

[Invited paper for the Second Euroconference and NEA Workshop on Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources, held in Grenoble, France, Sept. 10-13,2000]

THE PRESSURE BEHAVIOR OF ACTINIDES VIA SYNCHROTRON RADIATION

R. G. Haire¹, S. Heathman², T. Le Bihan³ and A. Lindbaum⁴

¹ Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375 USA

² Institute for Transuranium Elements, Karlsruhe, Germany

³ European Synchrotron Radiation Facility, Grenoble, France

⁴ Institute for Experimental Physics, Technical University of Vienna, Austria

A contractor of the U.S. Government under contract DE-AC05-00OR22725 has authored this manuscript. The U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this document, or allow others to do so, for U.S. Government purposes.

THE PRESSURE BEHAVIOR OF ACTINIDES VIA SYNCHROTRON RADIATION

R. G. Haire¹, S. Heathman², T. Le Bihan³ and A. Lindbaum⁴

¹ Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375 USA

² Institute for Transuranium Elements, Karlsruhe, Germany

³ European Synchrotron Radiation Facility, Grenoble, France

⁴ Institute for Experimental Physics, Vienna University of Technology, Austria

Abstract

Various aspects of performing high-pressure studies with radioactive f-elements using synchrotrons as sources of X-rays are discussed. For ultra-high pressures, intense well-focussed beams of 10 to 30 microns in diameter and a single wavelength of 0.3 to 0.7 Å are desired for angle dispersive diffraction measurements. Special considerations are necessary for the studies of transuranium elements under pressure at synchrotron facilities. Normally, with these actinides the pressure cells are prepared off-site and shipped to the synchrotron for study. Approved containment techniques must be provided to assure there is not a potential for the release of sample material. The goal of these high-pressure studies is to explore the fundamental science occurring as pressure is applied to the actinide samples. One of the primary effects of pressure is to reduce interatomic distances, and the goal is to ascertain the changes in bonding and electronic nature of the system that result as atoms and electronic orbitals are forced closer together. Concepts of the science being pursued with these f elements are outlined. A brief discussion of the behavior of americium metal under pressure performed recently at the ESRF is provided as an example of the high-pressure research being performed with synchrotron radiation. Also discussed here is the important role synchrotrons play and the techniques/procedures employed in high-pressure studies with actinides.

Introduction

Electromagnetic radiation has long been employed for characterizing materials, and third generation synchrotrons offer unparalleled opportunities in this regard. In the area of X-ray diffraction, a classical tool for structural determinations, synchrotrons offer not only a very intense X-ray source but also provide beams of superior dimensions and stability that can be customized readily. These are the characteristics that have expanded greatly the ability to perform ultra-high pressure research, and have attracted researchers wishing to investigate actinides under pressure at synchrotron facilities.

There has been increased interest in the effects of pressure on f-elements and compounds, especially as pressures in the megabar region are now easily attainable. An important issue in these studies is to determine how the decreasing interatomic distances, brought about by applying pressure, can effect the electronic nature and/or bonding in these materials. Specifically, for the f-elements, the question is whether such changes effect the normally non-bonding (localized) f-electrons themselves and incorporated them in some manner into the bonding of the materials. The 5f electrons of the actinide elements, which are all radioactive to varying degrees, are particularly intriguing in this regard.

Whereas it is accepted that the actinide elements from protactinium through plutonium have f electrons involved in their bonding at normal pressure, in contrast the transplutonium elements are considered to be more lanthanide-like and do not. Thus, one goal for investigating transplutonium

metals is to determine if pressure can bring about delocalization of their f electrons and thereby alter the nature of the bonding in the materials.

The spatial extent of the 5f electrons is greater than that of the 4f-electrons, and close in energy to the 6d, 7p and 7s electrons. Altering certain parameters, such as pressure, may then change the total energy of the system. An especially interesting element in this regard is americium (element 95), the near neighbor of plutonium (element 94). At room temperature and pressure, plutonium is accepted as having overlapping orbitals, which involve its 5f electrons (hybridized band structure), while americium has localized 5f electrons (e.g., 5f electrons in a narrow region). The question becomes whether pressure can reverse this sudden change in 5f-electron behavior that is observed in this region of the actinide series. That is, can pressure cause the 5f electrons of americium to participate in bonding? There is also interest in the behavior of different actinide compounds and alloys under pressure. These latter materials present an additional complexity in that more than one kind of atom is involved.

