Additional Resources for Practical and Successful High Temperature X-ray Diffraction and Structural Studies by XRD

Andrew Payzant & Camden Hubbard
High Temperature Materials Laboratory
Metals & Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN, USA 37831-6064

e-mail: payzanta@ornl.gov
hubbardcr@ornl.gov
web: http://html.ornl.gov

Objectives

- Review resources that are valuable to use during determination of crystal structures by XRD methods
- Review resources readily available that can be helpful in analysis of HTXRD data
  - Some are in books or journal format
  - Many of these are web, Internet or CD-ROM based

Note: Many are free!
- but sometimes you get what you pay for
- Generally, more comprehensive and edited data are not free

Books and Reference Data?

- For those who long for the days before Google when looking up an answer meant reading books and journals, these are all very useful (and accessible even today and easier to read for many):
  - B.D. Cullity, *Elements of X-ray Diffraction*, Addison Wesley
  - R. Jenkins and R. Snyder, *Introduction to X-ray Powder Diffractometry*, Wiley-Interscience
  - Bish and Post, *Modern Powder Diffraction*, Min Soc Amer, Reviews of Miner. Vol 20
  - R.A. Young, *The Rietveld Method*, IUCr/Oxford
  - F.H. Chung and D.K. Smith, *Industrial Applications of X-ray Diffraction*, Marcel Dekker
  - __, International Tables for X-ray Crystallography, IUCr
  - P. Villars and L. Calvert, Pearson's Handbook, ASM Intl
  - __, Phase Equilibria for Ceramists, Am Ceram Soc
  - __, Binary Phase Diagrams, ASM International

Journals & Conference Proceedings

- Advances in X-ray Analysis (CD-ROM from ICDD)
  - yearly proceedings of the Denver X-ray Conference, ICDD
- EPDIC Conference Proceedings (book)
  - periodic proceedings of the European Powder Diffraction International Conference
- Powder Diffraction
  - Printed & electronic formats of ICDD journal via APS
- Journal of Applied Crystallography
  - Printed and electronic

Newsgroups and Mailing lists

- **Internet/Usenet Newsgroups:**
  - **sci.techniques.xtallography**
    - **Netscape: via the Communicator, Newsgroups menu**
    - **Internet Explorer: via the Tools, Mail and News**

- **Mailing Lists:**
  - **Rietveld users mailing list**
  - **Clay Minerals Mailing list**
  - **SDPD (Structure Determination from Powder Diffractometry)**

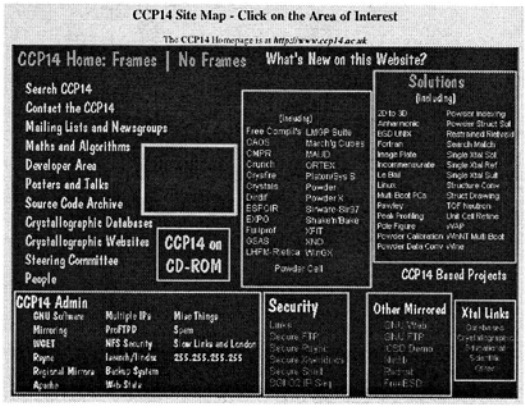
- ***But Internet advice may be worth exactly what you paid for it!***

Additional Resources in Appendix to the Presentation

The CCP14 Website

An essential website for software resources is the Collaborative Computational Project Number 14 (CCP14) for Single Crystal and Powder Diffraction. <http://www.ccp14.ac.uk>

The website provides links to software, tutorials, and other resources, and is regularly updated. Most is free.



