial representation of nuclear orbiting. The target and projectile nuclei are shown in part 1. In the center-of-mass coordinate system, both target and projectile are in motion, as indicated by the arrows. In part 2 the two nuclei are shown to clutch and rotate together. Their separate identities are essentially maintained. Part 3 shows the reseparation that may occur after one or more rotations. Note the intrinsic spin of the reseparating nuclei.

Recently, Shapira and his co-workers, including B. A. Harmon from the University of Virginia, B. Shivakumar from Yale University, and one of the leading authorities on fusion reactions, M. Beckerman, who came to ORNL from the Massachusetts Institute of Technology and is now a guest of the HHIRF Joint Institute, have confirmed the above finding by making careful measurements of fusion products from the same reacting systems for which the investigations on orbiting were carried out. The entrance channel limiting angular momenta governing both fusion and orbiting are indeed the same. Thus, orbiting, itself a form of nuclear capture, can be considered to be a doorway to fusion. At, or below, the limiting angular momentum, the colliding nuclei stick to form a dinuclear complex which, after a few rotations, proceeds either to reseparate into the two constituent nuclei or to amalgamate into a compound nucleus.

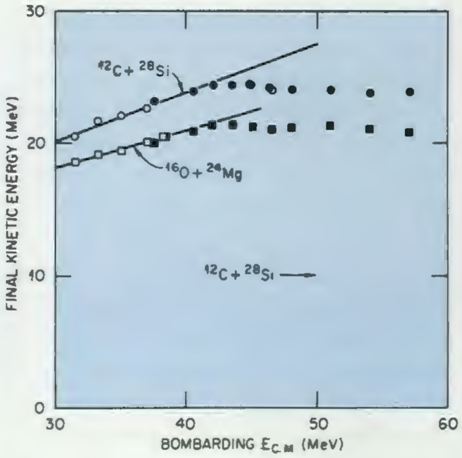


Fig. 4. Variation of the final kinetic energies of reaction products (resulting from orbiting) as a function of the bombarding energy for the two systems shown. Note the initial linear dependence (indicated by the straight lines) followed by a saturation plateau (leveling-off) in both cases.

For the crowning touch, Shapira and Shivakumar collaborated with theorist S. Ayik of Tennessee Technological University at Cookeville. Together they have developed a theory that describes the formation of a dinuclear complex in collisions between light nuclei and its subsequent decay, resulting in fusion or reseparation. Their approach has two underlying assumptions: (1) the dinuclear complex, once formed, evolves primarily by means of an exchange of nucleons between the two constituent nuclei, while the shape undergoes little change, and (2) the only two possible final outcomes are fusion or reseparation. In addition, the numerical solution of the relevant equations governing the evolution processes was performed at the limit at which equilibrium has already been reached.

Using this theory, Shapira and his associates have been able to predict the probability that light nuclei colliding at specific energies will fuse or orbit and reseparate. The success of their approach thus far, in terms of a quantitative description of observed fusion and orbiting cross sections, has been both gratifying and promising. More work, however, is needed. For example, the question of the dynamic nature of the process, which starts with two clutching nuclei rotating together and ends with a single nucleus, needs to be resolved. Does the contact point between the nuclei grow into a "neck" that continues to "thicken" until only one nucleus is observed? Alternatively, is a "window" opened up between the two sticking nuclei through which nucleons pass back and forth, but preferentially in one direction, until one nucleus "sucks up" the contents of the other? The evidence favors the former conjecture, but time, and more work, will tell.

Quark-Gluon Plasma: The Meltdown of Nucleons

Future studies of nuclear reactions by ORNL physicists include an exciting project that departs from "business as usual" in several ways: the energy regime of the projectiles that we use is changing from tens of millions of electron volts (MeV) per nucleon to hundreds of billions of electron volts (GeV); the size of our research teams is increasing from about 10 individuals to as many as 50; our detectors of several grams will be replaced by detectors weighing several tons; and the preparation time required for an experiment is changing from a week or two to several years. Our field of research, which is currently central to traditional nuclear physics, will span the boundary between particle and nuclear physics. We are entering the new field of ultrarelativistic heavy-ion reactions by becoming partners in the WA-80 collaboration at the European Laboratory for Particle Physics, CERN, in Geneva, Switzerland.

Our motivation goes back to the time of early Greek philosophers, who realized that, if matter is divided into ever smaller constituents, one must, at some point, reach an indivisible, fundamental "building block" of nature. Indeed, the word atom has its roots in this philosophical concept. In our current era of modern science, the quest for the fundamental constituent of matter has been pursued relentlessly. Molecules were found to consist of atoms, atoms of nuclei and electrons, and nuclei of nucleons (protons and neutrons). Now, nucleons (recognized to be members of the baryon class, which is itself a subclassification of the hadron category—see sidebar) are believed to be made up of quarks and of gluons. (Quarks are the basic constituents of nuclear particles, and gluons are the massless particles that act as the "glue" that binds the quarks together.) Until the current stage was reached, it had always been possible to isolate the entity which was believed to be the fundamental building block. It turned out to be relatively easy to isolate single molecules, atoms, nuclei, and nucleons. Quarks, however, have never been observed in their free, unconfined form. They seem to exist only in groups of either three, as in the case of nucleons, or in pairs, as in the case of mesons.

The evidence for the existence of quarks is so overwhelming as to be incontestable. It is even known that the three quarks that make up every nucleon move about freely within the nucleon's confines. However, the energy required for a quark to break loose from this confinement appears to be infinite, and the deconfinement of quarks has never been achieved.

The branch of theoretical physics that deals with the properties of quarks and gluons is known as quantum chromodynamics (QCD), which is analogous to (but much more complicated than) the more familiar quantum electrodynamics (QED), which describes atomic systems. The prefix "chromo," meaning color, refers to the labeling of the attributes of individual quarks by colors and flavors, for lack of better adjectives. (See sidebar on page 218.) The complicated nature of QCD has made theoretical progress slow. Thus, physicists have only recently started to understand why quarks are confined.

With these new insights has come a new revelation: If the energy density of a large system of quarks and gluons can be made large enough (at sufficiently large temperatures and pressures), a phase transition may be reached, resulting in the formation of a new state of matter. In this new phase, the confinement of the quarks to pairs and triplets may be broken, and the quarks (and gluons) may be free to move throughout the region of high energy density. This ensemble of deconfined (free) quarks and gluons is referred to as the quark-gluon plasma, and it is believed that the entire universe existed in this state in the first few instants following the "Big Bang." The formation of this fascinating state, which we think can be achieved in collisions between ultrarelativistic heavy ions, and the observation of "signatures" indicating that this new state of nuclear matter has been produced, are the primary goals of the CERN experiments. (The term relativistic heavy ion refers to an energy range of about 1 GeV per nucleon where relativistic corrections start to become important. The term ultrarelativistic refers to even higher energies, in the 10 to 100 GeV per nucleon range.)

It is easy to understand our fascination and intellectual motivation. But why should we, at ORNL, engage in the difficult task of participating in research on another continent? How does all of this fit in with the national policy on fundamental research in nuclear physics? Although my personal interests in the problem outlined here go back perhaps ten years, the first time that official consideration was given to it at ORNL was in 1982–1983 by a committee of staff members of the Physics Division, which was given the charge to consider alternative future research directions in nuclear physics. The ad hoc committee consisted of Cyrus Baktash, Jim Beene, Curt Bemis, Karl Erb, Jorge Gomez del Campo, Georg Leander, I-Yang Lee, and Dan Shapira, and it was chaired by Glenn Young.

The thoughtful document that this committee produced, entitled "Future Prospects in Nuclear Physics at ORNL," includes an extensive discussion of this emerging field of research and of

The Terminology of Fundamental Particles

Subatomic particles may be divided into two broad categories: the hadrons (from the Greek adjective meaning robust or heavily built), which are subject to the strong (nuclear) force, and leptons (from the Greek word meaning small or light), which do not participate in the strong force.

Hadrons. Neutrons and protons (nucleons) are members of the hadron class. The strong force binds them together to form nuclei. In addition to these two well-known hadrons, more than 100 other hadrons have been discovered over the last three to four decades. Hadrons are divided into three subcategories: baryons, mesons, and hyperons. Baryons, derived from a word meaning "heavy," include the nucleons. Mesons, from the Greek word for "middle," refer to hadrons that are lighter than baryons but heavier than (most) leptons. Hyperons, based on a word meaning "over" or "excess," include those particles that have a mass between that of a nucleon and a deuteron. (A deuteron consists of one proton and one neutron.)

Quarks. The quark model was introduced in 1964 by Murray Gell-Mann and George Zweig as a scheme for classifying the growing number of hadrons. The acceptance of the physical reality of the quark as the fundamental "building block" of nature came about gradually, as evidence continued to accumulate.

Six basic types of quarks are known or thought to exist. They are distinguished from one another by their quantum properties, known as flavors. The quarks are called up, down, charmed, strange, top (or truth), and bottom (or beauty), or *u, d, c, s, t,* and *b*. All but the top quark have been observed experimentally; the existence of this lone quark has been only postulated, but there is little doubt that it exists.

Quarks have fractional electric charges: the *d, s,* and *b* quarks have a charge of one-third of that of an electron (i.e., $-\frac{1}{3}$), and the *u, c,* and *t* quarks have a charge of $+\frac{2}{3}$. In addition, each quark can be found in three different quantum-mechanical states, known as colors. (These are somewhat similar to electrical charge and are sometimes arbitrarily designated as red, purple, and green.) Thus, if each colored quark is counted as a separate entity, 18 quark varieties exist altogether. Finally, for each quark there is an antiquark having the same mass but opposite values of electrical charge and color.

All hadrons are made up of combinations of quarks. Baryons are made up of three quarks (e.g., the proton consists of two *u* quarks and one *d* quark, and the neutron, of one *u* quark and two *d* quarks). Mesons are made up of quark-antiquark pairs (e.g., the positive pi-meson consists of a *u* quark and a *d* antiquark).

Leptons. Leptons are fundamental particles that are not subject to the strong force. Like quarks, they are believed to be indivisible building blocks of matter. Scientists have identified six leptons: the electron, the muon, and the tau and their associated neutrinos (e.g., the electron neutrino). The electron, the muon, and the tau each have an electrical charge of -1, whereas the neutrinos are electrically neutral. Like quarks, each of the leptons has its associated antiparticle, but they lack color properties. Leptons can exist in isolated states in nature (i.e., they are not subject to confinement).

Photons and Gluons. The electromagnetic force acts between any two charged particles. It is transmitted by the massless photon, a quantum of electromagnetic radiation. Photons do not interact with each other. By analogy, the strong force that acts among quarks is transmitted by massless gluons, so-named because they can be regarded as the "glue" that binds quarks together into hadrons. Gluons carry color charge and can interact with each other. Thus, quantum chromodynamics (the study of quarks and gluons in hadrons and in nuclear systems) is vastly more complicated than the analogous quantum electrodynamics (the study of atomic systems).

the opportunities that it offers. At about the same time, the important Nuclear Science Advisory Committee (NSAC), which advises both the Department of Energy and the National Science Foundation on all matters (policy, priorities, new facilities, etc.) relating to research in nuclear physics, completed the development of a long-range plan. Key elements of this plan were (1) the recognition of the importance of research using ultrarelativistic heavy ions and (2) the high priority that was given to the production and study of the quark-gluon plasma. In fact, NSAC concluded that the next major facility to be funded by DOE should be a "collider" for ultrarelativistic heavy ions in which heavy nuclei, having energies of hundreds of billions of electron volts, would collide with each other and produce sufficiently high energy densities to form the quark-gluon plasma.

At this point it was clear that the time was ripe for us to enter the field. The way this actually came about illustrates, once again, the importance of personal connections and of past collaborations. In 1981, two research centers with significant experience with relativistic heavy ions, LBL and GSI (the Gesellschaft für Schwerionenforschung; literal translation: Company for Heavy-Ion Research), in Darmstadt, Federal Republic of Germany, joined forces to see if an existing high-energy particle accelerator could be made available for the acceleration of heavy ions. After some initial frustration, they concluded an important agreement with CERN. LBL and GSI agreed to build an oxygen-ion source and an injecting accelerator, and CERN agreed to accelerate the oxygen nuclei through their accelerator complex. Under the plan, the oxygen ions will first be accelerated in a linear accelerator, then injected into the Proton Synchrotron (PS) for further acceleration, and, finally, into the Super Proton Synchrotron (SPS), where they can achieve energies of up to 225 GeV per nucleon. CERN has also agreed to allocate two ten-day periods of precious SPS time jointly to GSI and to LBL. This time is earmarked for studies to be performed with the newly developed ultrarelativistic oxygen beams.

The first of the two heavy-ion runs was scheduled for November 1986. The second will take place in the second half of 1987, by which time sulfur or calcium ions may be available in addition to oxygen for bombarding various targets ranging from aluminum to gold. The number of collaborations has grown to five, involving more than 300 scientists from over 60 institutions located in 18 nations. How did ORNL get involved in such a huge effort?

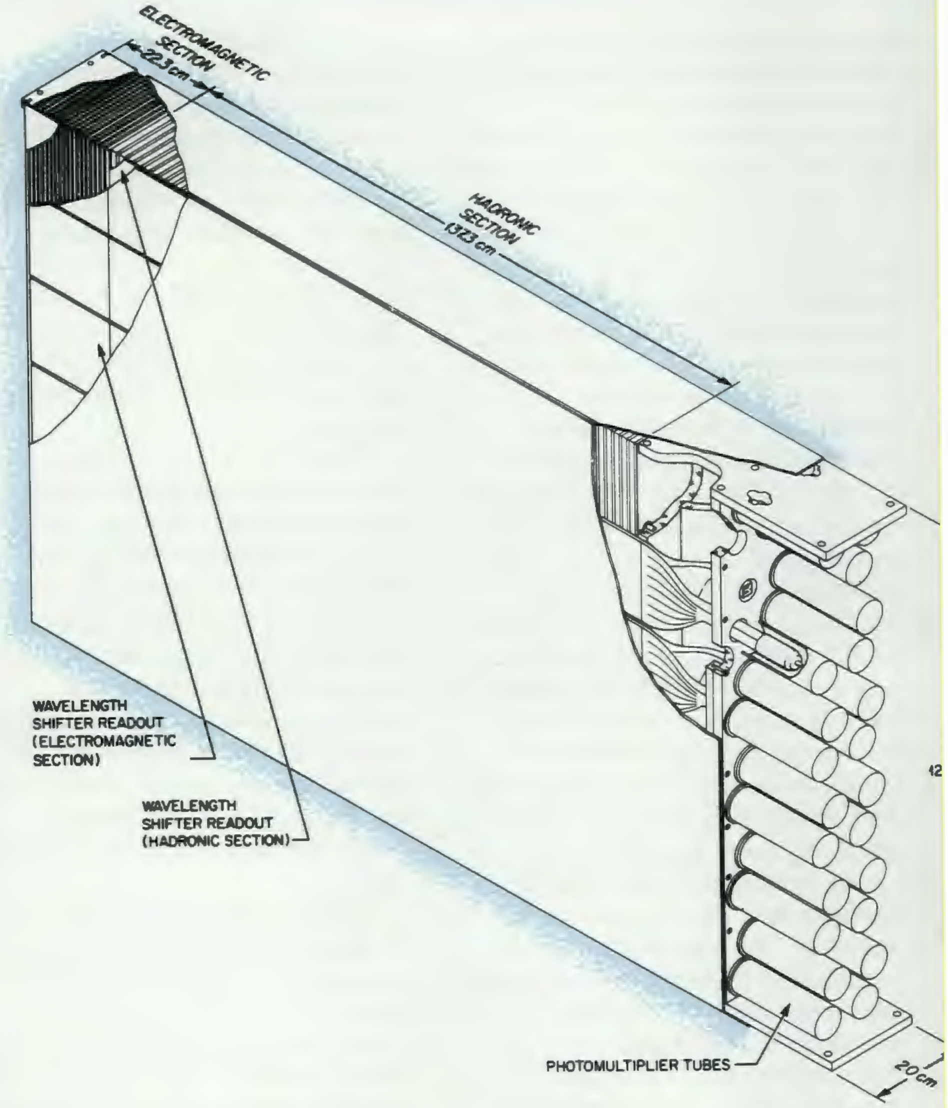
Hans Gutbrod (GSI) and Art Poskanzer (LBL) are two of the experimenters who were eager to make use of CERN's ultrarelativistic oxygen beams. Since the mid-1970s, they have been jointly providing the leadership for a group engaged in research with relativistic heavy ions at the LBL Bevalac. When it appeared that ultrarelativistic heavy ions at CERN were to become a reality, they obtained permission to move their primary experimental device, the Plastic Ball, from LBL to CERN. Such a move is difficult and complicated because the Plastic Ball consists of 655 two-element scintillators. At that time, their CERN plans were known as "the Plastic Ball collaboration."

I have known both Gutbrod and Poskanzer very well for some time and have, over the years, kept up with their professional activities. Poskanzer and I overlapped at BNL in the mid-1960s when he was a junior staff member there and I was a postdoctoral fellow. I met Gutbrod somewhat later when he was a postdoctoral fellow with Marshall Blann at the University of Rochester. In the early 1970s, Blann, Gutbrod, and I initiated a collaborative program of heavy-ion fusion measurements at the LBL SuperHILAC. With these background interactions acting as a catalyst, an agreement was reached for ORNL to join the Plastic Ball collaboration late in 1983. Since that time, the collaboration has grown as the universities of Lund (Sweden) and Münster (Germany) have become members. The collaboration has the official CERN designation of WA-80 (the 80th experiment in the SPS *W*est *A*rea). Gutbrod has become the official spokesman. It is interesting to note that, with the exception of ORNL (where other ties exist), each of the participating WA-80 institutions includes on its staff at least one alumnus of the old LBL Bevalac group.

After the major collaborating institutions were signed up, detailed planning began in earnest. I remember the excitement and exhilaration that we felt at our first collaboration meeting held at GSI in January 1984. I also remember how incredibly naîve we were (one device that we estimated to cost $50,000 ended up costing $200,000) and what a steep portion of "the learning curve" we found ourselves on. The first realization the group came to was that the Plastic Ball was suitable for detecting only one category of reaction products—those that are emitted in the backward direction. All other products will have energies that are much too large to be contained within the ball. Whole new detection systems would have to be built.

Responsibilities were quickly assigned to the various institutions.

Calorimeters from ORNL: Measurement Tools for High-Energy Physics



The measurement of energies of products from reactions performed at ORNL's Holifield Heavy-Ion Research Facility is relatively simple. The products have energies ranging from a few MeV to as high as 100 MeV. Such products can be stopped in solid materials of thicknesses from a fraction of a millimeter to a few centimeters. The energies of products resulting from reactions with ultrarelativistic heavy ions at CERN, however, will be as high as tens of GeV, and their range of propagation in matter will be several meters.

Energy measurements at low energies usually rely on collisions of the product nuclei with atoms of the detecting medium (semiconductors or scintillators), and the energy is approximately proportional either to an electrical pulse or to emitted light. At GeV energies, the stopping of nuclei proceeds via a cascade, or "shower," of increasingly lower-energy particles.