Structural information in high-pressure studies is basically obtained in the classical manner using X-rays, except that a diamond anvil cell (DAC) is employed for applying pressure on the sample. The DAC imposes some restrictions in the diffraction studies, but the nature and flexibility of the synchrotron radiation makes it the preferred choice for pressure work, especially at the higher pressures. There are several obvious advantages to using synchrotron radiation for pressure studies, but for pressures of one or more megabars, the small (10-30 micron diameter) X-ray beams of high intensity are very significant, in some instances even being a necessity.

This work will cover different aspects, both positive and negative, of performing high-pressure studies with radioactive f-elements at synchrotron facilities. The important role synchrotrons play in studies with actinides, together with the needs and responsibilities of scientists performing such investigations will also be addressed. Some of the science being pursued with actinides will be outlined and demonstrated by a brief discussion of selected studies, which includes the investigation of americium metal under pressure performed recently at the ESRF (Grenoble, France).

Experimental Aspects

Materials

The actinide elements are all electropositive metals and display variable reactivity toward water and air. They are prepared by various techniques [1-3], depending on their particular physicochemistry and availability. In experiments with the limited quantities of the element and with isotopes having short half-lives, the preparation of the metals becomes an integrated part of the high-pressure studies. Reactivity of the metal is a concern, especially considering the small amounts of the sample employed in the high-pressure study. In most cases, sample loading of the DAC must be done in inert atmosphere gloved boxes to protect the sample from moisture and air, as well as to provide containment for the radioactive materials. Thought must also be given to the pressure-transmitting medium being used, to assure that it will not bring about sample degradation, especially with a lengthy transportation period. Generally, silicon oil, liquefied gases (Ar, He, N₂, etc.) are acceptable, whereas alcohol (e.g., mixtures of methanol and ethanol) can react with some actinide metals, especially those with higher radiation fields that decompose the alcohol to more reactive products.

Diamond Anvil Cell (DAC)

There are a number of diamond anvil cell (DAC) designs and it is not the purpose here to compare these designs. Nor is there an attempt to discuss the preparation or loading/unloading techniques employed. Rather, the discussion is aimed at operations necessary to allow radioactive samples in a DAC to be studied at a synchrotron.

In our work we have employed three cell designs: (1) Cornell design [4]; (2) Syassen-Holzappel design [5]; and the Megabar design [6]. The first design is best suited for pressure of a megabar or more, whereas the second design is limited to pressures of ~ 60 GPa. The DAC by necessity (for alignment, installation of parts, etc.) has several openings to the diamond anvil area. These openings must be "sealed" when using radioactive samples at a synchrotron. The diamonds and gasket provide the first level of containment. In addition, other containment must also be provided. For the latter perspective, some cell designs are more adaptable than other. We have found that the Cornell DAC design lends itself nicely for such containment. A photograph of two views of the Cornell cells is shown in Figure 1.