Powder diffraction software & calculations you likely need to use to get quality data

- Brian Toby's absorption correction
- X-Ray attenuation lengths
- Steffan Krumm's XRD slit settings calculator

Crystal structure databases on the Web or on CD-ROMs (http://www.iucr.org/iucr-top/data/)

- ICSD - Inorganics Crystal Structure Database
  - Inorganic phases (http://www.fiz-informationsdienste.de/en/DB/icsd/)
  - on the web (4% of it can be freely accessed)
- CSD - Cambridge Structure Database
  - Organic and metalorganic phases (http://www.ccdc.cam.ac.uk/products/csd/)
- Mincryst - mineral structures (comprehensive)
  - http://database.iem.ac.ru/mincryst/index.php
- American Mineralogist - mineral structures
  - http://www.geo.arizona.edu/AMS/amcsd.php
- Linus Pauling File
  - Binaries - CD-ROM via ASM (includes phase equil. and properties)
  - Multinaries - CD-ROM tbd (release likely in 2005 or 2006)
  - Web - http://crystdb.nims.go.jp/
- CRYSTMET - Metals and intermetalic structures
  - http://www.tothcanada.com/Crystmet.htm
- PDF-4 from ICDD (separate inorganic and organic db's)

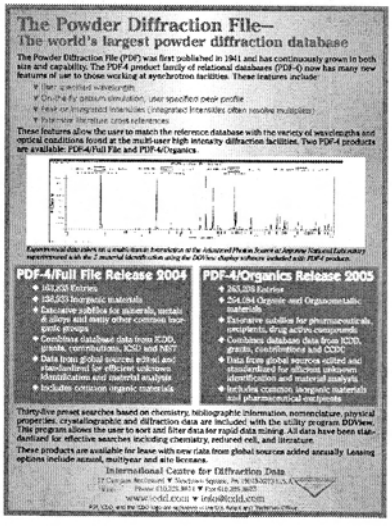
The Powder Diffraction File (PDF) Is By Far the Largest in Terms of Unique Entries
& ICDD is Adding Atomic Coordinates in 2005

Nearly all laboratory XRD instruments are purchased with a PDF database licensed from ICDD.

http://www.icdd.com

You should plan to keep yours up-to-date!

The 2004 release contained nearly 430,000 unique entries! The database is updated annually and is estimated to grow by ~100,000 with atomic coordinates in 2005 and then ~40,000 entries per year for the foreseeable future.



PDF is Available in Several Versions, all Updated Yearly

- **Powder Diffraction File**
  - PDF2 is most commonly available format, more limited in content
  - PDF4 with database software is more extensive
  - Full File (inorganics) & Organics (includes pharaceuticals+incipients)
- **PDF4-Release 2004 on CD-ROM/DVD**
  - **Excellent version for data mining, finding isostructural, cell searches, …**
  - XRD pattern as d-spacing, intensity and hkl
  - Names, chemical and empirical formula,
  - Cell and SG info; reduced cell and SG
  - References, comments and editorial assessments
  - F^2_{hkl} for CuKα (if patterns is from calculation based on atomic structure)
- **PDF4-Release 2005 for inorganics**
  - Addition of atomic coordinates, thermal parameters, site coordination, graphics
  - Much more

What Is In the PDF4 Regarding Temperature?
(Ambient/Non Ambient/Tmp Flags)

Information	PDF-4/ Organics 2005	PDF-4/ Full File 2004 (inorganics)	PDF-4/ Full File 2005 +Linus-Pauling
# of Entries	**265,208**	**163,835**	**~250,000**
Ambient	**201,364**	**152,119**	
T (non-amb.)	**63,811**	**9,984**	**~20,000**
P (non-amb.)	**33**	**1,507**	
T+P (")	**0**	**221**	
Tmp<19 (C)	**544**	**47**	
Tmp 19-100	**13,453**	**1,165**	
Tmp 100-500	**64,436**	**5,382**	
Tmp 500-5,000	**73**	**2,632**	

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

What's In the PDF About Crystal Structures?
(Commentary-Searchable)

Info.	PDF-4/ Organics 2005	PDF-4/ Full File 2004	PDF-4/ Full File 2005 w/ Linus-Pauling File (LPF)	PDF-4/ Full File 2006 w/ LPF
Atomic Coords.	**147**	**47**	**~80,000**	**~110,000**
Crystal Habit	**67,409**	**25**		
Wyckoff Sequence	**1,104**	**46,783**	**~130,000**	**~160,000**
ANX coding		**49,110**	**~135,000**	**~165,000**