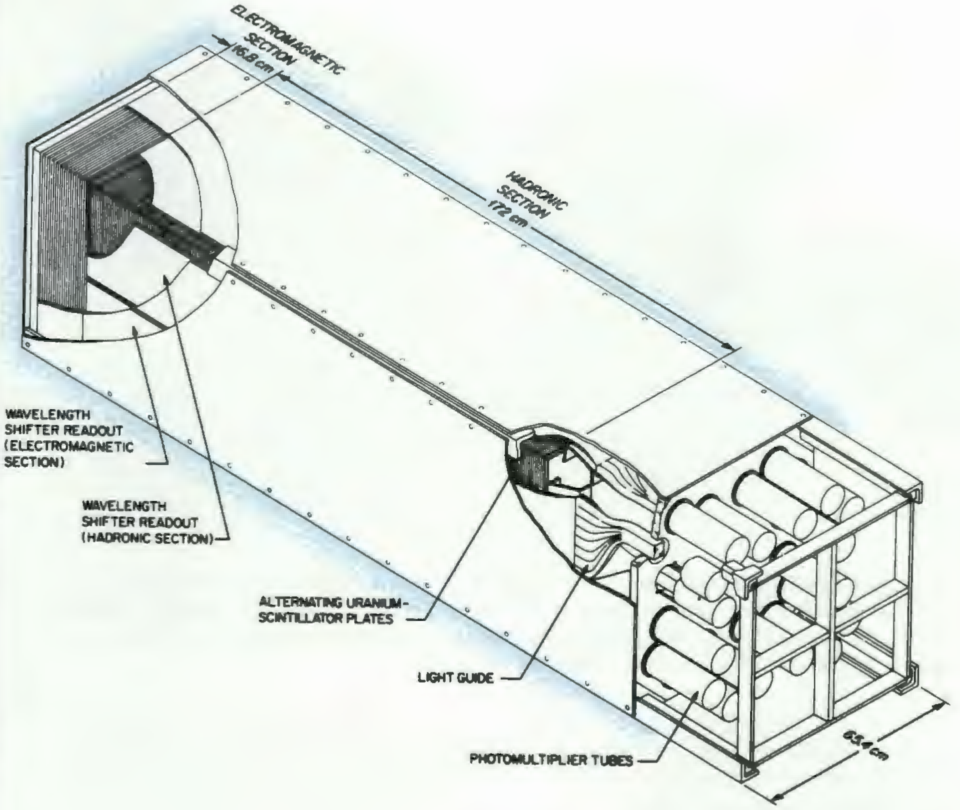
Two types of showers are produced: electromagnetic and hadronic. Electromagnetic (em) showers are produced by gamma rays, electrons, and neutral pi-mesons (which decay to pairs of gamma rays). Hadronic showers are propagated, as the name implies, by hadrons, such as charged pi-mesons, protons, and neutrons. The mechanisms of propagation and the physical characteristics of the two types of showers are very different from each other. This information is used to determine the category of the detected particle.

The mechanisms associated with em showers are pair production (in which electron-positron pairs are produced from gamma rays), bremsstrahlung (or braking) radiation, and Compton scattering. Hadronic showers, on the other hand, propagate through successive collisions between nuclei and generate broad spectra of secondary particles. The longitudinal range of propagation of a hadronic shower is much larger (about a factor of 10) than that of an em shower, and the radial containment of the em shower is much smaller than that of a hadronic shower.

A calorimeter is a detector in which the primary particles are intercepted in a large bulk of matter and in which they deposit all of their energy by means of subsequent showers. The size of the calorimeter is dictated by values of radial and longitudinal containment. Scintillation light, Cerenkov light, and ionization charge are among the practical calorimeter signals from which the energy of the primary particle may be deduced. (Heat, as implied by the term calorimeter, is actually not one of the useful signals.)

The energy resolution of calorimeters is inversely portional to the square root of the energy of the primary particle—that is, the resolution improves as the energy of the detected particle increases. The required length of the detector scales only logarithmically with the energy of the incident particle, making it possible to design practical detectors for particles having the highest energies (greater than 100 GeV).

Calorimeters can be of either the homogeneous or sampling type. Homogeneous calorimeters consist of



only one kind of material that must be active—that is, must be capable of producing the required signal such as Cerenkov light or ionization. Sampling calorimeters consist of active materials interspersed with passive ones. The signal (e.g., light) is produced by the active material (e.g., scintillator), and the bulk of the stopping is done by the passive absorber material (e.g., iron or uranium). For the containment of particles of a given energy, sampling calorimeters are more compact than homogeneous calorimeters.

ORNL has designed and built major portions of two types of sampling calorimeters for WA-80—the Wall Calorimeter and the Zero-Degree Calorimeter. Both calorimeters have a front em section, sensitive to both em and hadronic showers, and a hadronic section, which is penetrated only by hadronic showers. The Wall Calorimeter consists of lead absorber plates in the em section and stainless steel absorber plates in the hadronic section, both interleaved with plastic scintillator plates. The calorimeter is divided into 30 independent units called stacks (see drawing at left). The area covered by a stack is 1.2 × 0.2 m, and the stack is divided into six 20 cm × 20 cm segments. Each stack, which includes 150 metal and 150 plastic scintillator sheets, weighs two tons. The stacks were designed at ORNL and assembled at CERN.

The Zero-Degree Calorimeter is a depleted uranium–plastic scintillator sampling calorimeter, covering an area of 60 cm × 60 cm. It is more than 2 m long and weighs 8 tons (see drawing above). Uranium was used to obtain the best possible energy resolution, and the size was chosen to ensure essentially complete containment of particles having energies of up to 200 GeV. This calorimeter will be used as a trigger and will intercept beam particles after they have passed through the target. To determine whether an interaction has taken place in the target, the calorimeter must be capable of distinguishing between projectiles that consist of either 16 nucleons (oxygen-16) or 15 nucleons (oxygen-16 minus either a proton or a neutron). The Zero-Degree Calorimeter was designed and built at ORNL and shipped to CERN in June 1986.

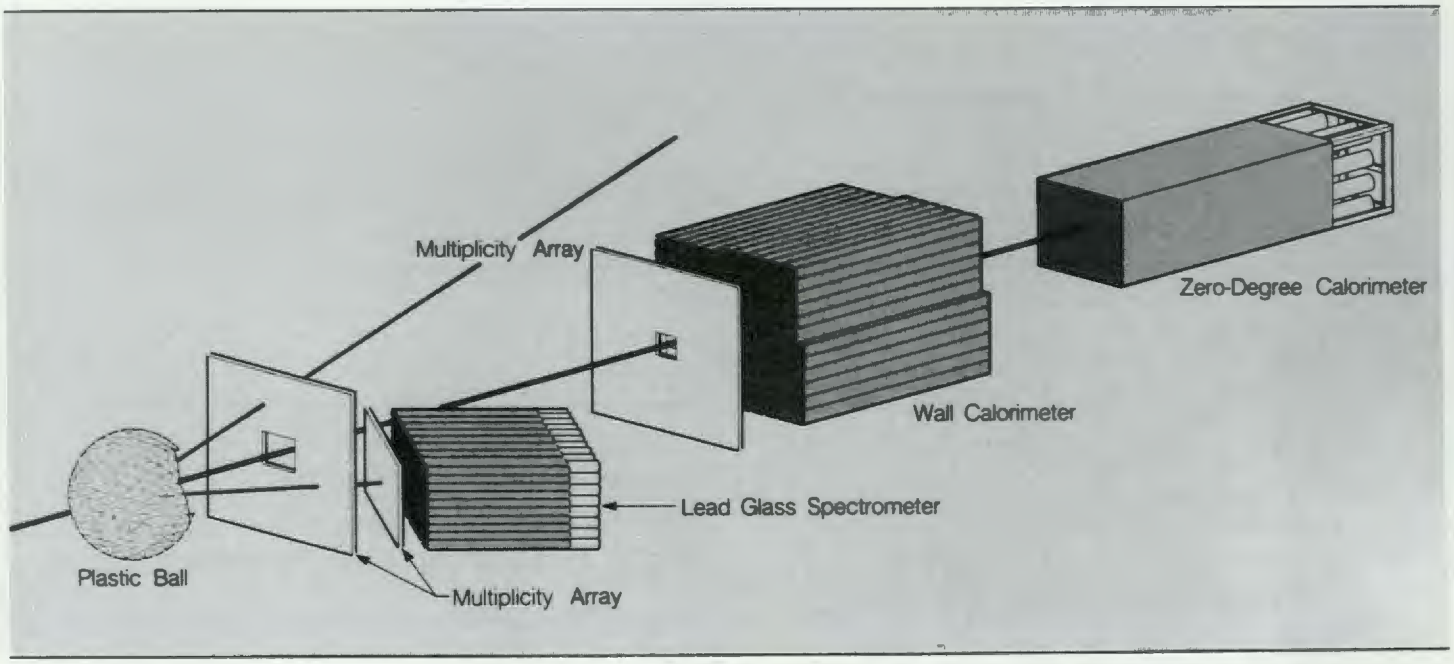


Fig. 5. Experimental arrangement of the CERN WA-80 experiment. The individual detector systems are described in the text. The target (either aluminum, copper, or gold) is located inside the Plastic Ball. The overall length from the entrance to the Plastic Ball to the rear of the Zero-Degree Calorimeter is about 15 m.

The Plastic Ball remained the responsibility of GSI and LBL. It was decided that the major new detector was to be the Wall Calorimeter, which was to consist of 25 two-ton stacks of lead, stainless steel, and plastic (see sidebar on page 220). ORNL was assigned the primary responsibility for this device, and help was promised (and later delivered) by LBL and Lund University. ORNL was also assigned the responsibility for the design and construction of an 8-ton uranium-plastic scintillator trigger calorimeter (see sidebar). In addition to the Plastic Ball and the calorimeters, two other systems were to be built: SAPHIR, under the leadership of the University of Münster, and various multiplicity arrays, under GSI's direction.

Each detector system has a unique purpose and specialized capabilities. The Plastic Ball is capable of identifying moderately energetic, light, charged particles (e.g., protons, deuterons, and helium nuclei, or alpha particles) and measuring their energies. The Wall Calorimeter, which is divided into 150 separate 20 cm × 20 cm segments, measures the total energy of the reaction products emitted in the forward direction—up to energies as high as 50 GeV. The energy is deduced from the light produced in the scintillator, not from the heat generated, as the name calorimeter might imply. The calorimeter can also provide some information on the type of product that was detected (hadronic or electromagnetic, see sidebar on page 218).

SAPHIR is an array of 1350 lead-glass modules designed to detect intrinsic gamma rays and to pick them out from a large gamma background produced by the decay of neutral pi-mesons. The spectrum of intrinsic gamma rays may provide one of the most direct indications of whether the quark-gluon plasma was formed. Finally, the multiplicity array indicates whether a charged particle passed through it and localizes the particle to a small area of space (fine granularity). To accomplish this task, 25,000 separate readout pads are needed. From this set of detection devices, we hope to reconstruct the nature of each event. (The layout of the experiment, indicating the various detector systems, is shown in Fig. 5.)

The ORNL WA-80 team consists of the following Physics Division staff members: Terry Awes, Cyrus Baktash, Jim Beene, Dick Cumby, Bob Ferguson, Ed Gross, Jim Johnson, I-Yang Lee, Felix Obenshain, Søren Sørensen, Glenn Young, and me. Very valuable design help was provided by Tony Gabriel of the Engineering Physics and Mathematics Division, who is a leading world authority on cascade propagation and calorimeter design. He performed the calculations that enabled us to optimize the calorimeter composition and configuration. The effort of Jim Johnson also merits special mention. He has been in charge of the mechanical design and in-house fabrication of all calorimeter components—a very demanding job that he has performed very well.

What do we expect to happen when an oxygen nucleus, traveling with a total energy of 3200 GeV (200 GeV/nucleon), impinges centrally on a stationary heavy nucleus such as gold? Although 213 nucleons are involved in this collision, as many as 1000 particles (mostly pi-mesons) will be produced as a result of "hadronization"—the conversion of energy into matter, as postulated by Einstein's famous equation, $E = mc^2$. How will our detectors respond when confronted with multiplicities as high as 1000? These questions are being addressed by extensive simulation calculations, which are performed in two stages. First, our colleagues at Lund University calculate a large number of collisions and provide us, for each collision, with the number and types of particles produced, as well as with their energies and their distribution in space. At ORNL, our colleague and University of Tennessee professor, Søren Sørensen, inserts the Lund results into his computer program that predicts the response of our Wall Calorimeter. Many practical questions are addressed by such simulations. What should be the gain settings of the various segments of the Wall Calorimeter? How big should the hole-in-the-wall be to allow the beam to pass through? How can we hope to disentangle events in which several particles hit the same calorimeter segment? (An example of the type of result obtained by Søren is shown in Fig. 6.)

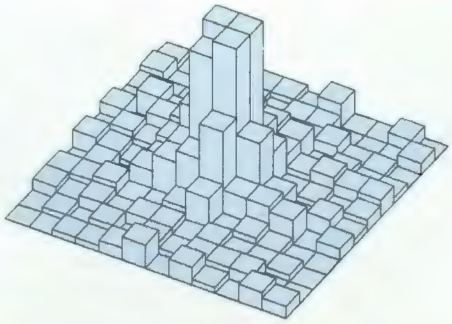


Fig. 6. Results of simulation calculations depicting the number of particles incident on the Wall Calorimeter in one typical central-collision event. The total yield of particles and their direction of emission were calculated by means of the LUND simulation model. Each square indicates one of the independent 20 cm by 20 cm segments of the Wall Calorimeter. The height of the rectangular solid built upon any particular square is proportional to the number of particles incident on that calorimeter segment. Note that the highest density of incident particles is located near the center of the Wall Calorimeter, in the vicinity of the center hole (not shown) through which the beam passes.

As of this writing, almost three years have passed since the first collaboration meeting. It has been a period of intensive activity, which is just reaching its peak. We have been fortunate to have had the help, support, and understanding of ORNL management at all levels, as well as that of our colleagues in the Physics Division. In this way, for example, we were able to come up with more than half of the $800,000 needed to build the calorimeters. The stacks of the Wall Calorimeter (30 were finally built) were assembled at CERN under the able leadership of Hans-Ake Gustafsson of Lund University (an LBL Plastic Ball group alumnus). It did not turn out to be practical to assemble the 30 units of the 60-ton device here at ORNL and then to ship them to CERN. This was, however, what we did with the 8-ton uranium trigger calorimeter. An official milestone was achieved on schedule when the assembly of the calorimeter was completed at ORNL in April 1986. All experimental devices are now installed at CERN, and we have started to take test data. Various ORNL staff members take turns in being assigned at CERN. (As of this writing, Terry Awes, Dick Cumby, Bob Ferguson, Felix Obenshain, and Glenn Young are in Geneva. Oxygen ions have been accelerated through all accelerators and have been extracted.) The great event—two weeks of prime oxygen-beam time—was to have occurred in November 1986.

It is not known if the quark-gluon plasma will be formed in this round of experiments. The energy at our disposal and the size of the projectile may not be sufficient. However, much can be learned in this virgin territory even if the plasma formation is not achieved. In any case, we at ORNL are already looking toward the future. For example, in 1987, an injector for heavier ions will become available at CERN. But the most exciting long-term prospect for us is the possible funding of the Relativistic Heavy-Ion Collider (RHIC) proposed for Brookhaven. The energy densities that can be achieved when two heavy nuclei collide head-on are an order of magnitude higher than those that are reached when the target nucleus is stationary. It is our hope that RHIC will be funded and that ORNL physicists will play a major role in exploring the research field that will be opened up. Life will certainly be easier for us at ORNL if we can help field big experiments so much closer to home. ornl

ORNL's nuclear-structure program has shifted techniques—from gentle excitation of nuclei by bombardment with light ions to highly stressing nuclei by bombardment with energetic heavy ions from the Holifield Heavy-Ion Research Facility. By giving a nucleus high-excitation energy and high spin, ORNL physicists stress it until it assumes characteristics very different from those it had in its quiescent state. Current research in the Physics Division addresses the structure of the nucleus at excitation energies of 10 to 100 MeV and with spins of 10 to 50 units of angular momentum. Among the nuclear-structure findings at ORNL that have stimulated research throughout the world has been the discovery of the giant quadrupole resonance.

Nuclear Structure of the Stressed Nucleus

By FRED BERTRAND, DAN HOREN, AND NOAH JOHNSON

The study of nuclear physics involves two broad aspects: the investigation of the structure of the nucleus and the investigation of the interaction between nuclei (reaction mechanism studies). Because both these aspects depend on the interaction between the constituents of nuclei—the nucleons (neutrons and protons)—they are intimately related. Thus, a comprehensive program of nuclear physics research must study both interrelated aspects. In a broad sense, the nuclear physics basic research program in the Physics Division at Oak Ridge National Laboratory is organized to study nuclear structure and reaction mechanisms. Studies of nuclear reactions and studies of nuclear theory carried out by ORNL scientists are described in other articles in this issue of the *Review*. Because of space limitations, we discuss only two of ORNL's major ongoing programs pertaining to nuclear structure.

In the simplest terms, the problem of nuclear structure is one of placing the neutrons and protons of a nucleus in ordered levels by means of an energy that we usually call excitation energy. These ordered levels are classified with the aid of theoretical quantum mechanics in terms of (1) an orbital angular momentum confined to integer values (this arises from a motion similar to the rotation of a ball on the end of a string), (2) an intrinsic angular momentum (spin, or rotation about an axis through the ball), and (3) a total angular momentum (given by the vector sum of the orbital and intrinsic angular momenta).

More than 1900 nuclei have been identified out of the 7000 predicted nuclei. The ordering, or

Fred E. Bertrand is the head of the Nuclear Structure Section of ORNL's Physics Division. When he came to the Laboratory in March 1970, he was no stranger. In pursuit of his Ph.D. degree in physics, which he obtained from Louisiana State University in 1968, he had conducted his doctoral thesis research at ORNL under an Oak Ridge Associated Universities fellowship. His mentor was Bob Peelle in the Neutron Physics (now Engineering Physics and Mathematics) Division. A native of New Orleans, Bertrand has long been interested in nuclear-structure physics and has devoted most of his research career to the experimental study of nuclear giant resonances and direct nuclear reactions. He has performed his research on accelerator facilities at Vancouver, Canada; Los Alamos; Indiana University; Groningen, The Netherlands; and Caen, France. He is a Fellow of the American Physical Society (APS).

Dan Horen, a senior research staff member in the Reaction Spectroscopy Group of the Physics Division, came to ORNL in 1969. He has a Ph.D. degree in physics from Stanford University. His studies of nuclear structure at various accelerators have focused on the nuclear continuum, including giant resonances. He is a Fellow of APS.

Noah Johnson is leader of the Nuclear Structure Group in the Physics Division. In 1956, when he received his Ph.D. degree from Florida State University, he came to ORNL to work in the Chemistry Division as a nuclear chemist. In 1980 he moved to the Physics Division. As a Guggenheim Scholar and a Fulbright Fellow, he spent 1962–1963 at Niels Bohr Institute in Copenhagen. He has coauthored a book and edited another. In the past several years of his career in nuclear structure research, he has focused on nuclei excited to high energy and high angular momentum. Johnson is an APS Fellow.

Here, Bertrand (right), Dan Horen (center), and Noah Johnson view an illuminated map of the Oak Ridge Isochronous Cyclotron beam lines and magnets (curved symbols).

structure, of the nuclear levels is different for each of these 1900 nuclei. During the past three decades, nuclear physicists have focused on determining experimentally the properties of the levels of all known nuclei, searching for systematic trends among the properties of the levels, and theoretically interpreting such trends. The known levels and their properties fill the pages of nuclear physics journals and are reviewed and compiled in such journals as *Nuclear Data Sheets*, edited by Murray Martin, a member of ORNL's Physics Division.

For example, the level structure of the lead-208 (^{208}Pb) nucleus was recently compiled by Martin for *Nuclear Data Sheets*. In this nucleus alone more than 200 levels have been experimentally observed. In fact, in all nuclei combined, over 100,000 levels are known to exist. The experimental work to identify and catalog these levels has been formidable and has made up a large portion of the total effort in nuclear physics from about 1950 to the present. The work carried on at the University Isotopes Separator of Oak Ridge (UNISOR) facility located at the Physics Division's Holifield Heavy-Ion Research Facility (HHIRF) is an example of sophisticated efforts in the study of nuclear levels having low-excitation energy (see sidebar on page 228).