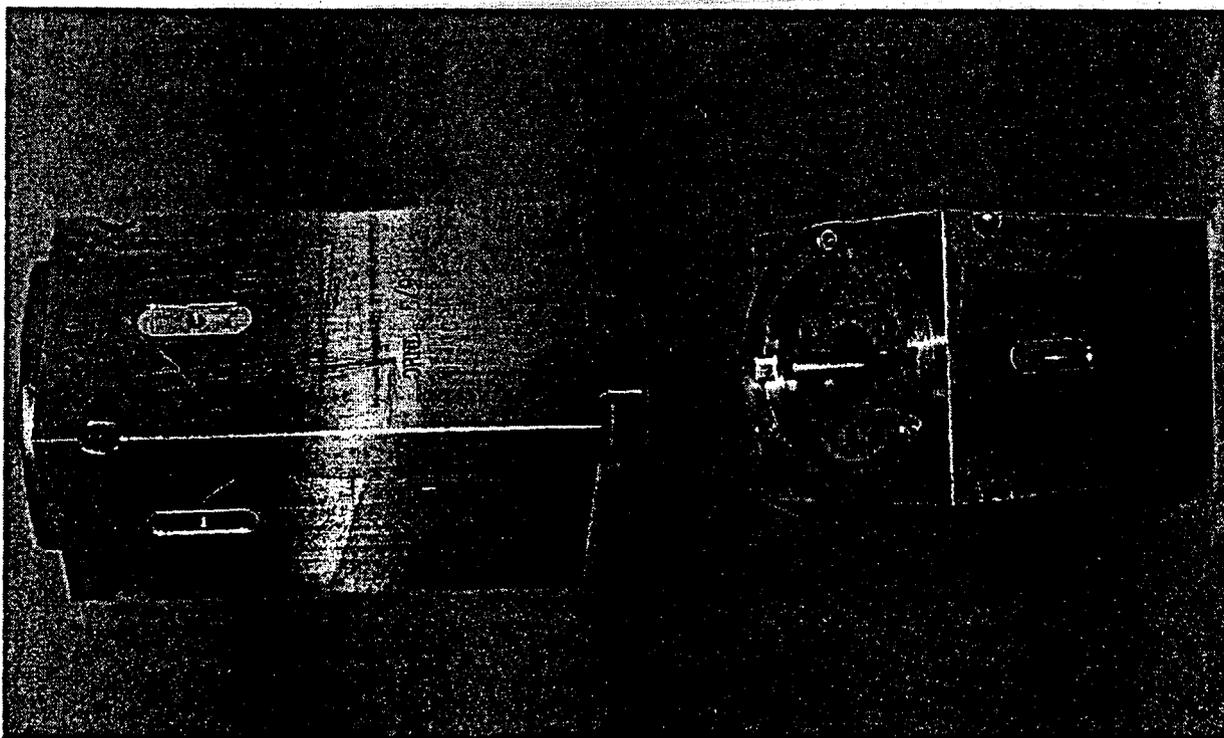


Figure 1. Two Cornell-type, Diamond Anvil Cells with Special Containment Pieces for Studying Radioactive Samples (A beryllium window inside of the housing of the moveable piston is not shown).

This DAC is essentially a precision-bored, block of stainless steel that contains a fixed diamond anvil and is fitted with a movable piston containing a matching diamond anvil. The piston is associated with the large nut on the right side of the left-hand cell in Figure 1. The accesses through the block are sealed with oval aluminum plugs (threaded hole in center) and a second Allen screw in each corner. A brass piece fitted with a 6 mm diameter beryllium window is screwed and sealed into the movable piston (visible only as a nut on the left cell), and rests just before the base of the diamond. The X-ray beam enters the piston opening and then passes through a beryllium window. After passing through this window, the moveable diamond, the sample and the fixed diamond, the X-rays exit pass through the end slit.

The exit slit is visible in the right hand cell (Figure 1) and provides limited two-theta angle of some twenty degrees. The exit slit is fitted with a large brass ring, which has a high strength plastic (Melinex^R, a polyester film by Dupont) sealed to it. The ring is held on the DAC by three screws. The plastic window was chosen both for its strength and its ability to transmit the ruby's fluorescence, when the latter is used for pressure determinations. Either ruby fluorescence or the equation-of-state

for platinum were the techniques used for the pressure determinations. Using a plastic film over an aluminum frame also provided additional containment for the cell.

Containment for the other two cell designs was similar in principle, though both were more difficult given the different cell constructions. Containment for these two cell designs is not discussed here, but a similar approach was used for the other cells.

Special techniques have been developed for loading/unloading the DAC at ORNL. Experience has shown these cells can be loaded with radioactive samples, used in the studies and then unloaded without contaminating the DAC, except for the gasket and diamond surfaces. It has been found that the diamonds can easily be de-contaminated and re-used in other studies.

DAC and Synchrotron Radiation

High-pressure studies with a DAC can employ either energy dispersive or angle dispersive techniques. Both techniques have advantages and disadvantages but overall we have preferred the angle dispersive technique for studies with synchrotron radiation. This approach provides excellent resolution, most flexible operational conditions, and given the high intensity of the radiation, does not suffer with regard to the collection time for the diffraction data. Angle dispersive studies with a DAC do have some special requirements, and these vary with the properties of the specific cells being used.

Provided here are a few comments relative to the study of f-elements in a DAC at synchrotrons. With the angle dispersive technique, X-rays of a wavelength shorter than $\sim 0.7 \text{ \AA}$ (e.g., $0.7 - 0.3 \text{ \AA}$) is used to maximize the diffraction data that can be collected. A wavelength of 0.7 \AA is sufficient to pass through the two diamonds and the sample. Shorter wavelengths allow "compressed" diffraction data to be collected to favor higher angles. Altering the sample to detector distances and/or rotating the cell relative to the beam are other approaches that can be done at advanced facilities. These techniques help overcome the limitation of having relatively small diffraction angles provided by the DAC ($\sim 20\text{-}25$ degrees two theta). Finally, the rapid image plates and readout used at the ESRF facility is very important, and allow complete diffraction patterns to be obtained with the synchrotron radiation in a less than a minute.