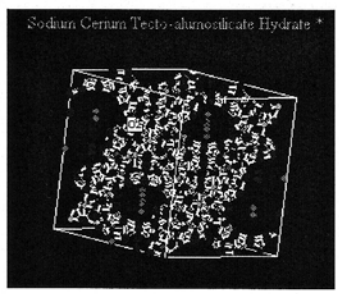
OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Examples of New Features/Fields in PDF-4/Full File 2005 (inorganics)

- Atomic Coordinates
- Thermal Parameters (anisotropic when available)
- Rationalized Mixed-Site Occupancy
- Absolute Configuration
- ANX
- Bond Distances
- Isomorphism Comments
- Polymorphism/Phase Transition
- Wyckoff Sequence
- Calculated Pattern Quality Marks
  - Based on current PDF editorial review plus the R-factors, missing electron density, bond distances, etc.
  - Identification of primary entry and lower quality reports to reduce multiple entries for common phases

- 3D structure display (powerful)
- On-the-Fly Digitized Powder Pattern Calculator
  - User Instrumental Function
  - X-rays
  - Electrons
  - Neutrons
  - Any wavelength

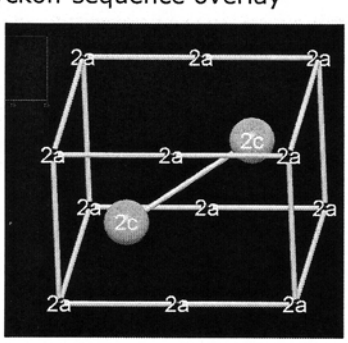


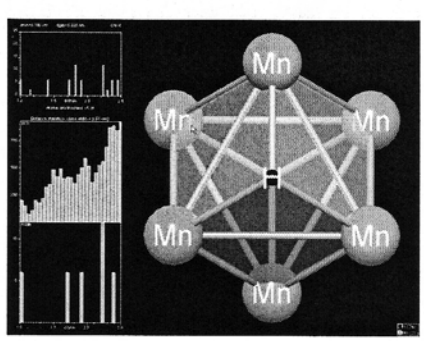
New Features in PDF-4/Full File 2005

3D structure

Structure type

Wyckoff sequence overlay





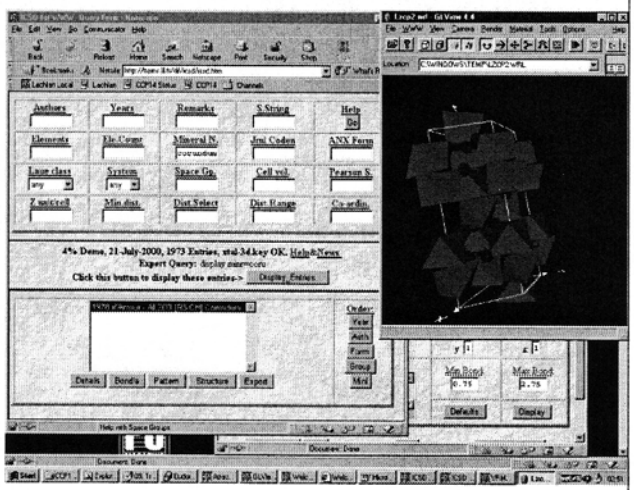
Atomic Environment

ICSD via the Web

Using an Interface created by Alan Hewat

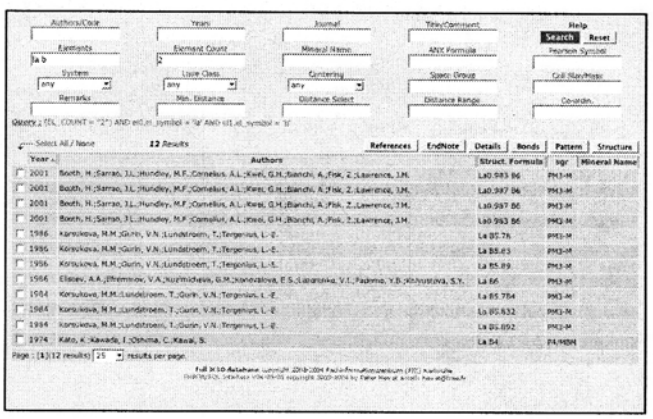
4% of the database is available for public access
http://http://icsd.ill.fr/icsd/