The Physics Division at ORNL has a long history of nuclear structure research, both experimental and theoretical. The identification and systematization of the properties of states in nuclei throughout the periodic table have been accomplished by measuring radioactive decay and detecting products of nuclear reactions induced by accelerated ions.

In recent years the emphasis of the Physics Division's nuclear-structure research program has shifted. Instead of "gently" exciting nuclei by bombarding them with light-mass particles at low energies, we employ highly energetic heavy ions. As a result, we impart to these nuclei what we call high excitation energy and high spin (angular momentum). It is our goal to stress the nucleus. That is, we cause the nucleus to assume characteristics very different from those of the quiescent state (referred to as the ground state). Studies of nuclear levels over the past three decades have generally considered states having excitation energies below a few million electron volts (MeV) and spin below 10 units of angular momentum. Current research in the Physics Division probes the structure of the nucleus at excitation energies of 10 to 100 MeV and at spins of 10 to 60 units of angular momentum.

At these higher nuclear excitation energies we have found evidence for large-scale oscillations of the surface of the nucleus when it is bombarded with highly energetic ions. We call these oscillations giant resonances. The word giant is used to indicate that the oscillation of the nucleus is so large that a large fraction of the nucleons in the nucleus are simultaneously involved in the motion. Observation of these special states has been one of the most vigorously pursued goals of ORNL's nuclear structure program during the past ten years.

The most common method of imparting very high spin to nuclei is through a compound-nucleus reaction in which the incoming ion fuses with a target nucleus. The compound-nuclear system emits various particles, resulting in the formation of several final product nuclei in highly excited states. The energies of gamma rays emitted by such a nucleus are measured to provide information on its nuclear structure. Although a multitude of gamma rays is emitted in cooling the nucleus down to its ground state, a typical gamma-ray spectrum will cover an energy range of only about 5 MeV. Even then, most of the discrete resolvable lines in the spectrum will appear below 1.5 MeV. One particularly interesting aspect of the information from such measurements on high-spin states is that it has begun to supply answers to a long-standing question: How do the structure and shape of a nucleus change as it is forced to carry ever-increasing amounts of angular momentum?

The advent of high-energy particle accelerators has allowed nuclear physicists to study the behavior of the stressed nucleus. Accelerators such as those available at the HHIRF can produce intense beams of almost any stable ion, and because of this flexibility, nuclear reactions can be fine-tuned to elucidate various properties of the stressed nucleus.

This article discusses the results of ORNL's nuclear physics research on giant resonances at high excitation energies and on the shapes of nuclei at very high spin. In addition, sidebars provide information on the study of low-lying states using the UNISOR facility at the Laboratory and on two experimental devices heavily used for nuclear structure physics at HHIRF.

Giant Resonances in Nuclei

Giant resonances are highly collective modes of nuclear excitation in which an appreciable fraction of the nucleons of a nucleus move together. The motion is so collective that it is appropriate to think of these modes of excitation in terms of the hydrodynamic oscillations of a liquid drop.

Figure 1 shows a representation of several modes of nuclear oscillation, where L represents the orbital angular momentum quantum number of the modes. The monopole ($L = 0$) mode is a spherically symmetric oscillation, or compression, of the nucleus; the dipole ($L = 1$) is pictured as a motion in which the neutrons and protons oscillate in bulk against each other, whereas the quadrupole ($L = 2$) mode is an oscillation of the spherical nucleus to a prolate (football) shape and then to an oblate (pancake) shape. Oscillations with $L > 3$ are, of course, possible but are not shown.

The nuclear fluid can be considered to have four parameters: neutron, proton, and two spin parameters indicating the direction of the nuclear rotation—spin-up and spin-down. Hence, for each angular momentum (L) four combinations of these parameters are possible (see Fig. 1). Modes in which neutrons and protons oscillate together are called isoscalar modes (denoted as $\tau = 0$ here), whereas those modes in which the neutrons and protons oscillate out of phase are called isovector ($\tau = 1$). Similarly, spin-up and spin-down nucleons oscillating in phase yield $s = 0$ modes, and the so-called spin-flip modes ($s = 1$) are produced by spin-up and spin-down nucleons oscillating out of phase. The electric modes can have either $s = 0$ or $s = 1$ oscillations, whereas the magnetic modes must have $s = 1$. The electric modes observed thus far are mainly of the $s = 0$ type. For example, the electric dipole mode of nuclear excitation is one in which the neutrons oscillate against the protons in the nucleus and in which the spin-up and spin-down nucleons oscillate together. We denote the electric dipole by the symbol *E1*, where E stands for electric and the 1 means $L = 1$; another mode of excitation (magnetic dipole) is known as *M1*.

The treatment of giant resonances as large oscillations of a "nuclear fluid" has led to the theoretical prediction of many properties of the resonances based upon the hydrodynamical model of the nucleus. For example, the excitation energy E_x of the various giant resonances can be expressed as a simple function of the mass of the nucleus as

$E_x = C \times A^{-1/3}$ MeV,

where A is the nuclear mass number and C is a constant. For the giant electric dipole resonance that was discovered in the 1940s, it has been found that $C \sim 77$. This simple dependence of the resonance energy upon the mass of the nucleus indicates that giant resonances are fundamental properties of all nuclei and should be theoretically understood in a manner that is general to all nuclei. The study of giant resonances provides an excellent proving ground for theories of nuclear structure. In other words, any nuclear force set forth by theorists must correctly predict the location of the various types of giant resonances. This requirement places strong constraints on the nuclear force and has, in fact, already led to several refinements in the theory of nuclear forces.

Of particular interest is the giant monopole resonance, which we have described as a nuclear oscillation in which the nucleus alternately compresses and expands. We call this oscillation the nuclear compressional or breathing mode. A measurement of the excitation energy of the monopole resonance can be directly related to a quantity of fundamental significance to nuclear physics—the compressibility of nuclear matter.

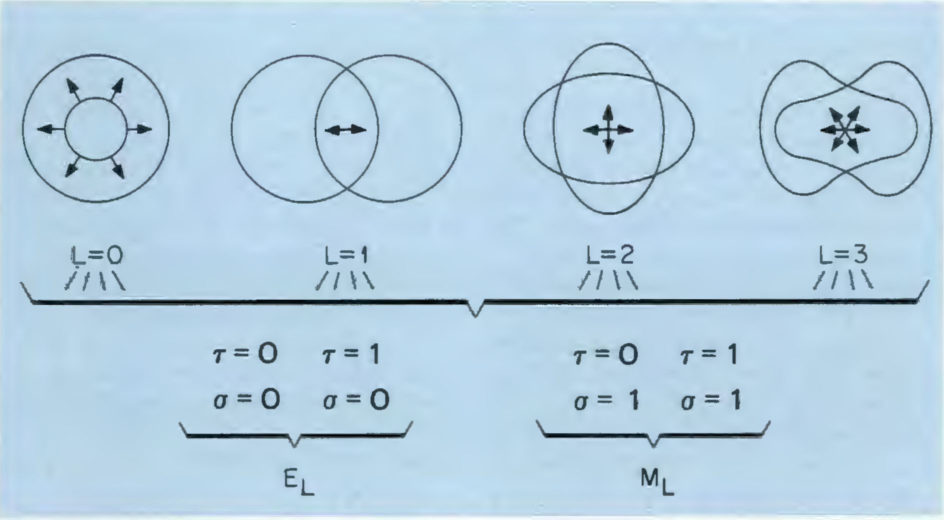


Fig. 1. Modes of oscillation of a nucleus. The orbital angular momentum is denoted by L. $\tau = 0$ or 1 denotes isoscalar or isovector mode, respectively, and $\sigma = 0$ or 1 denotes non-spin-flip or spin-flip mode, respectively.

The compressibility of nuclear matter can be pictured as analogous to the spring constant of a common spring—a constant that describes the compressibility or tension of the spring. In our case the spring is nuclear matter. The value of the compressibility of nuclear matter is crucial to our understanding of the interaction between pieces of nuclear matter and affects, for example, descriptions of the formation of nuclear matter in the Big Bang theory of the formation of our universe.

As previously mentioned, giant resonances are created by collective nuclear oscillations that involve a very large fraction of the nucleons in the nucleus. How collective is the vibration? Can the collectivity be measured? The collectivity of the various modes can be deduced by measuring the probability (cross section) of their excitation in nuclear reactions. The measured cross sections are then compared with theoretically calculated expectations. A useful benchmark to which the measured cross section can be compared is the sum rule, which indicates the total cross section expected for excitation of a particular resonance. In general, for a nuclear level to be considered collective, it should exhaust an appreciable fraction of the sum rule for the mode in question. Giant resonances are found to exhaust 20 to 90% of their sum rules in a rather narrow region of nuclear excitation energy (another explanation of the use of the word giant).

From these brief background comments, a complicated picture of possible giant resonances is derived. For each multipolarity (*L*) there may be four different combinations of the quantities, isoscalar ($\tau = 0$), isovector ($\tau = 1$), spin flip ($\sigma = 1$), and non-spin flip ($\sigma = 0$); in other words, in giant resonance studies, four independent fundamental modes of vibration exist.

How do we sort out this complicated picture? The answer lies in choosing the nuclear reactions that selectively excite the giant resonances for which we are searching. Using different nuclei as projectiles provides a great deal of variety for the reactions, and through this variety we obtain selectivity.

How are the properties of the resonance experimentally deduced? The excitation energy of the resonance is obtained by measuring the position of the resonance peak in a spectrum of particles which are detected in the chosen nuclear reaction. The best device for making this measurement is a magnetic spectrograph (see sidebar on page 232). The angular momentum (*L*) of the resonance is deduced by measuring the cross section for excitation of the resonance in a given reaction at a number of angles to obtain an angular distribution. The experimentally measured angular distribution is then compared with theoretically calculated distributions for various values of *L* to determine which calculation best describes the data.

The Physics Division program studies two broad categories of giant resonances: isoscalar ($\tau = 0$) giant resonances, using inelastic scattering of different incident projectiles, and spin-flip (($s = 1$) giant resonances, using charge-exchange reactions, most notably the exchange of protons and neutrons between projectile and target nuclei—the (p,n) reaction.

The giant dipole resonance was discovered in 1947 by G. C. Baldwin and G. S. Klaiber (General Electric Company) using reactions in which a photon is absorbed by the nucleus, which then becomes excited and cools down by emitting a neutron (or other particle). It was not until 1972 that another giant resonance was discovered. At ORNL, the isoscalar giant quadrupole resonance was discovered by Monty B. Lewis and Fred E. Bertrand using inelastic scattering of protons from the Oak Ridge Isochronous Cyclotron (ORIC). As a result, research in this area was initiated at laboratories throughout the world.

Isoscalar Giant Resonance Studies

Over the past dozen years, ORNL researchers have observed isoscalar giant resonances using a very wide variety of nuclei as projectiles. Recently, we have measured the inelastic scattering of 334-MeV protons by ^{208}Pb nuclei. The inelastically scattered protons were detected in a magnetic spectrograph. The protons were obtained from the Los Alamos Meson Physics Facility (LAMPF) accelerator at Los Alamos National Laboratory (LANL). The spectrum obtained (see Fig. 2) shows narrow peaks at low excitation energies that arise from excitation of many of the levels known to exist in the ^{208}Pb nucleus. At energies above ~8 MeV, several broad peaks are observed that arise from excitation of giant resonance states in the ^{208}Pb nucleus. The peak located at about 10 MeV is from excitation of the giant electric quadrupole resonance ($L = 2$ mode in Fig. 1) and the peak at 14 MeV is from excitation of the giant electric dipole ($L = 1$) and monopole ($L = 0$) resonances. Observation of the

High-Sensitivity Studies of Exotic Nuclei at UNISOR

The stability of nuclei depends on a number of factors, some of which are understood and some of which we are just learning about. The balance between protons and neutrons is a dominating factor, resulting in only 279 stable nuclei in nature. Through modification of the proton-neutron ratio, up to 7000 radioactive nuclei can be produced. Of this number, approximately 2000 have been observed to date; however, information on many of these is still very sketchy. Thus, the store of information regarding the dominant force in nature, the nuclear force, and the resulting nuclear structure is indeed vast.

The properties of nuclei can be studied in numerous ways. Two important ways are through (1) identification of reaction products that result when one nucleus is bombarded by another energetic nucleus or other probe and (2) measurement of the energies of gamma rays, electrons, positrons, and alpha particles emitted by radioactive decay. The ORNL programs include both reaction studies and studies of nuclei far from stability by radioactive decay.

These exotic nuclei are produced by bombarding targets with heavy-ion beams from the Holifield Heavy-Ion Research Facility (HHIRF). Because many different nuclear species are produced in these reactions, a mass filter is needed to achieve the sensitivity required to adequately study these particular radioactive nuclei. About 15 years ago, the University Isotope Separator at Oak Ridge (UNISOR) collaboration was organized to install and operate such a facility at the HHIRF. The collaboration currently involves eight universities, ORNL, and Oak Ridge Associated Universities (ORAU). It maintains a small staff at Oak Ridge and has approximately 20 active university and ORNL users. The isotope separator acquired by this group produces different beams for different masses from the reaction products by stripping a single electron from each atom, accelerating each resulting ion to a constant energy, and deflecting the fast ions in a magnetic field.

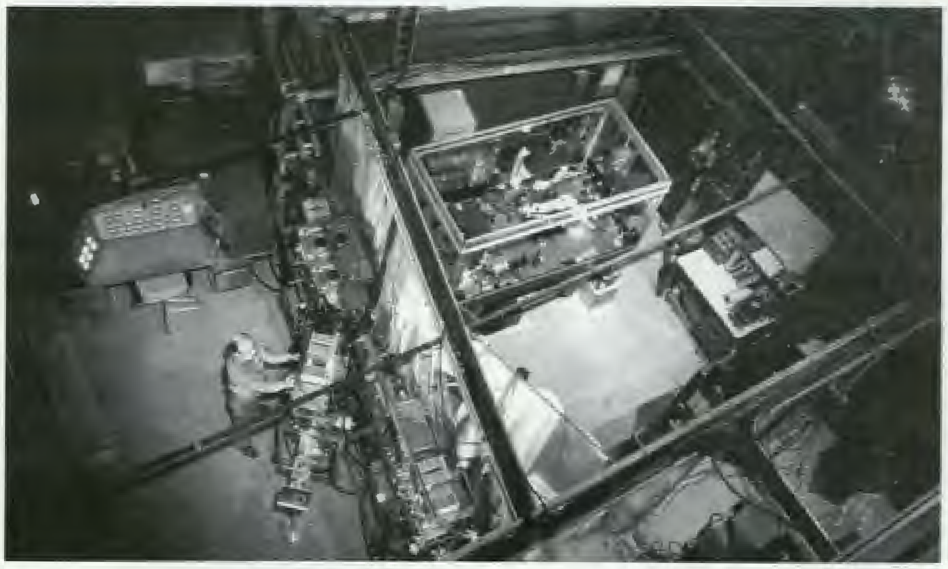
The aim of the UNISOR research group is to advance the understanding of nuclear structure and the factors affecting nuclear stability. Although the nuclear force between two nucleons (protons and neutrons) is strong and the nucleons are closely packed in a nucleus, they still seemingly move with a minimum of collisions because the nucleons are fermions and, thus, obey the Pauli Exclusion Principle. The nucleons of a nucleus in its lowest energy state (ground state), basically occupy the orbitals that result in the lowest total energy. An important factor in determining these orbitals is the shape of the nucleus. For some proton and neutron numbers (Z and N), the most stable shape is spherical; for others, however, a deformed nucleus is more stable. In a case in which the protons favor a spherical shape and the neutrons a deformed shape or vice versa, a "tug-of-war" ensues, leading to cases of coexisting spherical and deformed shapes at low excitation energies in a single nucleus.

Two basic theoretical approaches have been taken to understand deformed shapes in nuclei. The simpler one is the independent-particle approach, which assumes that the average field in which the nucleons move within the nucleus is allowed to deform. In this concept, the nucleons of a nucleus in its lowest energy, or ground, state occupy the deformed, or single-particle, orbitals, which result in the lowest energy. The deformation is adjusted to give the lowest possible energy for the nucleus.

The more difficult and more microscopic approach is the correlated-particle model in which a two-body force is used to bring about correlations between the nucleons such that a deformed shape "builds up" from the correlations. The magnitude of the resulting deformation is determined by the number of protons and neutrons that are beyond the closed shells. Shell structure imposes bounds on these numbers. Promotion of pairs of protons or neutrons across closed shells increases the number of valence nucleons, thus introducing the possibility of states having different deformation in the same nucleus. Pairs of protons are favored by the two-body force known to act between like nucleons (producing such phenomena as odd-even staggering in binding energies). The study of nuclei exhibiting shape coexistence has been a general theme of the UNISOR program.

Nuclei have a variety of signatures indicating deformation. One of the easiest to observe is the spacing of the excited levels. A spherical shape is characterized by (almost) equally spaced levels in the band, whereas for a deformed shape the levels are spaced closely at the bottom but gradually spread apart higher in the band of levels. Until relatively recently, these dissimilar bands were not known to exist in the same nucleus.

At UNISOR nearly 10 years ago, we observed coexisting bands (indicating shape coexistence) in ^{184,186,188}Hg by measurement of gamma-ray transitions. This observation was significant because the nuclei of mercury isotopes are only two protons away from the closed proton shell of lead (Z = 82) and were considered, at the time, to be nearly spherical. A similar signature was the first clue that shape coexistence occurs also in the neighboring isotopes of gold (Au) and thallium (Tl). Further work at facilities in the United States and Europe has revealed an extensive region of coexisting shapes extending at least from the platinum isotopes (Z = 78) to the bismuth isotopes (Z = 83) and including the closed-shell lead isotopes (Z = 82). An emerging systematic picture suggests that the strongly deformed bands appear lowest in energy when the number of active, or valence, neutrons is maximal (the mid-shell point at N = 104 for these isotopes). Very dramatically, the strongly deformed structures become the ground states in the very neutron-deficient gold and platinum isotopes.



In this experimental hall at UNISOR, it was discovered that at very low energies, certain nuclei have coexisting shapes.

Recently, scientists at UNISOR have more directly "fingerprinted" nuclear deformation by measuring nuclear electric quadrupole moments, which can be observed in a variety of ways. The method used at UNISOR depends on the fact that atomic electrons are held in their orbits by the electrostatic properties of the nucleus. Changes in the charge distribution of the nucleus result in very small shifts in atomic energy levels. These can be observed by atomic (hyperfine) spectroscopy, specifically by observing the shifts in the frequency of a highly monochromatic tunable laser beam that will excite the electron levels. Briefly, light from a tunable dye laser is directed collinearly with an atomic beam resulting from an ion beam neutralized by passage through a charge-exchange cell. Detection is achieved by direct observation of photons produced as excited electrons return to their normal energy state. High sensitivity (one photon per 1000 atoms) is accomplished by observing a de-exciting transition with a frequency different from that of the laser (to give a low background) and by using a highly efficient light-collection system. In this way, the isotopes ^{189,191,193}Tl have been found to exhibit large nuclear electric quadrupole moments for the lowest states of the more deformed bands.

Another fingerprint looks promising. In some cases, strong electric monopole (E0) transitions appear between coexisting bands. These transitions are rather rare in nuclei in general and are observed through the internal conversion process whereby an atomic electron orbiting the nucleus carries off the energy of de-excitation. (A photon cannot do this because, by its very nature, it is spinning; and E0 transitions by definition do not involve a spin change.) In ^{185,187}Au a number of E0 transitions have been observed at very low energies, signaling that the nuclei of these isotopes have coexisting shapes.