The superiority of synchrotron radiation for high-pressure studies with actinides is in the machine's ability to provide intense, well-focussed and stable X-ray beams with of $10\text{-}30$ microns in diameter. As the desired pressure region for the studies increases, there is the need for smaller diamond anvils, small gasket openings and smaller sample sizes. In many cases, diamond anvils with $70\text{-}100$ micron surfaces and having a gasket with a $30\text{-}60$ microns in diameter opening are used; only a few micrograms of actinide sample are employed. These conditions require the small, intense X-ray beams provided by synchrotrons in order to perform a complete study of the material at very high pressures in the allotted experimental time.

Specifically, the experimental procedure often uses micro-focussed beams of nominally $25 \times 25 \mu\text{m}^2$ (two bent mirrors in conjunction with a $30 \mu\text{m}$ pinhole filter) in many of the studies. Under these conditions, a 15-second exposure is sufficient (2/3 fill machine mode, at 200 mA) to yield excellent diffraction images. The images are captured with a Fastscan image detector [7] and the images can be viewed in $15\text{-}60$ seconds. This allows a large number of diffraction images to be collected in a short time.

Presently, facilities are not available at synchrotrons for loading and preparing DAC with radioactive samples, although facilities exist for preparing certain types of samples at the synchrotron. For high-pressure studies, this requires that the DAC samples be loaded, prepared for study at a synchrotron site and then transported to that site by official carriers. This transportation is costly, time consuming and the process is not forgiving if the sample is satisfactory upon arrival.

This transportation process also limits the number of samples and increases the inability to study successfully a particular sample. The DAC is an expensive sample device and only a limited number are normally available at one time. Transportation itself limits the number of cells that can be transported at one time. Thus, the experimenter must choose between having different samples or

having one to two materials with back-up samples. The total number of samples often falls into a range of one to six in these high-pressure synchrotron studies with actinides.

f Elements under Pressure

Over the past few decades there have been several studies of the lanthanides and actinides under pressure. Given recent advancements in high-pressure work and the use of synchrotrons, higher pressures have been attained and new concepts concerning behavior under pressure have been formed. The reader is referred to reviews [8-11] on high-pressure studies with f-elements and recent work on Ce metal [12]. There is strong evidence that the 4f electrons in the lanthanide series delocalize under pressure and that these metals adopt low-symmetry structure types known for the Pa-Pu metals, which normally have itinerant f-electrons. The pressure for this delocalization process increases as one moves across the lanthanide series (as the f electrons are "pulled-in" by the greater nuclear charge); it has not been reported for members of the second half of this series. The greater spatial extension of the 5f electrons in the actinides, as compared to the 4f electrons in the lanthanides, is expected to permit the delocalization process in the former to occur at lower pressures.

The physicochemical properties of the actinide metals at normal pressure vary considerably across the series. This is largely due to the changing role of the 5f electrons. It is accepted that the 5f electrons in the protactinium through plutonium metals are involved in bonding at normal temperature and pressure, and these metals display quite different properties than the lanthanide or transplutonium metals. The 5f electrons of the transplutonium metals are localized and their behavior is more like that of the lanthanide metals. In this regard, americium metal is in a pivotal position in the series and its behavior under pressure is especially interesting in this regard. The determination of whether pressure can bring about this delocalization is an important aspect of DAC studies with transuranium elements.

The concept of identical homologs between the lanthanide and the actinide metals is seriously limited, especially in terms of their pressure behavior, although some comparisons/relationships are valid and useful. In these pressure studies using X-ray diffraction, the approach is to monitor the structure of the metals as a function of pressure and extract the bonding behavior from established structure-bonding relationships. These structure-bonding relationships have both an experimental and theoretical basis. The goal is to use both theory and experiment to understand the pressure behavior and to promote the convergence of experimental and theoretical views of the metals under pressure.