Even 4% can be *very* useful, but a site license is not very expensive
*****where*****



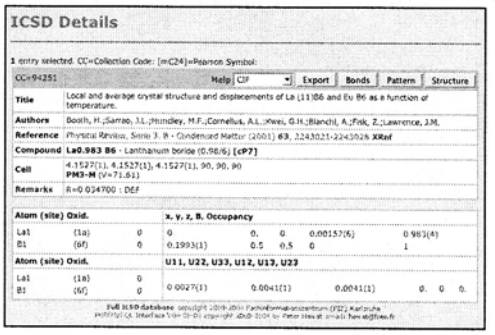
How to use the web-based ICSD server?

- **Menu-driven searches**
- **Can find lots of reference structures with complete data**
- **The example on the right is a search on La + B**
- **Note the numerous duplications!**



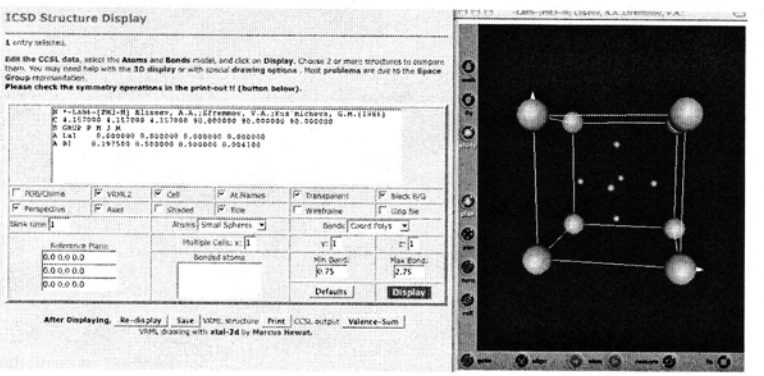
You can obtain useful CIF files directly from the ICSD web server

- Check the ICSD reference you are interested in and press "Details" button
- Again lots of information including atom sites, occupancies, and thermal parameters
- Note the CIF export option allows you to import this data *directly into many XRD packages*



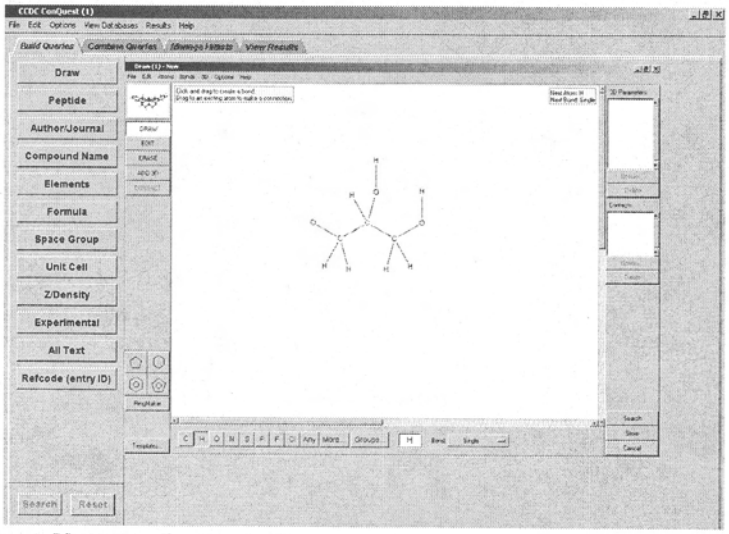
Note that it is important to double check this input (e.g. in some software packages the CIF data may not be imported correctly)