The emerging picture suggests that shape coexistence at low-excitation energy in heavy nuclei may be much more prevalent than previously expected. Both the independent-particle model and the correlated-particle model are nearly refined enough to make detailed predictions. The research scientists at UNISOR anticipate an exciting future exploring this fundamental facet of nuclear structure.—*C. R. Bingham, The University of Tennessee; J. L. Wood, Georgia Institute of Technology; and H. K. Carter, UNISOR, ORAU.*

giant monopole resonance was first reported in 1977 by Bertrand and collaborators from the KVI Institute in Groningen, The Netherlands. The observation of these resonances clearly demonstrates that the nucleus is undergoing very strong collective oscillations.

Figure 3 shows spectra similar to that of Fig. 2 for several different angles of experimental observation. The single broad peak seen in the data for 2.25° falls at the exact position of the dipole resonance as known from other types of measurements. At larger angles the strength of the dipole excitation should decrease and the quadrupole ($L = 2$) resonance should dominate. A strong peak, which is seen in the 5.25° data at about 10 MeV, is consistent with the expected location of the quadrupole resonance. At still larger angles, the quadrupole excitation should decrease in intensity and excitation from octupole ($L = 3$), and hexadecapole ($L = 4$) states should appear. Excitation of these states is indeed seen in the spectra. Note the very broad peak centered at about 20 MeV in the 9.25° data and the peak shown at 12 MeV in the 10.25° data. The octupole peak had been previously seen by LANL researchers. The peak at 12 MeV was identified in 1982 by ORNL physicists (Ed Gross, Dan Horen, Terry Sjoreen, and Bertrand with collaborators from the University of Oregon) as arising from excitation of the hexadecapole resonance.

The smooth solid curves drawn on the spectra in Fig. 3 indicate the shape of the resonance peaks, and the more or less horizontal solid curves show the estimate of the underlying spectrum that is not part of the giant resonance peak. Using these curves physicists can extract a cross section for each of the peaks and compare the experimental values with calculated values. Figure 4 shows angular distributions for the peaks found at 10 and 12 MeV compared with theoretically calculated angular distributions (solid lines). The peak at about 10 MeV is extremely well described by a calculation that assumes an angular momentum of two (i.e., a quadrupole excitation), and the 12-MeV peak is consistent with the calculation for an angular momentum of four but *not* with the calculations for $L = 2$. We thus have identified the giant resonance peaks arising from the nuclear quadrupole and hexadecapole modes of oscillation. The percentage figures shown on the curves are the percentages of the sum rule found for each giant resonance state. In the case of the quadrupole resonance, 70% of the sum rule is found, clearly fulfilling our expectations for giant resonances. In the ^{208}Pb nucleus, ORNL researchers have observed isoscalar giant resonances that correspond to

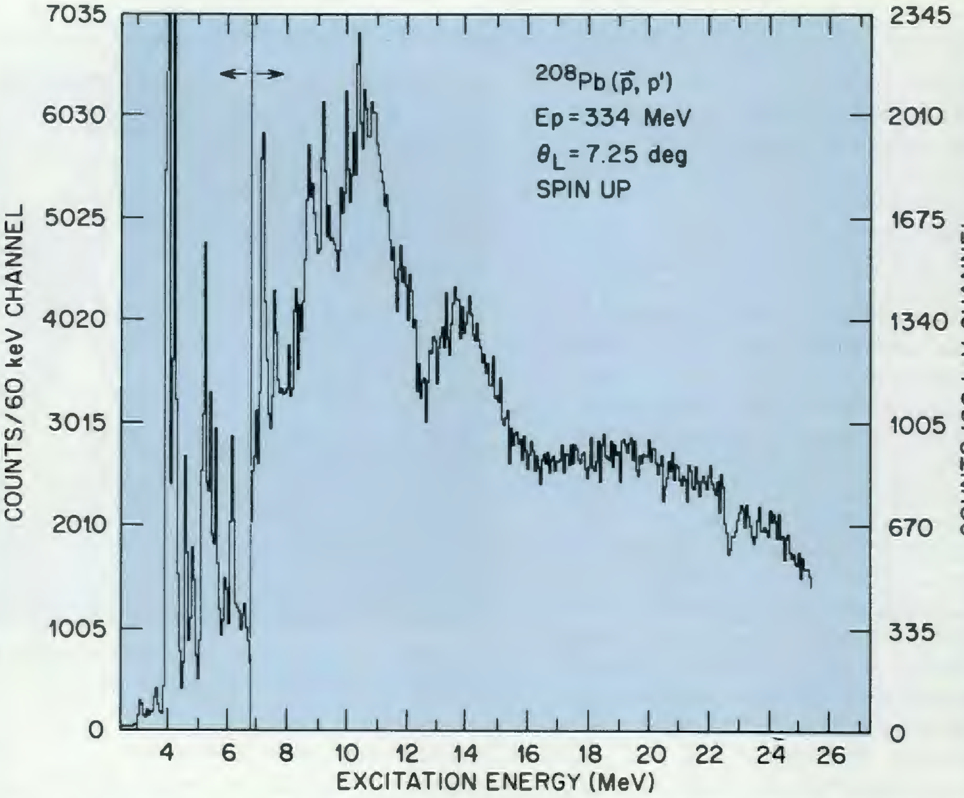


Fig. 2. Spectrum of protons from the reaction ^{208}Pb (p,p') ^{208}Pb, for an angle of observation of 7.25°.

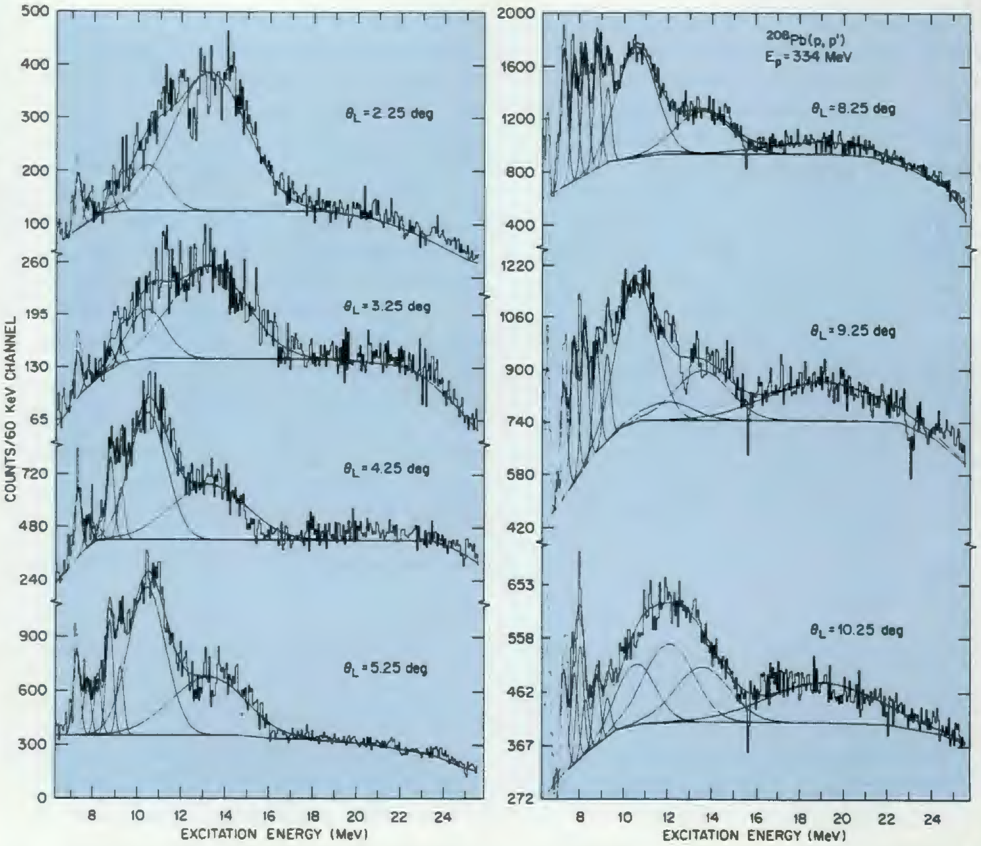


Fig. 3. Spectra of protons from the reaction ^{208}Pb (p,p') ^{208}Pb for several different angles of observation.

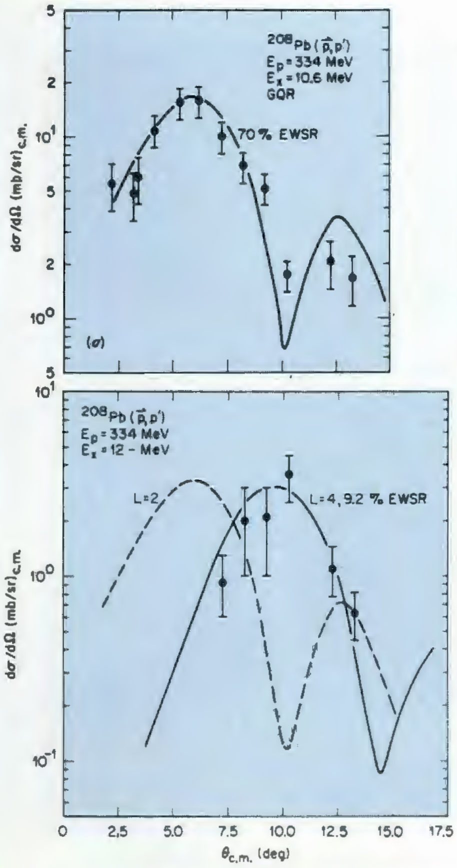


Fig. 4. Angular distributions for peaks in the lead spectra at 10.6 and 12.0 MeV.

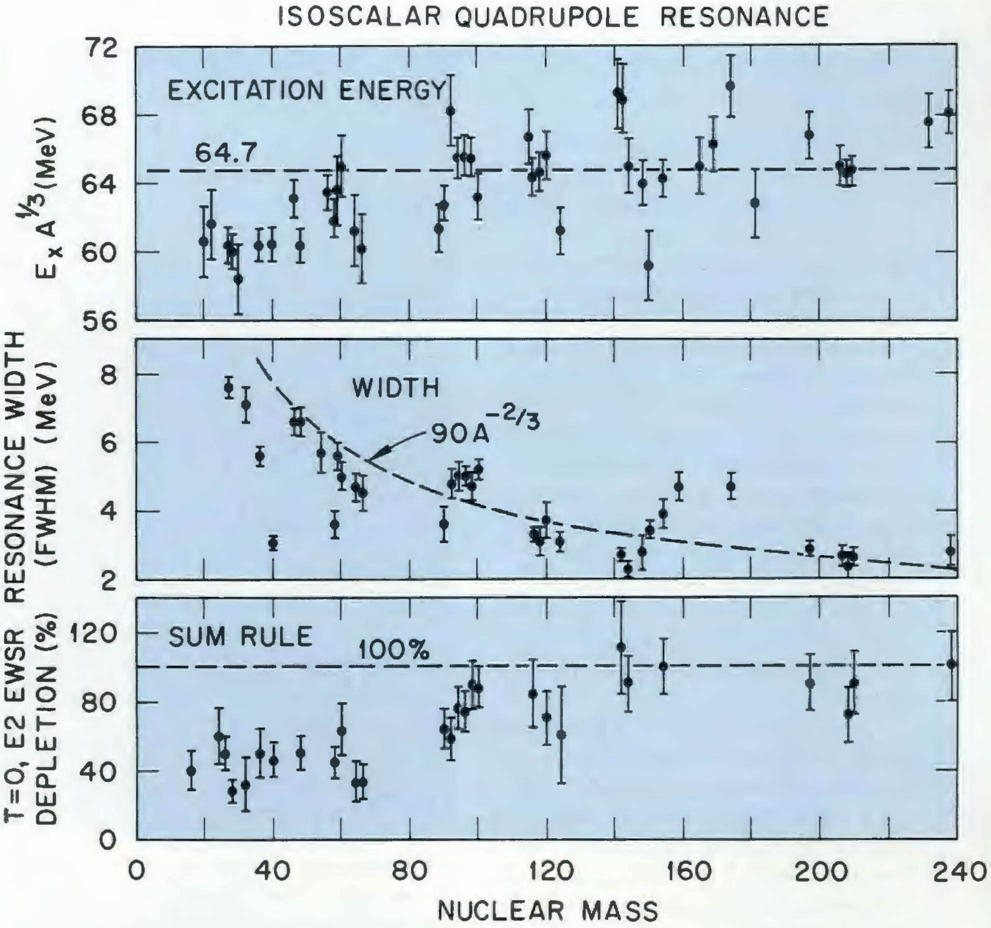


Fig. 5. Systematics from the excitation energy, width, and sum rule of the isoscalar giant quadrupole resonance.

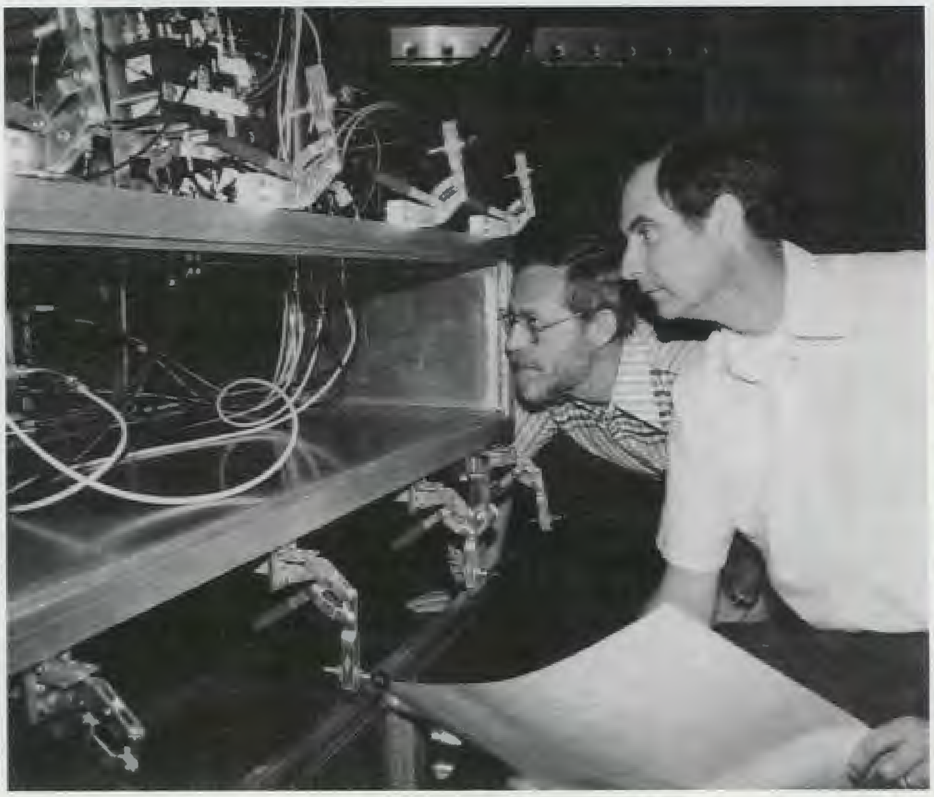
the quadrupole, octupole, hexadecapole, and monopole oscillations.

From research at ORNL and elsewhere, isoscalar giant resonances have been found in nuclei throughout the periodic table. Figure 5 shows the measured properties of the isoscalar giant quadrupole resonance (GQR) plotted as a function of the mass of the nucleus. The excitation energy of the GQR is given by the relation $\sim 65\,A^{-1/3}$ (A is the symbol for the nuclear mass number), except for the lightest nuclei, which are special cases. In general, the width of the resonance varies smoothly as a function of nuclear mass; and the sum rule for the resonance (called EWSR depletion in Fig. 5) is a substantial fraction of the theoretical maximum for all nuclei. These experimental results certainly fulfill the expectations for the properties of nuclear giant resonances.

Inelastic scattering of medium-energy protons and alpha particles has provided most of the data obtained on the isoscalar giant resonances. With the advent of medium-energy heavy-ion accelerators, such as those at HHIRF, physicists have found that the giant resonances can be excited with much larger (5 to 10 times) cross sections when heavy ions rather than lighter ions are used. The higher probability of exciting resonances using heavier ions is important because it makes possible the search for very weak, heretofore unobserved, giant resonance peaks. However, the most important advantage of the larger cross sections is that they open the possibility for the study of both the excitation of the giant resonances and the way in which they decay. We believe that much more detailed information about the nuclear structure of giant resonances may be obtained by identifying both the particles and gamma rays emitted when the resonance decays and the lower excitation states in the final nucleus to which it decays.

A recent experiment in the Physics Division, by Jim Beene, Mel Halbert, Fred Bertrand, and several others, was directed toward studying the gamma-ray decay of giant resonances, in particular, the giant quadrupole resonance. The resonances in heavy nuclei decay about only 1 part in 10,000 by gamma rays; the remaining decay is by emission of neutrons. In the new ORNL experiment, giant resonances in ^{208}Pb were excited by inelastic scattering of 375-MeV oxygen-17 ions from HHIRF. The

The HHIRF Broad-Range Magnetic Spectrograph for Studying Nuclear Structure



Fred Bertrand and Ron Auble check the operation of the Broad-Range Spectrograph (BRS), which is one of the major experimental devices available to users of the Holifield Heavy-Ion Research Facility. The versatility of the system has been shown in heavy-ion studies using projectiles as light as boron and as heavy as nickel, having energies from 100 MeV to over 1 GeV.

One of the tools commonly used to study nuclear structure is the magnetic spectrograph. This device offers higher resolution and better particle selectivity than do other types of charged-particle detectors. Magnetic analysis is based on the well-known property that a particle having charge q and momentum p, moving perpendicular to a magnetic field B, will follow a circular trajectory of radius r such that $p/q = kBr$, where k is a constant. For cases in which the identity of the charged particle is known, measurement of r and B will determine the momentum of the particle (p), from which various nuclear-structure properties can be deduced.

ORNL's Broad-Range Spectrograph (BRS), so named because of its large momentum acceptance, is one of the major experimental devices available to users of the Holifield Heavy-Ion Research Facility. Because a multitude of different particles can be produced in heavy-ion reactions, measurement of r and B will not fully determine the charge (q), atomic number (Z), mass number (A), momentum (p), and energy (E) of the particle. To provide additional information, ORNL researchers from the Physics and Instrumentation and Controls divisions (T. P. Sjoreen, J. L. C. Ford, R. O. Sayer, B. L. Burks, and F. E. Bertrand) have developed a powerful detector system, consisting of four separate elements, for the BRS.

The position at which the particle crosses the focal plane of the BRS determines the radius of the particle trajectory from which p/q is obtained. A vertical drift chamber (VDC) measures the location of the particle at several points near the focal plane. This measurement allows the experimenter to determine both the position and angle at which the particle crossed the focal plane. The angle determination allows the use of a large angular acceptance (up to 4°) into the BRS. Because the VDC relies on electron drift times for its position determinations, it is necessary to determine precisely when the particle crossed the focal plane. This information is provided by a parallel-plate avalanche counter (PPAC) mounted directly behind the VDC.

To determine the atomic number (Z) of the particle, we rely on the well-established technique of measuring the energy (E) and rate of energy loss (ΔE) with modest resolution using an ionization chamber. This chamber, which is located behind the VDC and PPAC, is used to stop the particle. For particles having mass less than about 20, the information provided by this detector, when combined with the position information from the VDC, allows a unique identification of the particle. The VDC, PPAC, and ionization chamber are all located *near* the focal plane of the BRS.

For heavier particles, the mass identification becomes ambiguous; to obtain the additional information needed to make a precise identification, we installed a fourth detector near the scattering chamber. This detector, either a small PPAC or secondary electron detector, determines the time when the particle exits the scattering chamber. By combining this time measurement with that from the PPAC located at the focal plane, we obtain a measure of the time-of-flight or, equivalently, the projectile velocity. This technique has been applied very successfully to identify particles having a mass as heavy as 60.