There are at least two different processes envisioned for the 5f electrons when the metals are subjected to pressure. One effect is for the 5f electrons to combine/overlap with other electron orbitals to form a hybrid-type of bonding band (as exists with the Pa-Pu metals at normal pressure). In essence, the 5f electrons become delocalized and become involved in bonding, either in totally or partially. In this situation, it would be expected that lower symmetry structures would form, perhaps similar or identical to the structures exhibited by the protactinium through plutonium metals.

The second process is for the pressure to cause promotion of the f electron to another state (e.g., f→d) and then this new state would become involved in bonding. This does not seem to have been observed experimentally in pressure studies to date. A potential example would be to apply pressure on divalent einsteinium metal ([Rn core] 5f¹¹7s²) and force it to become trivalent einsteinium metal ([Rn core] 5f¹⁰spd). Simple calculations indicate this could occur at relatively lower pressures.

The primary structural effects of pressure are: dynamic compression; structural transformations; and volume collapses. In many of the structural transformations involving high-symmetry, common metal structures, s-d interactions are the driving force, as the relative energies of these orbitals change with pressure. Transformation from a high to lower symmetry structure can suggest potential incorporation of f-electron character. A sudden volume collapse is indicative of the onset of f-electron involvement.

The above discussion provides a snapshot of what investigations of actinide metals under pressure are pursuing in high-pressure studies at synchrotrons. The studies require the application of

established structure-bonding concepts/relationships. Other complimentary analysis under pressure would of course be useful/informative, and some have been done at lower pressures. However, the situation is that these other analytic probes (magnetism, resistivity, etc.) are far more limited in the pressures that can be obtained. The DAC probably provides the highest pressure that can be experimentally obtained in static measurements. The types of changes being pursued very likely require these high pressures.

In the subsequent section, important aspects of americium's behavior under pressure, determined in recent studies at the ESRF [13], will be discussed. Studies of americium under pressure have been reported previously at lower pressures using conventional X-ray radiation sources. The recent work on americium [13] differs significantly in the structures observed in the mid- to high-pressure regions, and these new findings were made possible through the use of synchrotron radiation.

Recent Studies on Americium Metal

Americium metal was studied recently at the ESRF high-pressure diffraction facility (ID 30) and the initial findings reported [13]. These studies extended greatly the pressure range examined previously, from 60 GPa to the reported limit of 100 GPa. In addition, the high quality (resolution) and extensive diffraction data acquired at the ESRF resolved previous disagreements about the high-pressure behavior of americium. These new data have allowed a new understanding of the behavior of americium under pressure. These data are shown in graphical form in Figure 2 as a plot of relative volume (volume at pressure/volume at normal pressure) versus pressure. The insert in the figure displays the atomic volume of the different actinide metals versus the atomic number, showing the sharp increase in volume in going from plutonium to americium. This increase reflects the change from having delocalized electrons in plutonium (smaller than expected atomic volume) to having localized f-electrons found in americium. If the localized f electrons in americium suddenly became delocalized (e.g., by applying pressure), a sharp reduction in its atomic volume would be expected (e.g., the volume for americium in the insert would drop down toward the volume shown for plutonium). Conversely, if f-electron involvement could be removed in alpha-plutonium (generation of localized f electrons), its volume should increase towards that of americium. This can be partially accomplished by heating or alloying of plutonium with small amounts of other metals.

Figure 2 displays that four phases were observed for americium metal under pressure in a recent study [13] at the ESRF. Previous researchers have reported data and interpretations about the behavior of americium metal under pressure below 60 GPa [14-21]. The main differences in Figure 2 from earlier work are found in the two phases labeled Am (III) and Am (IV). Differences included both the structural assignments and the transition pressures for these two phases. In addition, a second, small volume collapse was observed for the first time at the transition between the Am (II) and Am (III) forms (Figure 2).