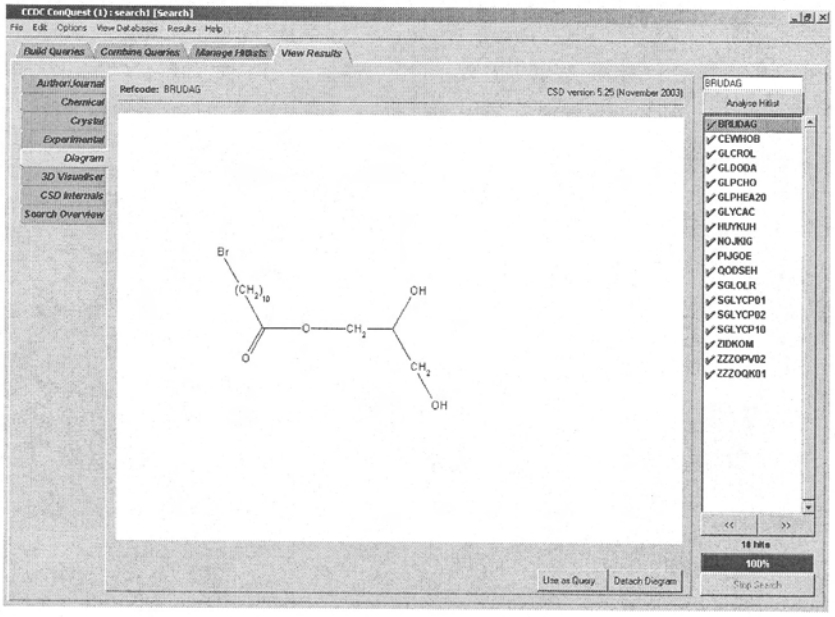
It may be worth your while to license the full ICSD database

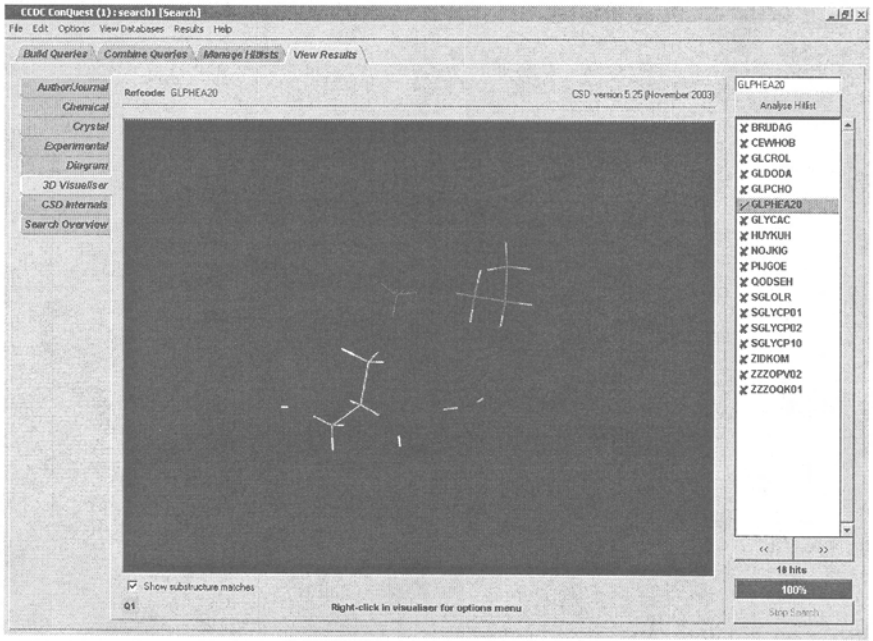


- You can calculate diffraction patterns for x-ray and neutron sources with selectable wavelength and profile parameters
- As shown above, you can do 3-D modeling using VRML plug-in

Cambridge Structure Database 5.25 with ConQuest 1.6 (2004) Software - *www.ccdc.cam.ac.uk*