Adapting the BRS from its original use for light ions to a high-resolution, heavy-ion instrument has been rewarding work. We are pleased that the excellent position and angle determination provided by the VDC allow energies and scattering angles to be determined to ~1:6000 and 1.4 mrad, respectively. The versatility of the system has been demonstrated in heavy-ion studies using projectiles as light as boron and as heavy as nickel, having energies from 100 MeV to over 1 GeV.—*Ronald L. Auble, Physics Division.*

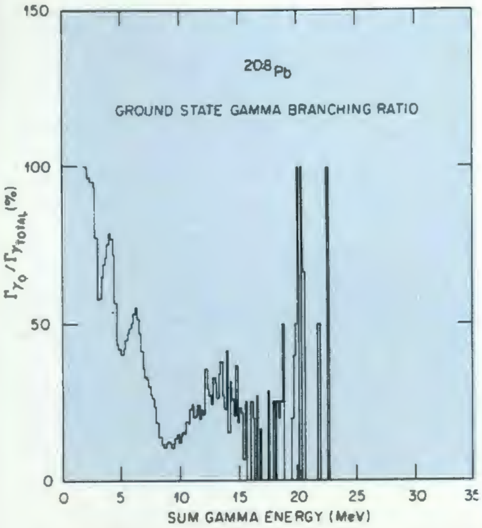


Fig. 6. Spectrum of ground-state γ-decay plotted as a function of excitation energy of the ^{208}Pb nucleus.

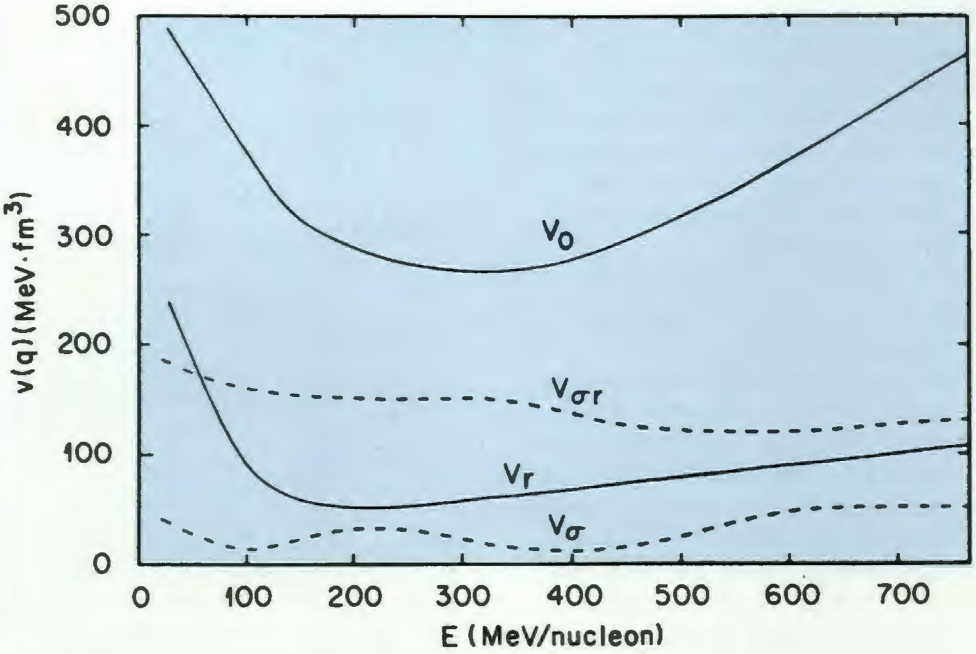


Fig. 7. Energy dependence of the central components of the nucleon-nucleon interaction. The subscripts on V indicate whether the interaction is isoscalar or isovector (τ) and involves spin change (σ).

deexcitation gamma rays were detected in the Spin Spectrometer (a 70-detector, nearly 4π gamma-ray spectrometer), which measured the number and energies of gamma rays and their direction of emission with respect to the incident beam direction.

We then analyzed a spectrum of all gamma rays that decay directly to the ground state of ^{208}Pb (see Fig. 6). The plot shows the excitation energy in ^{208}Pb vs the fraction of the total gamma rays that go to the ground state (called the ground-state branching ratio) plotted as a percentage. Between 10 and 15 MeV, a strong decay branch is observed that coincides with the energy of the giant quadrupole resonance and the giant dipole resonance.

This experiment marks the first time that the gamma-ray decay following inelastic scattering excitation has been measured for isoscalar giant resonances. The results of our ground-state decay measurement conclusively show that over 70% of the theoretically predicted quadrupole sum rule is located in the giant resonance state. Thus, we verified the theoretical expectation that most of the nucleons in the nucleus are participating in this giant vibration. More importantly, this verification is made independent of any effects of reaction mechanisms. Gamma rays were also observed in decays to low-lying excited states in ^{208}Pb. The strength of the decay to the various levels has shown for the first time that the nuclear structure of the different states making up the quadrupole resonance is not the same. The HHIRF accelerator, which provides high-energy heavy ions to excite the giant resonance, and the Spin Spectrometer provide an ideal experimental facility for the study of the gamma decay and thus the detailed nuclear structure of isoscalar giant resonances.

Spin-Flip Giant Resonances

The search for giant resonances that involve a spin change ($\sigma = 1$) has been somewhat more difficult than that for those in which $\sigma = 0$. Part of the reason for this difficulty can be seen in Fig. 7, where the relative strengths of the components of the interaction between two nucleons are plotted against energy. The part of the interaction (V_0) that excites states with $\sigma = \tau = 0$ (isoscalar) is several times larger than the parts that excite spin-flip states ($V\sigma$, $V\sigma\tau$). Normally, the spin-flip resonances are interspersed among a high density of non-spin-flip states. Thus, if the probe used to search for a spin-flip resonance is also capable of exciting $\sigma = \tau = 0$ states, the latter will dominate the observed spectra. The problem then becomes similar to the proverbial "needle in a haystack." The situation becomes even more complicated if the spin-flip strength is spread over several MeV of excitation energy.

At ORNL interest in spin-flip resonances developed in the latter part of the 1970s. From high-resolution neutron scattering measurements performed by Dan Horen, Jack Harvey, and N. W. Hill at the Oak Ridge Electron Linear Accelerator (ORELA), it was clear that much of the magnetic dipole (M1) radiation assigned to the ^{208}Pb nucleus had been incorrectly identified and was, in fact, of an electric dipole (E1) nature. This realization proved rather disturbing because the agreement between the data and theoretical predictions for M1 strength in ^{208}Pb had been fairly good and the problem was considered solved.

Although neutron scattering is a rather old technique, the unique features of ORELA allowed definitive measurements to be performed. The researchers also had a bit of luck because most of the M1 strength in ^{208}Pb lies at an excitation energy that is accessible to measurements at ORELA. The high-energy resolution achievable with ORELA made it possible to resolve the many levels in the excitation energy region where considerable M1 strength had been reported. The neutron-scattering measurements were capable of uniquely determining whether a given observed nuclear level should be classified as M1 or E1. When the results from the scattering measurements were combined with neutron-capture, gamma-ray measurements also performed at ORELA by S. Raman, M. Mitzumoto, and Dick Macklin, it became clear that the observed M1 strength above the neutron threshold was only a small fraction of that previously reported. Furthermore, the ORELA results prompted a re-examination of a bound state in ^{208}Pb that had been reported to contain about 50% of the M1 strength. This assignment was shown to be in error by measurements made at Princeton University by ORNL's Horen and collaborators. The ORNL finding suggested that very little of the expected M1 strength in ^{208}Pb had actually been observed experimentally. Consequently, numerous new theoretical and experimental investigations were set in motion.

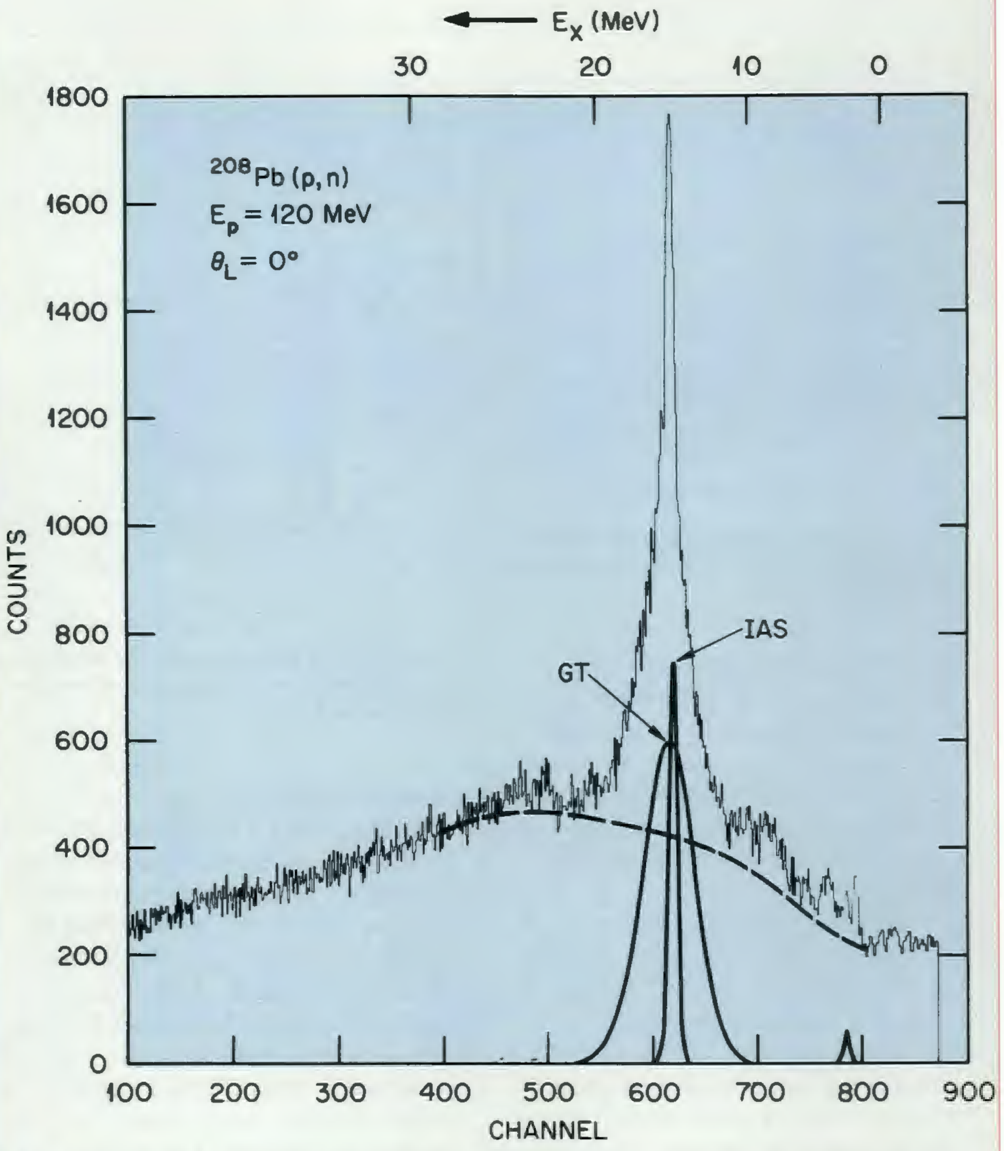


Fig. 8. Time-of-flight spectrum for the ^{208}Pb (p,n) ^{208}Bi reaction taken at an angle of 0° (i.e., the neutron is emitted in the same direction as the incident proton). The lower portion of the figure shows that the major portion of the peak arises for a GT transition.

The M1 resonance in a nucleus $_ZA_N$, where Z is the nuclear charge, N is the number of neutrons in the nucleus, and A is the nuclear mass ($A = Z+N$), contains both isoscalar ($\tau = 0$) and isovector ($\tau = 1$) components. Directly related to the isovector M1 transitions in the nucleus $_ZA_N$ are transitions between the $_ZA_N$ nucleus and the immediately adjacent nuclei that can be formed by changing a proton into a neutron, giving the $_{Z-1}A_{N+1}$ nucleus, or a neutron into a proton, giving the $_{Z+1}A_{N-1}$ nucleus. These latter transitions are called Gamow-Teller (GT) transitions. (The GT transition in the neighboring nuclei and the M1 transitions are so closely related that the GT transitions are usually called analogs of the M1 transitions.) GT transitions have been studied for many years by observations of radioactive nuclides. However, such transitions can be much more thoroughly investigated through the use of charge-exchange reactions $A(a,b)B$, where, for example, A is chosen as $_ZA_N$ and (a,b) as (p,n) or (n,p). These reactions are analogous to beta decay and have the important advantage that they excite all of the GT strength.

Historically, very little GT strength has been observed in studies of beta decay of radioactive nuclei. In 1963 it was theoretically predicted that most of the GT strength would be contained in a collective state (giant GT resonance) and reside at an excitation energy considerably above the ground state and, for this reason, would not have been observed through beta-decay studies.

The giant GT resonance was observed in 1975 in a study of the (p,n) reaction at $E_p = 45$ MeV using a "magnetic beam swinger" at Michigan State University. (The beam swinger is a system of magnets that allows changes to be made in the angle of incidence of the proton beam on the target.) The GT peak was seen as a broad bump rising above a large continuum background. C. D. Goodman (now at Indiana University) and co-workers began to design a beam swinger for installation at ORIC. At the higher energies available ($E_p = 60$ MeV), they thought that the GT peak should be enhanced. Meanwhile, Goodman and Dave Hensley of ORNL used ORIC to find out whether low-energy, heavy-ion reactions could provide useful information pertaining to GT transitions. The net conclusion was that although some GT transitions were observed, the incident heavy-ion energies were too low to deduce the strength of the transitions with confidence (i.e, the reaction mechanism was too complicated).

When the decision was made to use ORIC primarily for heavy-ion research, it was suggested that the beam swinger be used to develop a neutron time-of-flight facility at the intermediate-energy proton accelerator under construction at Indiana University. This facility was designed to accelerate protons to 200 MeV, an excellent energy with which to study spin-flip transitions (see Fig. 7).

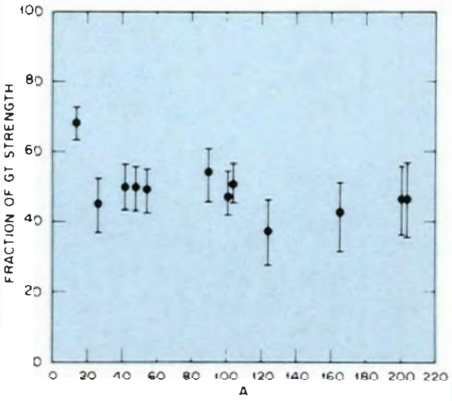


Fig. 9. Fraction of the observed Gamow-Teller sum rule plotted as a function of mass number.

When the beam swinger facility at IUCF began operating, the investigation of charge-exchange spin excitations proceeded with vigor. ORNL's Horen began conducting experiments there in collaboration with researchers from a number of institutions, including Indiana University, Ohio University, University of Colorado, and Florida A&M University.

Early experiments by the group showed clearly the enhancement of the GT resonance with increasing proton energy. A significant finding was that the giant GT resonance completely dominated the 0° neutron time-of-flight spectrum for the ^{208}Pb(p,n)^{208}Bi reaction at energies of 120 MeV and higher (see Fig. 8). The resonance occurs at an excitation energy of 15.6 MeV. Surprisingly, the resonance was found to have a relatively narrow width (~4 MeV).

During the past several years, a large body of (p,n) data has been recorded using the IUCF beam swinger, and we have been able to map out the energetics and the cross section of the GT resonances.

The sum rule for GT transitions can be expressed as

$$S_{pn} - S_{np} = 3(N - Z).$$

Here, S_{pn} represents the sum of all GT transitions that can be excited by the (p,n) reaction, and similarly S_{np} represents the GT transitions excited via the (n,p) reaction. Surprisingly, unlike the situation for isoscalar resonances, it has been found that the magnitude of the cross section observed in the (p,n) studies, S_{pn}, is less than the minimum expected [i.e., $S_{pn} > 3(N - Z)$] for all isotopes studied spanning the periodic table. If the observed sum rule is plotted as a function of the mass of the studied nucleus (see Fig. 9), only about 60% of the strength is found for all but the lightest nuclei.

A number of theoretical studies followed in an attempt to explain the missing cross section. One suggestion was that the nuclear GT transitions were mixed with excitations of the nucleons themselves. This idea was appealing because, if true, it would afford a bridge between nuclear physics and high-energy physics. Another line of thought was that the missing strength was, in fact, GT strength that is pushed to much higher excitation energies. Although it is now fairly well conceded that the latter explanation accounts for most of the missing strength, the suggestion that the GT transitions are mixed with excitations of the nucleons themselves has stimulated a new direction of experimental research.

Nuclear Structure at Very High Spins

Researchers in nuclear-structure physics have long been intrigued by the behavior of nuclei that contain large amounts of angular momentum (spin). This area of experimental investigation began its movement to the forefront of nuclear physics around 1970, primarily because of the availability of heavy-ion accelerators. ORNL scientists were in the initial wave of this research and have remained actively involved in this rapidly evolving area of study.

Until the late 1960s, very little was known about nuclear states beyond spin (I) and parity (π) of $I^\pi \sim 6^+ - 8^+$. The first opportunity at ORNL to explore a higher spin regime came in about 1970 when ORIC was modified to accelerate heavy ions. With the chance to use such beams as neon-20 (^{20}Ne), chlorine-35 (^{35}Cl), and argon-40 (^{40}Ar), Noah Johnson, the late Gene Eichler, and their colleagues launched a program to excite and study the properties of rotational states in deformed rare-earth and actinide nuclei. In these experiments, rotational states up to $I^\pi \sim 12^+ - 14^+$ could be populated by the Coulomb excitation process induced by bombarding nuclei with ^{40}Ar ions. Qualitatively, this process is a nuclear reaction in which an atomic nucleus absorbs energy from a swiftly passing charged projectile. The exchange of energy occurs because of the electrostatic forces acting between the incident charged particle and the target nucleus. The excited nuclear states produced can be studied by high-resolution measurements of the electric quadrupole (E2) gamma-ray transitions occurring between these rotational levels in the de-excitation process.

In exploring nuclei at what was considered at that time to be high angular momentum, ORNL researchers hoped to observe the possible influence of additional angular momentum on the shape of the nucleus. Actually, the shapes of nuclei had been a subject of interest in nuclear physics for many years. Even as early as the 1940s many nuclei having certain numbers of neutrons and protons were known to have near-spherical shapes. In the latter part of that decade, the properties of the ground and low-lying levels in many nuclei were well accounted for by Maria Mayer and others in their sophisticated theory of the nuclear shell model, a quantum mechanical description of individual protons and neutrons in the nucleus. For her work in this area, Mayer received the 1963 Nobel Prize for Physics.

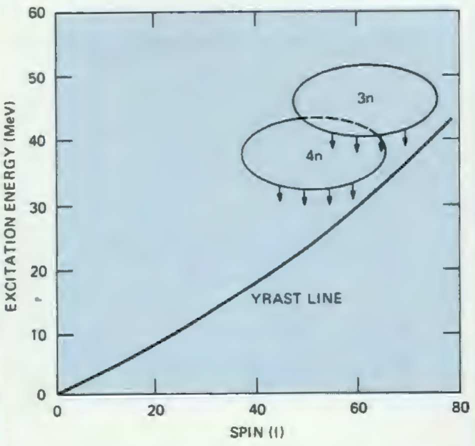


Fig. 10. Illustration of the entry-state distribution for two final nuclei produced in a compound-nucleus reaction. The accelerated heavy-ion and target nucleus fuse and in the case here emit three and four neutrons leading to the many excited states in each of the two final nuclei. From the entry-cloud of each final nucleus, decay proceeds toward and along the yrast line to the ground state by emission of a series of gamma rays.