The structures observed for the four forms were: Am (I) - dhcp (P63/mmc); Am (II) - fcc (Fm3m); Am(III) -orthorhombic (Fddd) and Am(IV) - orthorhombic (Pnma). The Am (IV) form is similar to the alpha uranium type structure (Cmcm) [13], while the Am (III) structure is isostructural with an elevated temperature form of plutonium metal (gamma plutonium). Both the Am (III) and the Am (IV) structures are believed to involve f-electron character, as do alpha plutonium and alpha uranium. A detailed discussion and experimental information can be found in the paper [13]. The results of the pressure study on americium metal can be looked at as a form of "modern structural alchemy". Under pressure americium (II) adopts first the structure of γ -plutonium and then a structure with a "slightly altered" arrangement of the atoms than found in α -uranium (loosely speaking, a slightly altered form

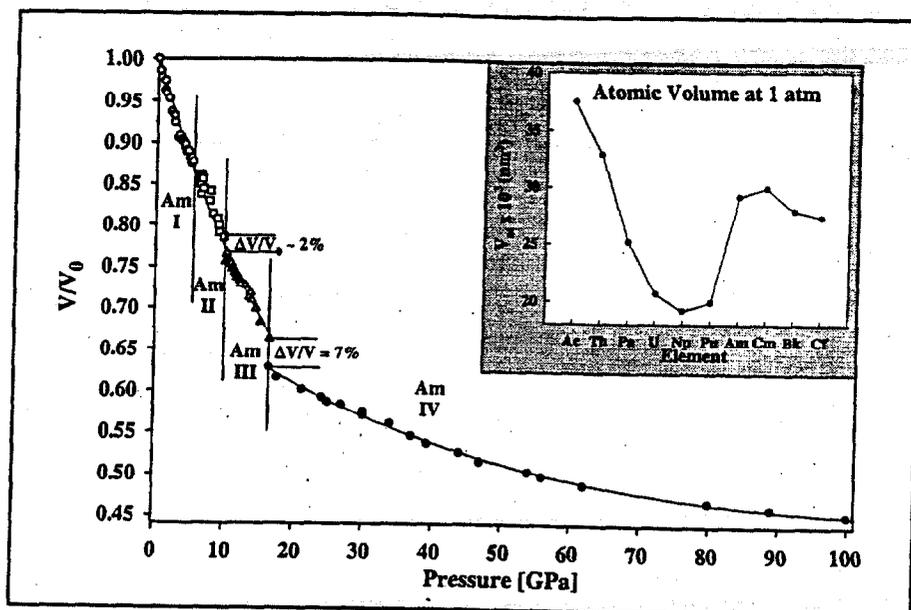


Figure 2: Relative Volume-versus-Pressure Curve for Americium Metal. Inset shows the atomic volume of the actinides as a function of element.

of α -uranium). The structures are displayed graphically in Figure 3, where the arrangement of the americium atoms in each form and the transformation processes between structures can be visualized.

The ability to resolve the behavior of americium under pressure was the result of high quality of the diffraction data obtained at the ESRF synchrotron facility. The quality of these data was confirmed in Rietveld analyses of the data at different pressures, and Bragg-R factors of 5-8 % were obtained for the derived structures. The results of the refinements for some data sets for the

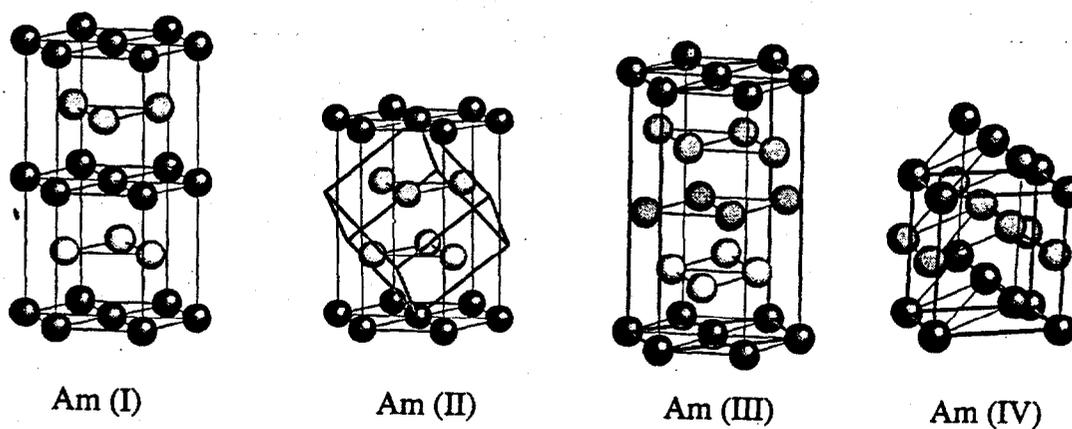


Figure 3: A form of modern alchemy. Under high pressure, americium (Am II) first adopts the structure of γ -plutonium (Am III) and then a structure that is "slightly altered" from that of α -uranium [Am IV].

face centered orthorhombic Am (III) and primitive, orthorhombic Am (IV) structures are shown in Figure 4. The space group for the Am (III) structure is Fddd and that for the

Am(IV) structure is Pnma. The latter space group has a lower symmetry than the Cmcm space group for α -uranium, which itself is a complex structure.