The interest in nuclear shapes was accelerated in the early 1950s by the theoretical developments of Aage Bohr and Ben Mottelson at the Niels Bohr Institute in Copenhagen, Denmark. It was recognized that, in some nuclei, the long-range forces between nucleons tended to concentrate their distribution in some directions and not in others, resulting in a permanent deformation of the nucleus. The most common deformed shape is that of a prolate spheroid (football shape) exhibited by many rare-earth and actinide nuclei. Drawing an analogy from the field of molecular spectroscopy, Bohr and Mottelson proposed in 1952 the now-famous rotational model of the nucleus. This theory, which in 1975 brought them the Nobel Prize for Physics, accounts for such properties as the spin-dependent rotational sequence of energy levels in deformed nuclei and the electromagnetic transition rates between them.

From many Coulomb excitation measurements carried out at ORIC and at Lawrence Berkeley Laboratory's Super HILAC, ORNL physicists have made many critical tests of the rotational model predictions for states up to $I^\pi = 20^+$ in a large number of nuclei. Results from these measurements on deformed nuclei showed that their behavior was very close to that predicted by the rotational theory. In most cases there was no evidence for changes in nuclear shapes, even when the nuclei contained as much as 18 to 20 units of angular momentum.

A major step forward in studying nuclei at still higher rotational frequencies came in 1981 when the 25-MV tandem accelerator at HHIRF became operational. The great variety of heavy-ion beams and energies offered by this device opened the door for investigations of a multitude of new nuclei. A notable advantage in using heavier ions to induce compound-nucleus reactions is that much more angular momentum can be pumped into the nucleus of interest. However, no attempt at making a nucleus rotate with more than 70 to 80 units of angular momentum has ever succeeded. This limitation is understood on the basis of the liquid-drop model of the nucleus. In the liquid-drop picture, when the nucleus rotates at very large frequencies, corresponding to about 70 to 80 units of angular momentum, the centrifugal forces simply separate it into two pieces, a process known as fission. Consequently, we must work within these angular momentum limits so that the nucleus under study can survive long enough for its properties to be measured.

Among the complex devices at

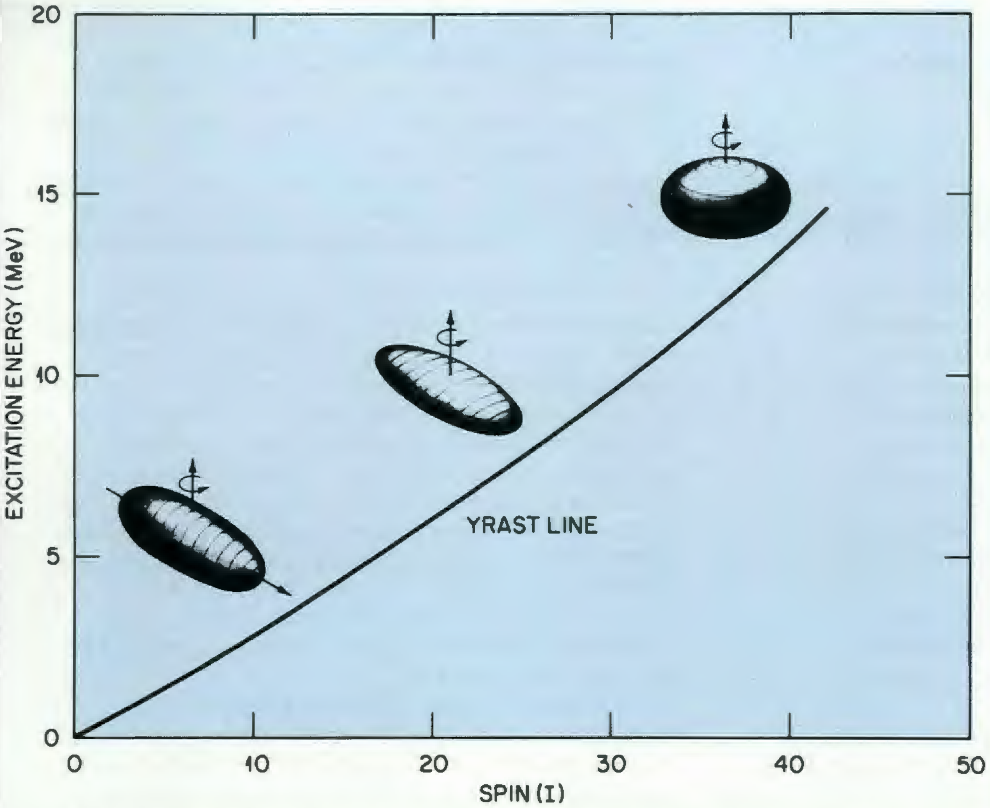


Fig. 11. Illustration of shape changes found to occur in the yrast sequence of ^{158}Yb. At low spin and low excitation energy, ^{158}Yb has a deformed shape close to that of a prolate spheroid (cigar shape). At about spin 14 to 16 and an excitation energy of a few MeV, the Coriolis effects, as a result of rotation, drive the nucleus to a triaxial shape (all three axes of the nucleus are unequal). In the region of spin 40, where the rotational frequency is very high, the nucleus is finally pushed to the shape of an oblate spheroid (disc shape).

HHIRF for the study of nuclei having high spin is the Spin Spectrometer (sometimes called the Crystal Ball). The Spin Spectrometer, built by Mel Halbert and Dave Hensley of ORNL and Demetrios Sarantites of Washington University, is a 4π array consisting of 72 sodium iodide detectors for measuring gamma rays. This versatile detector system simultaneously measures total energy and gamma-ray multiplicity (related to the total angular momentum). It has become a powerful tool for the study of highly excited nuclei. To illustrate the usefulness of this device, consider an example of a compound nucleus formed in a fusion reaction. The highly excited compound nucleus first "cools" by emission of particles, which in this example (see Fig. 10) are assumed to be three neutrons that produce one nucleus and four neutrons that produce another nucleus. The final nuclei are born in a cloud-like distribution of states called the entry states, which are centered at about 30 to 50 MeV of excitation energy above the ground state but only about 8 to 10 MeV above the "yrast" line.

The yrast line marks the boundary of the lowest energy for states of a given spin. The term yrast is based on the superlative form of the Nordic word *yr*, which means "dizzy"; literally, the yrast state is the most dizzy state of a given energy. The two final nuclei in this illustration will each decay from the entry states in its respective cloud down to the yrast line by emission of a multitude of gamma rays (see Fig. 10). For an even-mass nucleus, these gamma rays are predominantly composed of electric quadrupole (E2) transitions along with some electric dipole (E1) and magnetic dipole (M1) transitions. On reaching the yrast line, the nucleus decays toward its ground state of zero energy by further emission of E2 transitions, each of which removes two units of angular momentum from the system. Thus, by use of the Spin Spectrometer, ORNL physicists may isolate, or at least enhance, a single final nucleus for study by setting gating restrictions on the total decay energy and the total angular momentum associated with a given entry-state cloud.

The Spin Spectrometer's sodium iodide detectors have a resolution inherently too poor to resolve the many gamma rays typically encountered in our work. However, replacing some of these detectors with high-resolution germanium detectors produces an instrument of extreme power for tracking a nucleus from its birth at the entry cloud down to its ground state (see sidebar on page 238). For example, Cyrus Baktash and colleagues in the Physics Division used this unique capability recently to study the ytterbium-158 (^{158}Yb) nucleus during rotation up to very large frequencies.

An interesting new discovery emerged from these experiments. We found that the gamma-ray spectrum of ^{158}Yb behaves much like that of a prolate nucleus up to a spin of $I^\pi = 24^+$. However, from that point up to $I^\pi = 36^+$, there was evidence that the nucleus undergoes a striking shape transition, taking on a triaxial shape (i.e., all three shape axes are unequal). Furthermore, our data indicated that at $I^\pi = 36+$ the shape changed again to that of an oblate spheroid (disc-shaped nucleus). The evolution of these nuclear shapes along the yrast line of ^{158}Yb is illustrated in Fig. 11. With the aid of theoretical calculations by a group in Lund,

The Oak Ridge Compton Suppression Spectrometer System at HHIRF

In recent years at ORNL's Holifield Heavy-Ion Research Facility (HHIRF) and elsewhere, significant achievements have been made in understanding nuclei excited into states of very high angular momentum (spin). The complexities of experimental data obtained from these highly excited nuclei require a new level of sophistication in gamma-ray detection systems. Detector systems having both excellent resolution and high efficiency are required to sense the full energy of each gamma ray emitted by a nucleus as it "cools down" to a lower-energy state. Solid-state germanium detectors provide the needed high resolution of less than 2 keV full width at half maximum of the peak height for 1000-keV gamma rays. However, spectra from Ge detectors contain large background effects because many impinging gamma rays are Compton scattered from the detector, leaving only part of their true energy to be recorded. As a result, many weak transitions in the spectra may be masked by this Compton background.

What is needed is a detector having a resolution as good as that of the Ge detector but much larger stopping power. Unfortunately, no such detector exists. Nevertheless, an almost ideal situation can be achieved if a Ge detector is surrounded by a high-stopping-power medium that senses the Compton-scattered photons and provides a veto (cancellation) signal to the amount of energy left in the Ge detector. In this way, the Compton-background effects in the gamma-ray spectrum can be greatly suppressed.

To provide an improved level of sensitivity in gamma-ray spectroscopy studies of nuclei at high spin, a dozen researchers constructed a Compton-suppression spectrometer system at ORNL that is now operable with 17 fully implemented units and will later be expanded to an array of 20 detectors. The people involved in this project, which was launched about three years ago, are I. Y. Lee, Cyrus Baktash, D. C. Hensley, M. L. Halbert, F. K. McGowan, J. W. Johnson, R. P. Cumby, J. W. McConnell, M. E. Whitley, and Noah Johnson of ORNL's Physics Division; L. L. Riedinger from the University of Tennessee; and Demetrios Sarantites from Washington University.

A very good scintillator that can be used for the suppression shield around a Ge detector is sodium iodide (NaI); however, a relatively new scintillator, bismuth germanate (BGO), has a distinct advantage over NaI in that it has twice its stopping power for gamma rays. In our system the BGO suppression shield is a tapered pentagon or hexagon that has an annular opening extending to about 2.5 cm from its front lip section. The Ge detector is inserted into this opening, and around its 2-cm diameter cooling arm are attached two halves of an additional BGO cylinder to intercept forward-scattered (near 0°) photons. Gamma rays from the source are collimated through the window in the suppression shield and onto the Ge detector.

The power of this Compton-suppression unit is obvious from an examination of the spectra (see figure). The top spectrum contains the unaltered results (normal spectrum) from a cobalt-60 source as seen by the Ge detector. The middle spectrum shows that portion of the normal spectrum that is rejected by the suppression shield. (Note that the full-energy peaks at 1173 and 1333 keV are off scale, but they have been normalized in these data). The rejection of this useless and, in fact, harmful data attests to the real value of the whole idea. Finally, the bottom curve shows the net results that are recorded and used from such a Compton-suppression system. These data reveal that the suppression below the full-energy peaks averages greater than a factor of 5.

A large number of Compton-suppressed units is needed in the system because the two-fold coincidence

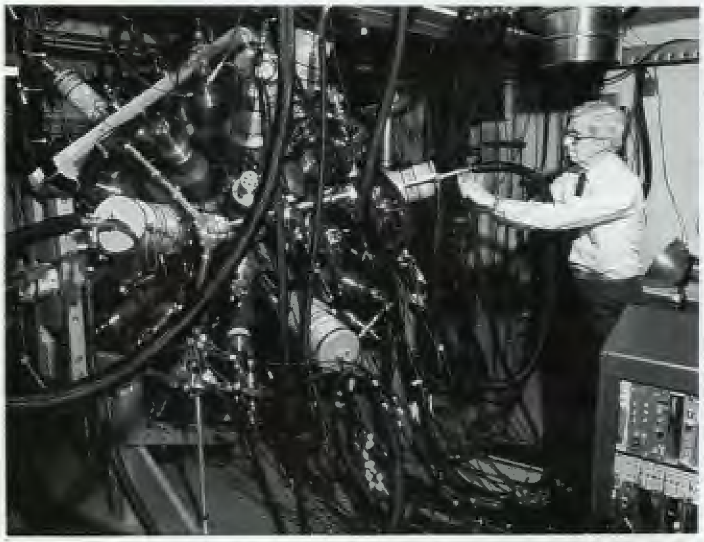
Sweden, Baktash and his colleagues concluded that between spins of 24^+ and 36^+, the coriolis forces caused a gradual decoupling of all the nucleons outside of closed shells and the subsequent alignment of their angular momenta along the rotation axis. The point at which this process was completed is referred to as a band termination. This marked the first such observation of this phenomenon in a deformed rare-earth nucleus.

Noah Johnson and his co-workers are also investigating other nuclei near ^{158}Yb to see if band termination is a general feature in this mass region. Work on one of these nuclei, ^{160}Yb, has been completed, and no evidence has been found for such an effect up to $I = 40^+$ in its yrast sequence. What has come from these studies on ^{160}Yb, which were done jointly with Lee Riedinger and his colleagues from the University of Tennessee, is a highly developed understanding of the intricate features of the level structure in this nucleus up to about 14 MeV of excitation energy. This level scheme, as shown in Fig. 12, illustrates the complex level structures that can be established with the aid of current detector systems.

Until now I have emphasized only the measurements on discrete resolved gamma-ray lines in the spectra; in addition, the gamma-ray spectra of nuclei produced in fusion reactions show a large continuum background under the peaks. Furthermore, the gamma-ray continuum background often extends several MeV above the last resolved peak, which is usually around 1 to 1.5 MeV in a spectrum. This continuum arises because of rate for gamma rays emitted within the sensing time of the detector plus the accompanying electronic circuitry is proportional to n $(n-1)/2$, where n is the number of detectors. To illustrate the situation, a 5-detector system will require almost a factor of 14 more time to collect data of a given statistical quality than will our 17-detector array. Currently, we are using a mixture of BGO and NaI suppression shields, but eventually we hope to use only BGO shields. The NaI units provide a Compton-suppression factor of about 2.5.

Flexibility in the Compton-suppression system is provided by organizing the individual units in any desired geometrical arrangement about the target in a stand-alone mode of operation. However, we recognized that an operational mode of unique power could be attained by substituting some of these units for the solid NaI detectors in the existing Spin Spectrometer at HHIRF. The Spin Spectrometer, sometimes referred to as a crystal ball, is a 4π array of 72 solid-tapered pentagonal and hexagonal NaI detectors. The geometrical considerations of this device dictated the geometry of the Compton-suppression units.

Although the NaI detectors in the Spin Spectrometer lack sufficient resolution to disentangle all of the gamma rays in a spectrum, this device does permit a measurement of both the number of gamma rays and the sum of all their energies resulting from the cooling of a highly excited nucleus produced in a nuclear reaction. In essence, it allows the isolation of a product nucleus at the point of its birth following a nuclear reaction and the tracking of its decay down to the ground state of zero energy. On the other hand, the excellent resolution and high gamma-ray coincidence efficiency of the Compton-suppression system provide the sensitivity to look at the microscopic details of this multitude of gamma rays. Therefore, the marriage of these two systems achieves the enormous power required to gain new insights into the ways nuclei adjust to contain these extreme amounts of energy and angular momentum brought into their systems in nuclear reactions. In fact, recent experiments carried out with this multi-detector array have already produced several important discoveries.—*Noah Johnson, Physics Division.*



Noah Johnson makes adjustments to one of the 17 units of the Compton Suppression Spectrometer System, which is incorporated into the Spin Spectrometer at the Holifield Heavy-Ion Research Facility. The combination of these two devices provides an arrangement of unique power for the study of nuclei excited to both high energy and high angular momentum. The Spin Spectrometer enables the isolation of nuclei at the point of their birth in a nuclear reaction. The Compton Suppression Spectrometer System makes it possible to look at the gamma-ray decay features of these nuclei with both high resolution and high sensitivity as they dissipate what in some cases may be as much as 30 to 40 MeV of excitation energy and 50 to 60 units of angular momentum.

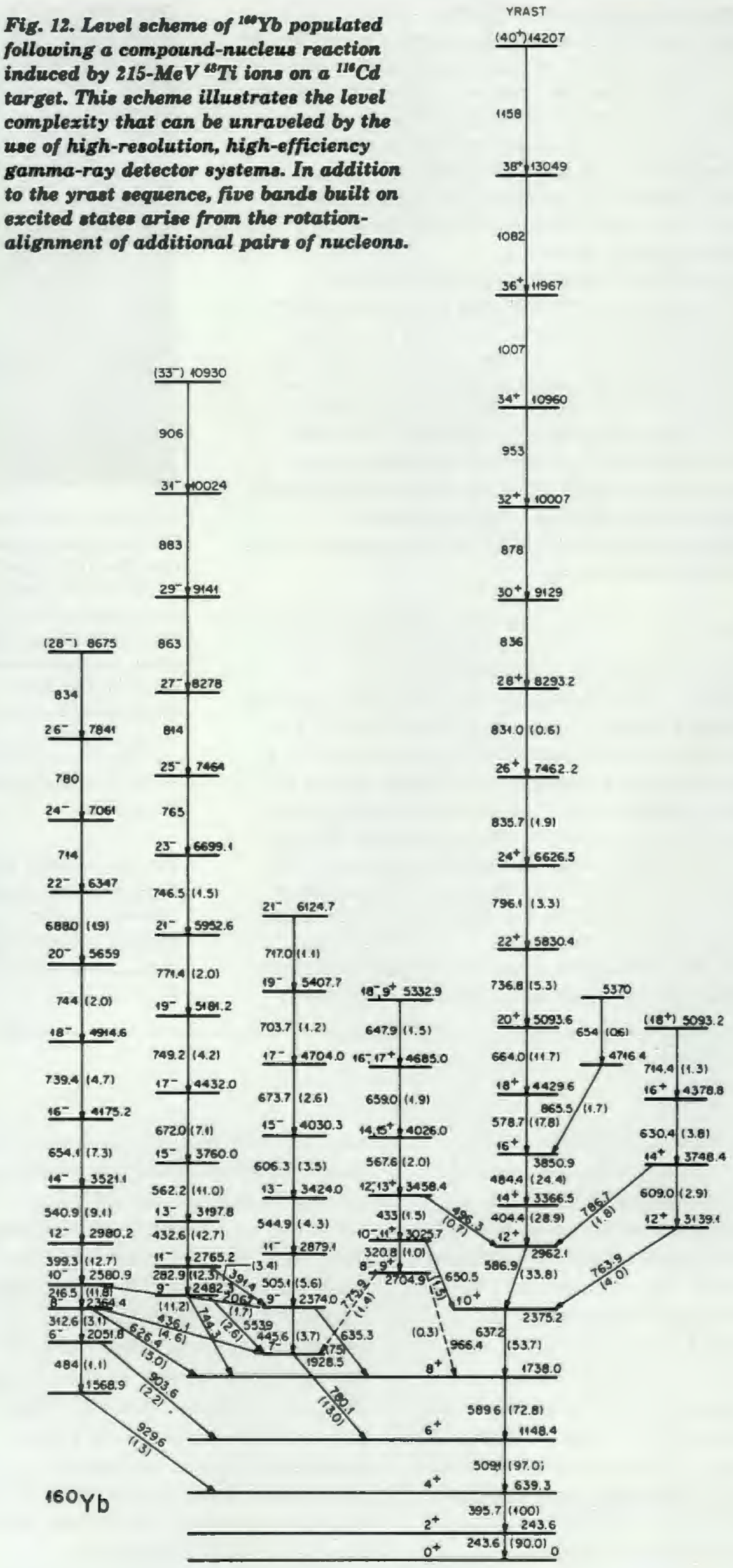
the high density of levels in the vicinity of the entry cloud, and this high density persists until the nucleus has cooled down to near the yrast line. Accordingly, the number of pathways the nucleus can take in this cooling process toward the yrast line is extremely large. The statistical distribution of the resulting gamma-ray energies is so intense and evenly spaced that, even with the high resolution of a germanium detector, they cannot be resolved.

To track the nucleus as it rotates to higher and higher angular momentum—to the point that it fissions—methods must be devised to extract the physics contained in the continuum. A few years ago, Bent Herskind at the Niels Bohr Institute in Copenhagen suggested an approach for analyzing the continuum gamma-ray spectrum known as the energy-energy correlation method. This method involves building a two-dimensional gamma-gamma coincidence map. At ORNL, I. Y. Lee and colleagues have used this idea to develop sophisticated analysis techniques that can be applied to the data taken with the Spin Spectrometer. Using these techniques they have isolated regions in the entry cloud and followed the route of decay from these regions down to the yrast line. Such data are now providing new insight into such properties as the moments of inertia of the nucleus along these routes and the multipolarity of many of the associated gamma-ray transitions. The latter feature has revealed, to the surprise of many, that some nuclei retain their collective behavior at these very large values of spin (i.e., the properties signify that the behavior is still governed primarily by the nucleons that move in concert vs behavior dominated by some of the individual nucleons).

To provide a more detailed understanding of the microscopic structure of these high-spin nuclear states, measurements must be made of the electromagnetic multipole moments of the transitions connecting the states. These moments are directly related to the wave functions (quantum-mechanical descriptions) of the states and, thus, provide pivotal information for a more microscopic probing of the collective behavior. These transition moments are obtained from a measurement of the lifetimes of the gamma-ray transitions connecting any two states. The mean lifetime is defined as the time during which the probability that the state will decay is 69%. In rotational nuclei these lifetimes range from less than one picosecond (10^{-12} s) for a state having spin 20 to possibly longer than 1000 picoseconds for a state having spin 2. Such short lifetimes can be measured by Doppler-shift techniques that take advantage of the large recoil velocity imparted to a product nucleus in a heavy-ion-induced reaction.

Noah Johnson, Francis McGowan, and their colleagues make such measurements using the recoil-distance method. In this technique a stopping medium (stopper) is placed at some variable distance from the target. Nuclei produced in the reaction recoil out of the target, and excited states may decay in flight or after the nucleus comes to rest in the stopper, depending on the lifetime of the state, the recoil velocity, and the distance between the target and stopper. If the state decays in flight, the gamma-ray energy is shifted to a higher value. Spectra obtained at various target-stopper

Fig. 12. Level scheme of ^{160}Yb populated following a compound-nucleus reaction induced by 215-MeV ^{48}Ti ions on a ^{116}Cd target. This scheme illustrates the level complexity that can be unraveled by the use of high-resolution, high-efficiency gamma-ray detector systems. In addition to the yrast sequence, five bands built on excited states arise from the rotation-alignment of additional pairs of nucleons.



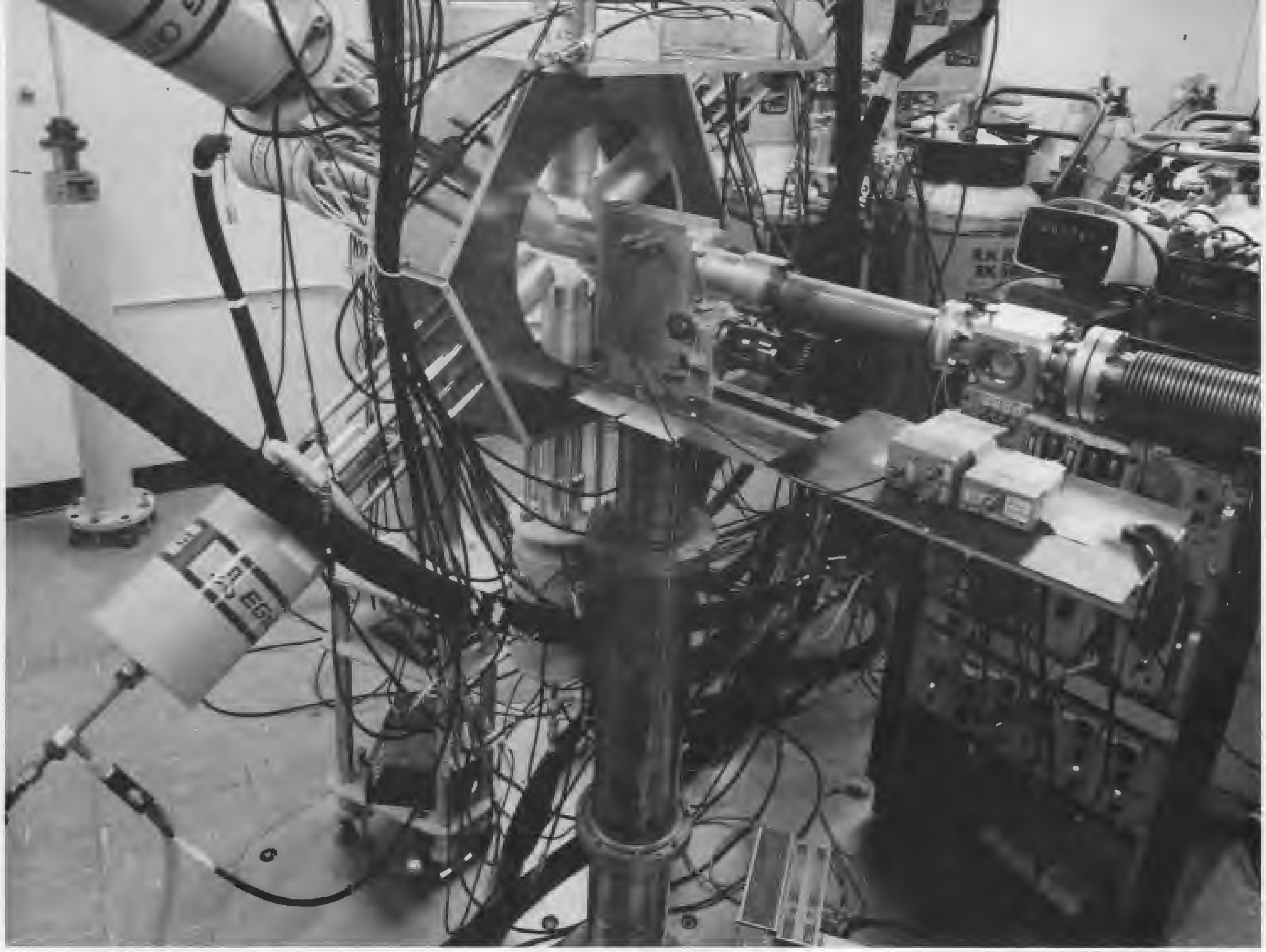


Fig. 13. Apparatus for carrying out Doppler-shift recoil-distance lifetime measurements of high-spin states in the gamma-gamma coincidence mode. The Doppler-shift apparatus is located at the center of the ring of six germanium detectors that are used for coincidence gating of the Doppler-shift spectrum. The latter is recorded in the germanium detector positioned just beyond the end of and in line with the Doppler-shift device.

separations provide the information necessary for extraction of the lifetimes. Data analyses are simplified considerably if the measurements are done in the gamma-ray coincidence mode. The Doppler-shift apparatus and an array of germanium detectors to accomplish this are shown in Fig. 13.

Some of the recent lifetime measurements were performed on deformed nuclei having about 90 neutrons (e.g., ^{160}Yb, ^{161}Yb, and ^{158}Er). All of these nuclei have prolate shapes near the ground state; however, the experimental results indicate that when stressed, each nucleus evolves into a triaxial shape. We conclude that these nuclei exhibit little resistance to deformation-driving influences, which is quite in line with recent theoretical calculations. A more visual description of the processes occurring in these nuclei is that in the low-lying states ($I < 12$), the rotational motion of the collective ensemble of nucleons dominates the pattern of behavior reflected in the very short lifetimes of the states. Beyond spin 14, where two neutrons have decoupled from the core, the decay rates of the states are slowed down because the nucleus is driven to a triaxial shape with less collective behavior as a result of the independent influence of this pair of particles.

Summary

These phenomena that occur when nuclei are stressed to high excitation energy and to high rotational frequencies are the basis for the current excitement in nuclear-structure physics. Much has been learned over the past few years, but we have only scratched the surface in understanding these rotating, highly excited nuclear systems. Early in 1986 the Physics Division completed a proposal to the U.S. Department of Energy for the construction of a major upgrade to the HHIRF accelerator system. The potential for new research if this facility is built is truly exciting and would certainly provide new insight into the mysteries of the stressed nucleus and its constituents. ornl

Jack Harvey is director of the Oak Ridge Electron Linear Accelerator (ORELA) in ORNL's Engineering Physics and Mathematics Division. He came to ORNL in 1955 and became an ORELA co-director ten years later. Before coming to ORNL, he worked for five years as a research physicist at Brookhaven National Laboratory. He has a B. Sc. degree from Queen's University in Canada and a Ph.D. degree from the Massachusetts Institute of Technology. At ORNL Harvey's research interests have centered on neutron cross sections and electron linacs. Between 1967 and April of this year, he served as secretary-treasurer of the Division of Nuclear Physics of the American Physical Society. Here, at the terminal of a data acquisition computer, Harvey studies a total cross-section measurement of uranium-235.

Probing Nuclei Using ORELA's Energetic Neutrons

By JOHN A. HARVEY

The structure of nuclei and the formation of the heavier elements in stars are being studied at Oak Ridge National Laboratory with the help of fast neutrons. These neutrons, produced at the Oak Ridge Electron Linear Accelerator (ORELA), are more energetic than those used in studies at research reactors (see Robert M. Nicklow's article on page 88) and are produced in very intense nanosecond pulses. Using the neutron time-of-flight technique, ORNL physicists have determined information about nuclei and the interiors of stars that cannot be revealed any other way.

Neutron Spectrometry and Nuclear Structure

Neutrons are an important probe of nuclear structure and reaction mechanisms, yielding information complementary to that obtained by high-energy photons and various energetic charged particles, such as protons, alphas, and heavier ions. Often results from neutron studies help interpret data obtained by these other probes.

Because neutrons do not possess an electric charge and, hence, undergo no Coulomb repulsion, the incident kinetic energy required to produce a nuclear reaction when nuclei are bombarded with neutrons can be very small. Neutrons having energies of only a few electron volts (eV), or velocities of $\sim 3 \times 10^4$ m/s ($\sim 10^{-4}$ of the velocity of light), can be absorbed by a heavy nuclide such as uranium-238 (^{238}U) to form the compound nucleus ^{239}U. The narrow peaks, or resonances (very narrow energy regions in which strong interactions occur) that are observed in a neutron cross-section measurement for this nuclide (i.e., the probability that a neutron will interact with the target nuclide) are separated on the average by only 5 eV and correspond to excited states <0.1 eV wide in ^{239}U at an excitation energy of 4.8 MeV(1 MeV $= 10^6$ eV). A similar situation occurs when a neutron interacts with a lead-207 (^{207}Pb) nucleus to form ^{208}Pb (see Fig. 1).

Neutron spectrometry, which is performed extensively at the ORELA, is a unique technique for examining the states of nuclei in a narrow energy region just above the neutron separation energy, S_n, the excitation energy at which a nucleus can emit a neutron. The excitation energy region from 5 to 10 MeV, depending on the nuclide, can be studied in extremely fine detail (see Fig. 1); such resolution, particularly for heavy nuclides, is

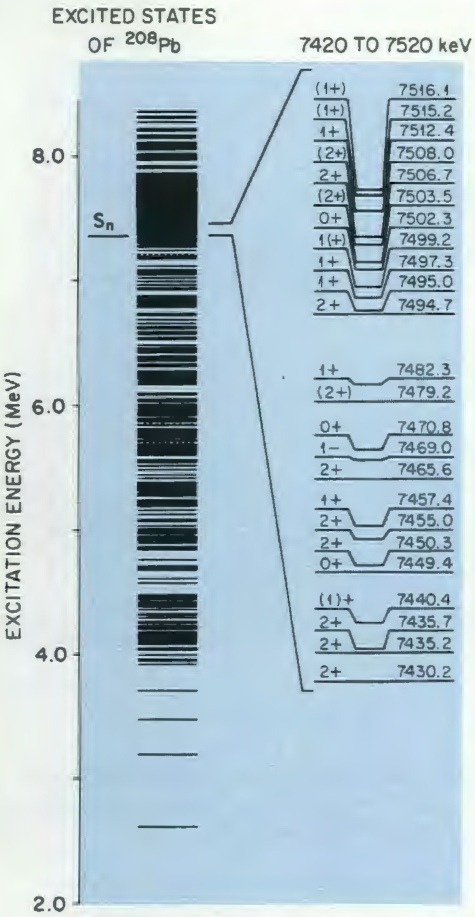


Fig. 1. This schematic shows the excited states of ^{208}Pb and the region above 7.4 MeV, which is studied with neutrons on ^{207}Pb. The numbers on the right are the excitation energies of the excited states of ^{208}Pb in keV (1 keV = 10^3 eV). The numbers to the left are the angular momenta (in units of ħ) and parity (+ or −) of the state.

Fast neutrons provide information about nuclei and the interiors of stars that cannot be revealed any other way. An important source of fast neutrons is the Oak Ridge Electron Linear Accelerator (ORELA) at ORNL. ORELA physicists have confirmed theories about the structure of nuclei, the neutron-induced fission for certain heavy nuclides, the heavy-element composition of stars, and the age of our galaxy.

not available with any other nuclear probe. The size of the nucleus, the level densities (the number of excited states per MeV), and the strengths (the average probability of decay by emission of neutrons, gamma rays, etc.) of the excited states of similar character can be obtained. Details of nuclear deformations and dynamics can be determined from a comprehensive study of the decay of these highly excited compound nuclear states by the re-emission of neutrons, by gamma-ray emission to lower-energy states, by fission of heavy nuclides, or by charged-particle emission (alphas or protons) from light nuclides.

Neutron Time-of-Flight Spectrometry at ORELA

Neutron spectrometry requires that the interaction strength between neutrons and nuclei be measured as a function of the energy of the neutron. A high-flux fission reactor such as ORNL's High Flux Isotope Reactor, which is an intense source of very low-energy neutrons (<0.1 eV), provides enough neutrons of higher energy to be usable for neutron spectrometry up to 10 eV with the use of a monochromator. Monoenergetic neutrons, which have an energy spread of $\sim 10^3$ eV when produced using monoenergetic protons on a thin target such as lithium-7 or tritium, are useful for measurements above 10^5 eV. The energy region between these limits can be studied in detail only by using the time-of-flight technique and a neutron source that is pulsed and has a wide range of energies. In this technique, the energy of the detected neutron is determined from the time required for it to travel a known distance.

ORELA, which was built over 16 years ago and is operated by ORNL's Engineering Physics and Mathematics Division, uses the time-of-flight technique for neutron measurements in the energy range from 10^{-3} to 10^8 eV. ORELA consists of a 180-MeV electron accelerator capable of producing intense nanosecond pulses of neutrons (5×10^{18} fast neutrons/s during the pulse) from a tantalum target surrounded by a water moderator to produce lower-energy neutrons; it has many evacuated flight paths up to 200 m long for high-energy neutron measurements. At ORELA, many types of neutron cross-section measurements (total, capture, fission, elastic scattering, and gamma ray and neutron production) that have an energy resolution as good as 0.05% for neutron energies below 1 MeV have been made using appropriate detectors at the ends of the flight paths. An example of the complexity and quality of the data obtained is shown in Fig. 2 for the neutron total cross section of calcium-40 (^{40}Ca + n). In addition to meeting basic research needs, many neutron cross sections have been made at ORELA to satisfy applied needs for nuclear data to guide the design and analyses of specific types of nuclear systems. These systems have included both fission reactors (particularly fast breeder reactors) and fusion devices.

Excited Nuclear States Having Simple Configurations

The location and properties of low-lying excited states for many nuclides have been measured at ORNL and other laboratories and can be understood from a simple shell-model theory that deals with a single nucleon moving in the nucleus under the influence of a "core" formed from all the other nucleons. More complicated nuclear theories have predicted excited states and their properties up to 10-MeV excitation energy for some light and closed-shell heavier nuclides. These theoretical calculations include not only the single-particle states described as a nucleon plus the core in its ground state but also these single-particle states and the core that has been excited to low-lying states. Neutron cross-section measurements and analyses at ORELA in recent years have provided the data needed to test the validity of various nuclear model calculations.

A recent neutron cross-section measurement of ^{48}Ca + n at ORELA (shown in Fig. 3) uncovered the presence of three strong resonances in the neutron energy range of 0.8 to 2.0 MeV for neutrons bombarding this calcium nuclide. Using a multilevel analysis code developed by Nancy Larson and Francis Perey of ORNL, Bob Carlton (a collaborator from Middle Tennessee State University) showed that these three strong resonances result from the interaction of incident neutrons having an orbital angular momentum, $l = 2$. These three strong resonances (at an excitation energy from 6 to 7 MeV) account for 45% of the single-particle strength predicted from the simple shell-model theory. Theoretical calculations by Boris Castel (an ORELA collaborator from Queen's University in Canada) using a more complicated theory gave three strong states in this energy region, representing 58% of the available single-particle strength, fragmented by particle-core excitation. Thus, Castel's results are in excellent agreement with the experimental data from ORELA.