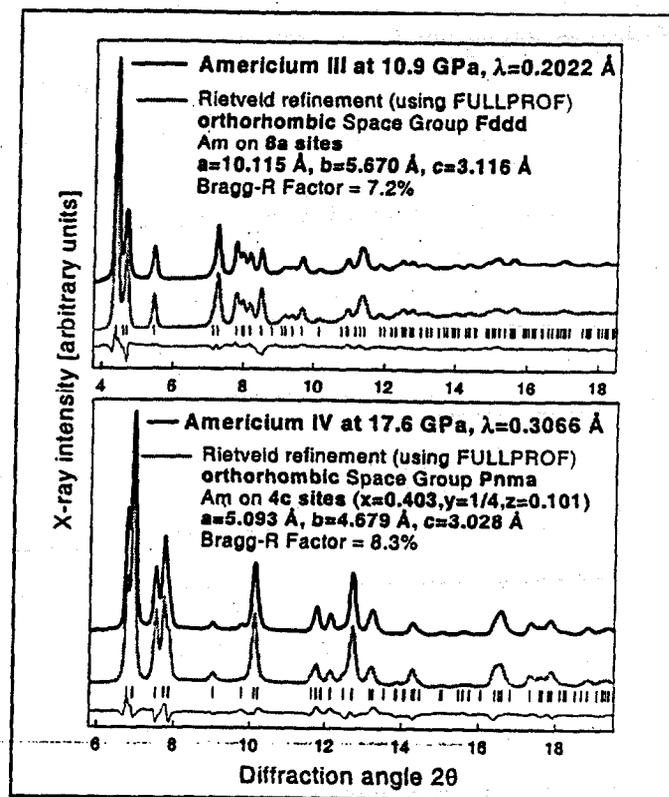


Figure3: Rietveld fits for the Am III and Am IV structures at 10.9 and 17.6 GPa. Shown are experimental (dark lines) and calculated (grey lines) diffraction patterns, reflection tick-marks and difference profiles (bottom line) [13].

Summarizing Comments

The attributes of synchrotron radiation have permitted and hopefully will continue to advance the high-pressure science of the actinides. Obtaining high-quality diffraction data is crucial to ascertain the proper structural behavior from which electronic and bonding nature of the material is extracted. Synchrotron radiation is very important when ultra-high pressures are sought, as it can provide the characteristics and the very critical beam conditions that are required for these particular DAC investigations. The flexibility/variability of the beams from modern synchrotrons are additional benefits.

Drawbacks to high-pressure studies with actinides at synchrotrons are the lack of on-site facilities for loading/unloading the DAC. These are not likely to be available, especially in the near term, given the requirements for handling DACs, as well as more extensive work needed with radioactive materials in DACs. In the absence of such facilities, it is necessary

to transport the DACs pre-loaded with sample and contained. This can be an expensive, difficult and time consuming, and the transport of radioactive materials is not likely to become easier in the future. This situation is made even less attractive by the fact that researchers are likely to only have a limited number of DACs for transportation at any one time. This reduces the number of samples that can be available for study during a particular allotment of beam time. In many instances, a choice must be made between having a back-up sample or another sample material for study.

The potential for new advancing actinide science is good for these high-pressure studies. In condensed matter studies, the large reductions in interatomic distances attainable with pressure are much greater than increases in such distances acquired by temperatures for conditions attainable in the laboratory. Hence, important changes can be induced in the bonding and physicochemical changes in actinide metals and compounds by applying pressure.

The recent studies of americium metal using synchrotron radiation provides an example of the type of new information that can be obtained with modern techniques. Properly identifying the Am (III) and Am (IV) pressure phases in recent studies at the ESRF allowed new insights to be obtained into the behavior of 5f electrons both under pressure and at normal pressure. Observing a partial delocalization of americium's 5f electrons in the Am(III) phase to form a gamma-plutonium type structure followed by a second delocalization step is perhaps the first example of the occurrence of a multi-step delocalization process in actinide metals which normally have localized 5f electrons.