Another example of the contribution of high-resolution neutron spectrometry is spin-flip giant resonances, as discussed by Fred Bertrand in the preceding article in this issue. From ORELA measurements and analyses, Dan Horen, Nat Hill, and I conclusively assigned the angular momentum and parity quantum numbers to hundreds of resonances corresponding to states in ^{208}Pb nuclei at excitation energies from 7.4 to 8.0 MeV (see Fig. 1). Of particular interest were the 1^+

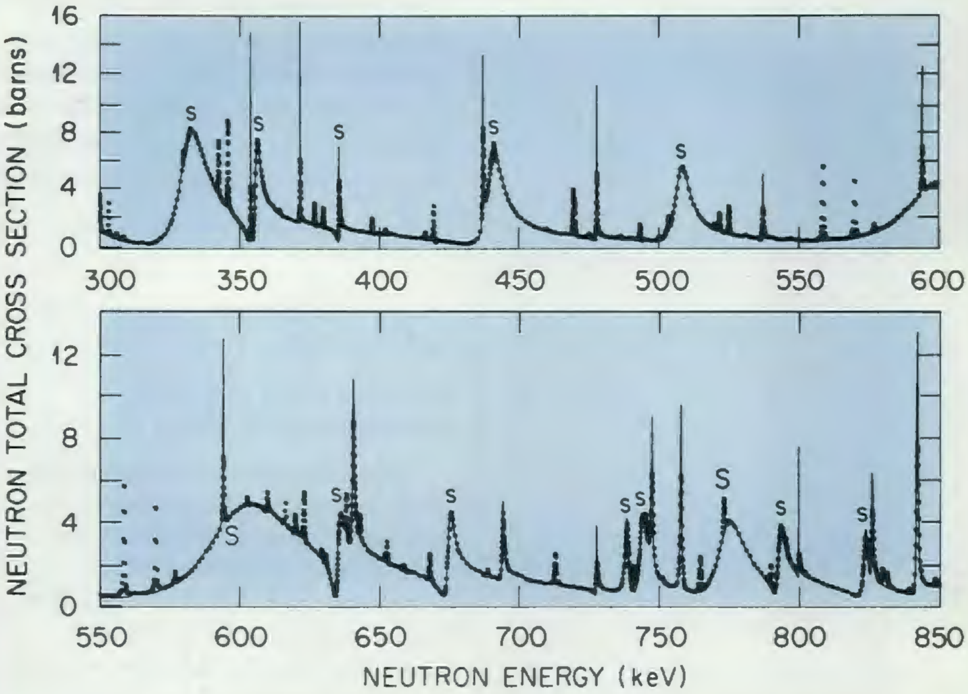


Fig. 2. Large **l** *= 0 resonances in the ^{40}Ca neutron total cross section are asymmetric and show interference. The extremely good energy resolution and low background available to researchers at ORELA permit detailed and precise resonance analysis.*

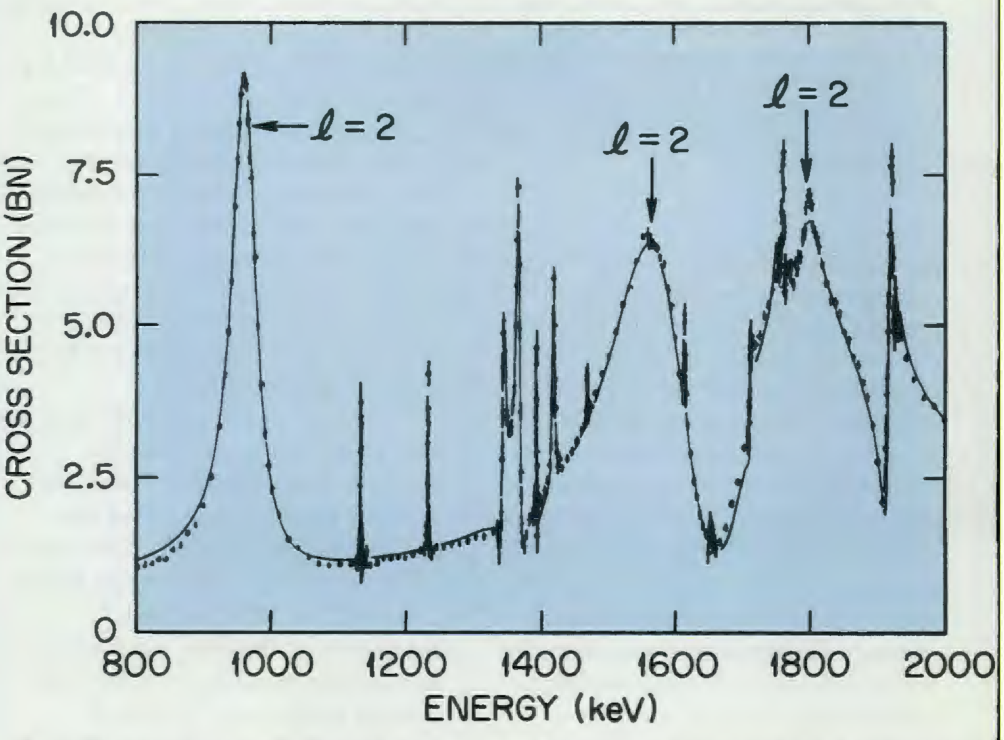


Fig. 3. The three large resonances for ^{48}Ca + n at 940, 1560, and 1770 keV (labeled **l** *= 2) result from incident neutrons having an orbital angular momentum of 2.*

On a collaborative experiment with Los Alamos National Laboratory, Nat Hill works on stabilizing the gain of photomultiplier tubes at high counting rates.

states (one unit of angular momentum and positive or even parity) in this region that can decay by gamma rays to the ground state (measured at ORELA by S. Raman and colleagues) by M1 transitions (a change of one unit of angular momentum and no change of parity). It was discovered from ORELA data that 1^+ resonances that absorb neutrons strongly also decay strongly by M1 gamma radiation to the ground state. A discrete group of resonances having enhanced neutron strength is known as a doorway state. Doorway states have been observed at ORELA by Horen, Hill, and me for several target nuclides, such as ^{207}Pb and ^{206}Pb; we saw the effect not only for incident neutrons having zero incident angular momentum but also for $l = 1$ and 2. However, the doorway state for $l = 1$ neutrons at 100 keV in ^{207}Pb + n, which is 20 keV wide and contains 7 resonances, is extra special because these same states possess a significant fraction of the M1 strength in this energy region.

Surface Effects in Nuclear Optical Model Potential

For many nuclides, microscopic theories as just discussed cannot predict the exact location and modes of decay of the complicated excited states above the neutron separation energy. However, the average over the detailed structure can be interpreted in terms of a "nuclear optical model potential." For many years the phenomenological optical model (in which the nucleus plus neutron system is considered analogous to a crystal ball that refracts and absorbs an incident light wave) has been valuable for describing nucleon-nucleus scattering, not only for low-energy neutrons but also for nucleons having energies up to several hundred MeV. Recent extensive theoretical studies have established the fundamental basis for the model for energies both above and below the nucleon separation energy and have pointed the way towards further measurements.

The high-resolution measurements at ORELA are making a unique contribution to the further development of the model because these measurements, in contrast to measurements at higher energies, reveal the contributions of individual partial waves of both even and odd parities. The bombarding neutron is treated as the sum of many partial waves having angular momenta $l = 0, 1, 2, 3$, etc. If a resonance is caused by an odd partial wave component, the parity of the nucleus is changed. This information has been obtained by measuring the cross section of ^{40}Ca when bombarded with neutrons in the energy range from 0 to 1 MeV (Fig. 2). Qualitatively, the resonances fall into two classes: the narrow resonances formed by $l = 1$ neutrons and the wide resonances formed by $l = 0$ neutrons, which are asymmetrical in shape. By a careful analysis, Cleland Johnson and colleagues deduced the neutron-scattering functions of the partial waves, which can then be energy averaged for each partial wave for comparison to the model. Even though only a few partial waves are measured, the results are significant because the wave functions for opposite parities behave differently in the region near the surface of the nucleus, where the part of the potential that causes absorption is at its maximum. Comparisons of the averages for the opposite parities provide information on not only the imaginary potential at the nuclear surface but also the related real potential at the nuclear surface. Measurements have been made and analyzed for several nuclides by ORNL's Horen and Johnson and Ron Winters (a collaborator from Denison University) and, with the help of Professor Claude Mahaux from the University of Liege, are being interpreted in terms of the recent theories.

Highly Deformed Nuclear Shapes and Neutron-Induced Fission

When certain heavy nuclei absorb neutrons, they may emit gamma radiation or break apart into two lighter nuclei. Neutron-induced fission of heavy nuclides is a powerful tool for studying these highly deformed nuclear shapes and the potential barrier for fission as a function of deformation. In the liquid-drop model the potential energy as a function of deformation is determined by surface tension and Coulomb repulsion, which results in a single humped barrier for fission. With the addition of a shell-energy correction arising from shell structure of the nucleus, the potential barrier as a function of deformation develops a minimum between two humps. In this second well are excited energy states, which are coupled to the excited states in the first well (i.e., tunneling through the first hump between the two wells). This shell correction gives rise to the intermediate structure (not a uniform distribution) that has been observed for many nuclides at ORELA over extended neutron energy regions. These nuclides include thorium, protactinium, uranium, and plutonium isotopes (^{232}Th, ^{231}Pa, ^{234}U, ^{238}U, and ^{240}Pu).

Detailed intermediate structure in subthreshold fission for ^{238}U was discovered and reported by F. C. Difilippo and others at ORNL (see Fig. 4). Although the capture cross section shows many resonances in the energy region shown in the figure, only a few of the resonances have appreciable fission components. The largest fission width (probability that a nucleus will decay by fission) in this energy region is 10^{-3} eV, but fission widths as small as 10^{-8} eV have been measured for other

Gypsy Tweed, a summer student, and Jack Craven plot the results of neutron experiments at terminals wired into the new Vax 11/785 at the operator console of ORELA.

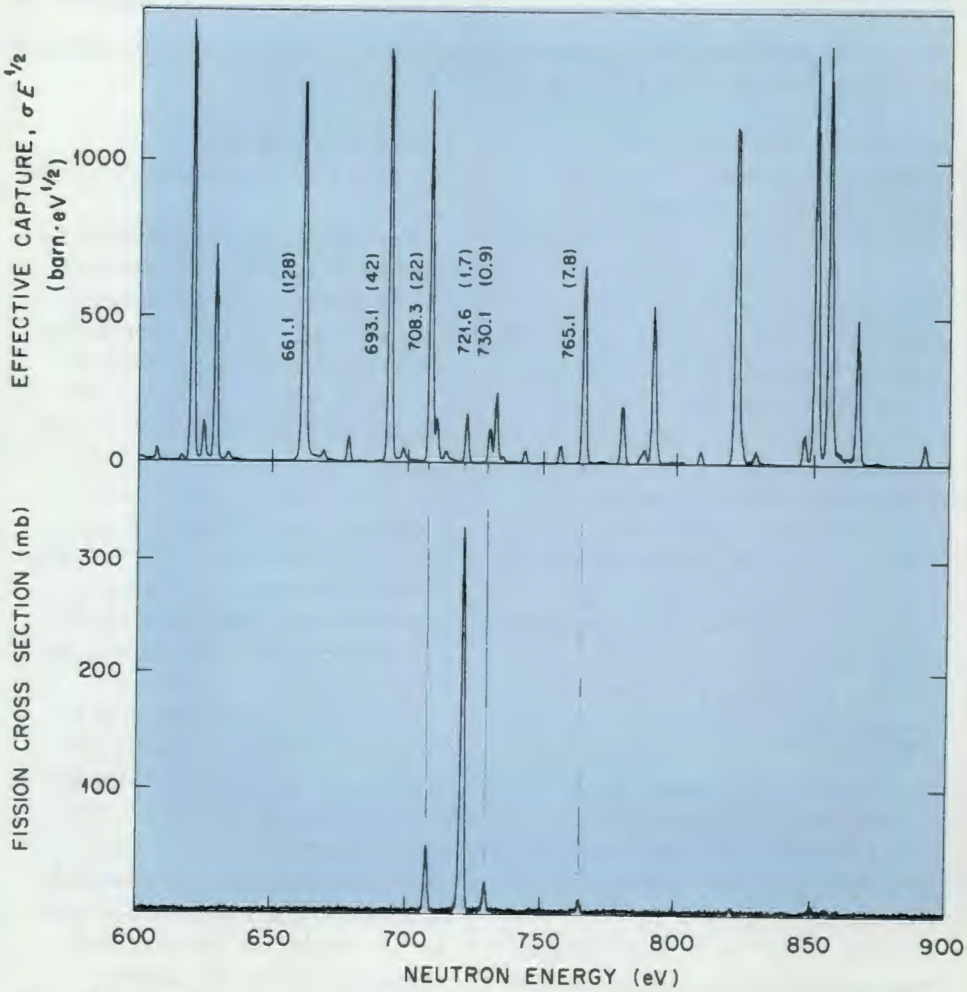


Fig. 4. Neutron capture in uranium-238 (upper curve) is particularly important to reactor physics because of the strong resonance structure. The presence of only a few of these resonances in subthreshold fission (lower curve) reflects a fascinating aspect of nuclear-structure physics.

resonances for ^{238}U. The striking phenomenon shown in Fig. 4 is understood in terms of the double-humped fission barrier in which the spacing of the fine-structure $l = 0$ resonances (~20 eV) is determined from the states in the first well; on the other hand, the spacing of the fission clusters (~1000 eV) is determined by the states in the second well.

From high-resolution ORELA data for many nuclides, a great deal has been learned about the properties of the first and second wells, such as barrier heights for the two wells, differences between well depths, and coupling between the states of the two wells. For example, using ORELA data obtained by ORNL's Gerard de Saussure, Dave Olsen, Rex Ingle, Rafael Perez and Dick Macklin, and George Auchampaugh (an ORELA collaborator from Los Alamos National Laboratory) found that the capture width of the strong fission resonance at 721 eV in ^{238}U is only about 20% of the average capture width (23×10^{-3} eV) of the fine-structure resonances in the first well (see Fig. 4). The fission width of the 721-eV resonance is 1.6×10^{-3} eV. This low value of capture establishes this resonance as one in the second well.

Measurements at ORELA of the angular distribution of fission fragments for ^{231}Pa have been interpreted in terms of a third well of the asymmetrically deformed potential energy surface for fission. Also, low-energy subthreshold fission and total cross-section measurements on ^{231}Pa showed that the fission strength for low-energy neutrons was randomly distributed over the fine-structure resonances and not in clusters, as for subthreshold fission for ^{238}U.

Formation of Heavy Elements in Stars

How heavy elements are formed in stars by the capture by lighter elements ($A > 56$) of neutrons at high temperatures (stellar nucleosynthesis) is of great interest to physicists and astronomers. Helping to answer this question is a highly productive program at ORELA (headed by Macklin) that measures neutron-capture cross sections in the 1-keV to 1-MeV energy region. These data are needed for interpretation of the stepwise buildup of elements by neutron capture at temperatures ($\sim 3 \times 10^8$ K or ~30 keV neutron energy) and densities typical of the interiors of stars.

When this capture process occurs with explosive rapidity (called the r-process), it proceeds by producing increasingly neutron-rich nuclides up to those that spontaneously fission or have very short beta-decay lifetimes. When the process is very slow (called the s-process), as in deep layers of old red giant stars, the rate is determined by neutron-capture cross sections of the stable nuclei for energies near 30 keV because most of the radioactive nuclei have time to decay by beta emission before another neutron capture occurs. This process terminates by alpha decay just beyond the synthesis of bismuth.

Neutron-capture cross sections have been obtained by Macklin and collaborators on more than 150 pure or highly enriched isotopes in the mass range from 56 to 209. The abundances of nuclides predicted by using these cross sections are in good agreement with the values found on the earth, on the moon, and in meteorites. Where the r-process can also contribute to an observed abundance, ORELA measurements allow this contribution to be singled out. This information is particularly important in a few cases in which an exceptionally long-lived decay step allows the age of our galaxy to be inferred from the abundance of the decay product. The beta-decay of rhenium-187 (^{187}Re), which has a half-life of 4.2×10^{10} years, to osmium-187 (^{187}Os) has long been recognized as a potential chronometer for stellar nucleosynthesis. Because ^{187}Os cannot be produced by the r-process, the present-day observed abundance is presumed to be the result of the decay of ^{187}Re, the production from s-process capture in ^{186}Os, and the depletion from s-process capture in ^{187}Os. The calculated abundance of ^{187}Os from nucleosynthesis depends on the abundance of ^{186}Os and the ratio of the average capture cross sections for ^{186}Os and ^{187}Os appropriate for the stellar temperature at the site of the s-process, 30 keV. This ratio has been determined from ORELA capture data and a correction based on an optical model calculation for capture by a low-lying excited state in ^{187}Os. From the excess abundance of ^{187}Os caused by ^{187}Re decay, a value of $(11 \pm 2.5) \times 10^9$ years is obtained for the age of our galaxy. This value is in good agreement with the value of $(13 \pm 4) \times 10^9$ years based on U/Th chronometers.

Macklin and Winters have derived a mean time between successive neutron captures from the s-process—~23 years—from a branch in the production chain at mass number $(A) = 204$ and from ORELA capture data. New data on the rubidium isotopes (^{85,87}Rb) obtained at ORELA are said to offer the only usable indication for neutron density in calculations of intermediate mass ($A = 56$–100) nucleosynthesis in stars that pulsate. More generally, the traditional interest in slowly simmering nucleosynthesis in the core of a star is giving way to more realistic models that involve changing conditions at boundaries of shells in stars. There remains a need for capture cross-section data on the more neutron-rich isotopes such as ^{48}Ca. Without a doubt, neutron-capture data from ORELA have been invaluable to the field of stellar nucleosynthesis.

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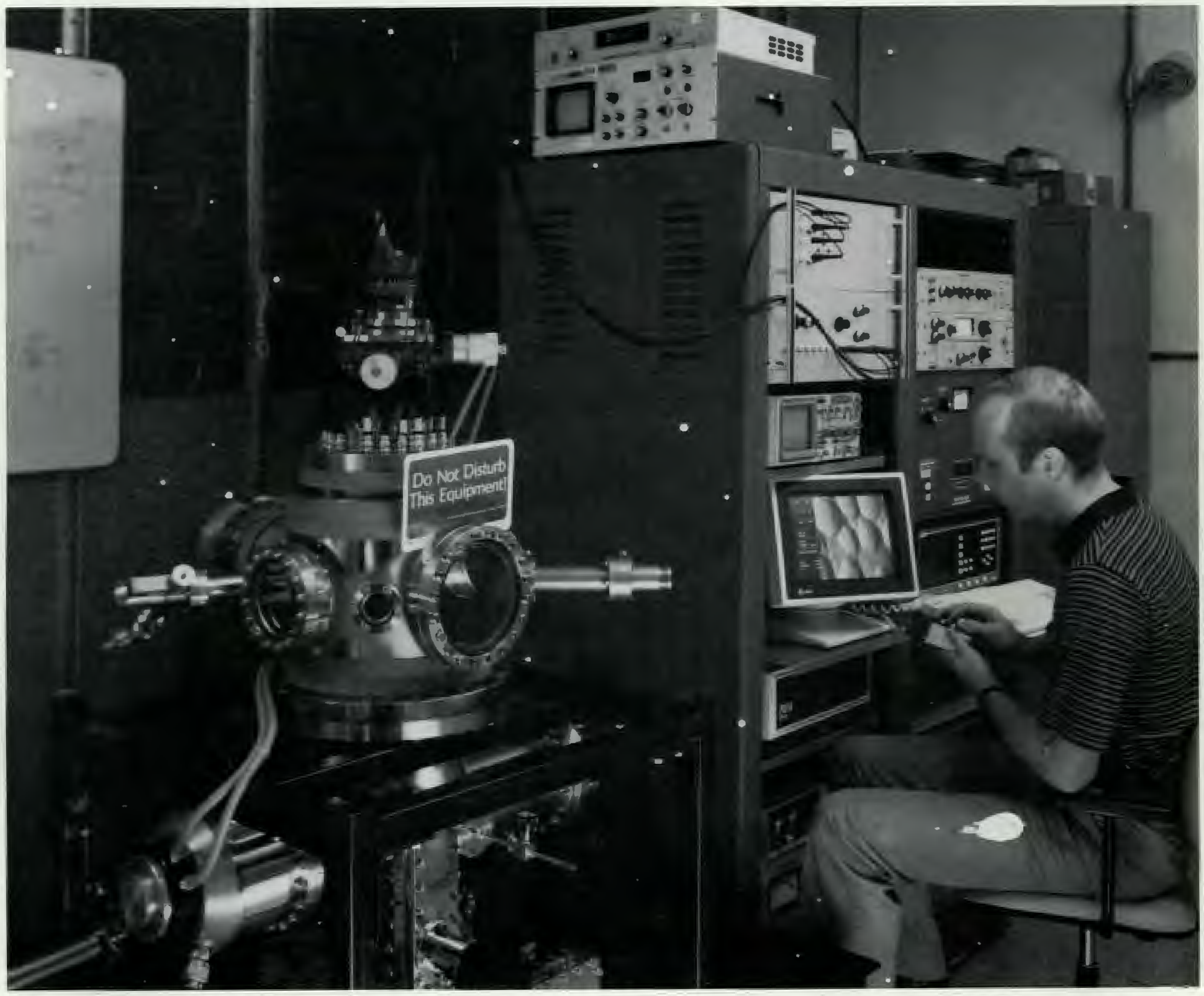

Bruce Warmack works at the controls of a scanning-tunneling microscope at ORNL, which recently imaged single atoms. For more details on the scanning-tunneling microscope (the invention of which was recognized by the 1986 Nobel Prize for Physics), see News Notes on page 127.