Overall, such high-pressure studies, which reach out to new pressure limits, require synchrotron radiation to obtain the quality data that are needed. Synchrotron radiation offers a new potential for establishing important structural and electronic behavior of actinides. Such studies are important not only for advancing actinide science, but also for providing new information for evaluating theoretical concepts/calculations. Hopefully, these studies will promote the convergence of experimental findings and theoretical views regarding the behavior of 5f electrons under pressure.

Acknowledgements

This work is supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U. S. Department of Energy, under contract DE-ACO5-00OR22725 with Oak Ridge National Laboratory, managed/operated by UT-Battelle, LLC, and also sponsored by the European Commission. The beam time allocated at the ID 30 beamline at the ESRF for performing the americium experiments is also acknowledged, as is the Health Physics coverage and cooperation provided by P. Berkvens and P. Colomp at the ESRF.

References

1. R. G. Haire, in N. M. Edelstein, ed. *Actinides in Perspective*, Pergamon Press, (New York, 1982), pp. 309-342.
2. R. G. Haire, *J. Less-Common Metals*, 121 (1986) 379-398.
3. J. C. Spirlet and O. Vogt, in A. J. Freeman and G. H. Lander, eds., *Handbook on the Physics and Chemistry of the Actinides*, North-Holland (Amsterdam, 1984) p 79; and references therein.
4. Design of Prof. Ruoff, Cornell University, NY.
5. Design of K. Syassen and Holzäpfel.
6. Mao-Bell Megabar Cell, Geophysical Laboratory, Washington, D.C.
7. M. Thoms, S. Bauchau, D. Häusermann, M. Kunz, T. Le Bihan, M. Mezouar, D. Strawbridge, *Nuclear Instruments and Methods In Physics Research*, A 413 (1998) 175.
8. U. Benedict, and W. B. Holzäpfel, in *Handbook on the Physics and Chemistry of the Rare Earths*, K. Gschneidner, Jr., L. Eyring, G. H. Lander, G. R. Choppin, Eds. (Elsevier Science, Netherlands, 1993), vol. 17, Chap. 113, pp. 245-300; and references therein.
9. R. G. Haire, in *Resources, Science, Technology and Applications*, R. Bautista, N. Jackson, eds. (TMS, Pennsylvania, 1991), pp. 449-462; and references therein.
10. U. Benedict, in *Handbook on the Physics and Chemistry of the Actinides*, A.J. Freeman and G. H. Lander, eds., (Elsevier Science, Netherlands, 1987) Chapter 3, pp. 227-269: and references therein.
11. K. A. Gschneidner, Jr. and F. W. Calderwood, in *Handbook on the Physics and Chemistry of the Rare Earths*. Vol.8, K. A. Gschneidner, Jr and L. Eyring, eds. (North-Holland, 1986) Chapter 54, pp. 156-160; and references therein.
12. M. I. McMahon and R. J. Nelmes, *Phy. Rev. Lett.*, 78 (1997) 3883.
13. S. Heathman, R. G. Haire, T. Le Bihan, A. Lindbaum, K. Litfin, Y. Méresse and H. Libotte, *Phy. Rev. Lett.*, 85, no.14 (2000) 2961-2964.
14. J. Akella, Q. Johnson, W. Thayer and R. N. Schock, *J. Less-Common Metals*, 68(1979)95.
15. J. Akella, Q. Johnson, and R. N. Schock, *J. Geophys. Res.*, B85(1980)7056.
16. R. L. Reichlin, J. Akella, D. Smith and M. Schwab, LBL-12441, (1981) pp. 218-219.
17. R. B. Roof, R. G. Haire, D. Schiferel, L. A. Schwalbe, E. M. Kmeto and J. L. Smith, *Science*, 207(1980)1353.
18. R. B. Roof, *J. Applied Cryst.*, 14(1981)447.
19. R. B. Roof, *Z. Kristallographie* B15 (1982) 307.
20. U. Benedict, J. P. Itié, C. Dufour, S. Dabos and J. C. Spirlet, in *Americium and Curium Chemistry and Technology*, N. M. Edelstein, J. D. Navratil and W. W. Schultz, (Reidel, Dordrecht, Boston, 1985) pp. 221-224.
21. U. Benedict, J. P. Itié, C. Dufour, S. Dabos and J. C. Spirlet, *Physica B*, 139/140 (1986) 284.