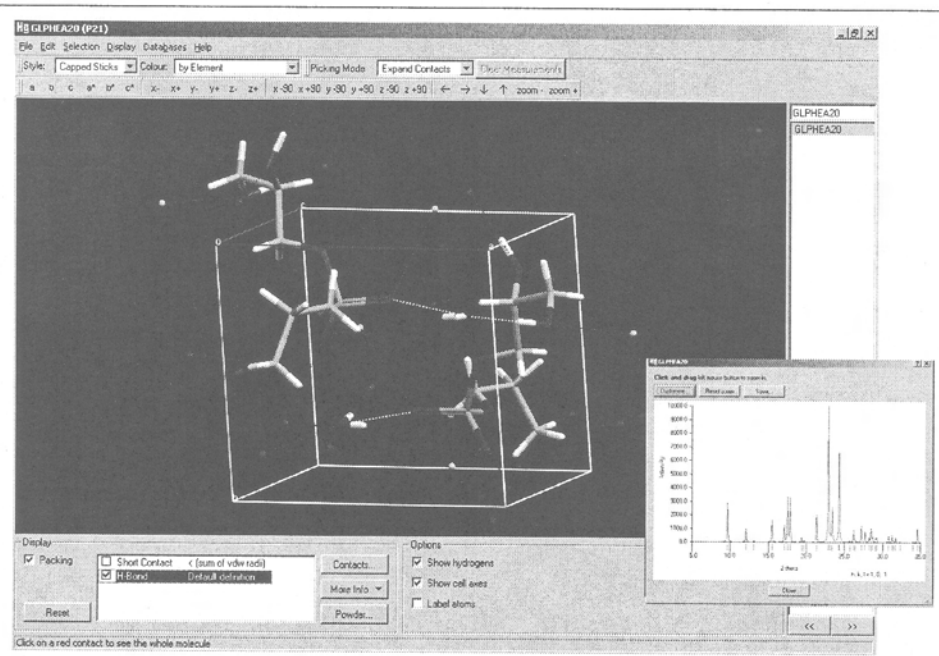






OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE



OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Phase Equilibria and Thermodynamic Databases are Very Valuable Particularly for HTXRD Studies

- Phase Diagrams for Ceramists, ACerS
- LPF Binaries, ASM
- ASM Phase Diagrams
- FactSage (software and databases)
- Thermocalc (software and databases)
- Many others

Thermal Expansion Knowledge Valuable for HTXRD

- Thermophysical Properties Research Laboratory (TPRL- Purdue) - not current!
  - Publications of evaluated data (library?)
  - One volume focused on thermal expansion
- CTE need not be "linear" with temperature
- CTE need not be isotropic with temperature
  - Non cubic typically are anisotropic
  - Diffraction lines can cross as temperature changes
- HTXRD can also be used to determine CTE from lattice constants as function of T

Training Opportunities and Workshops Are Widely Available

- ICDD Workshops - Beginners and Advanced
- Rietveld Short Course (Georgia Tech)
- Denver X-ray Conference Workshops (ICDD)
- ACA Special Interest Groups
- Argonne Workshops on neutron scattering
- Web based college courses (some for fee)
- …many others

Advanced Certificate in Powder Diffraction on the Web
Birkbeck University of London, UK

http://pd.cryst.bbk.ac.uk/pd/welcome.htm

Summary

- It is in your interest to check the resources out
  - Databases are a fast way to survey the literature and find related structures
  - Valuable software and web sites are amazingly useful
- Be continually looking for other resources to keep you up to date with the "hard" and "soft" scientific information relevant to powder diffraction and structure determination from XRD
- Use thermodynamic and structural resources in your HTXRD to help explain the observed patterns and what the changes with time and temperature mean.
- Refer to resources on thermal expansion
  - Anisotropic expansion can easily have lines cross with temperature

Appendix to Presentation

Content includes focus on Rietveld structure analysis

sci.techniques.xtallography

- Accessed via using "news reading" software such as provided within Netscape and Internet Explorer
- Very useful for posting general crystallography queries
- Can often get an answer within the day - depending on how fast the news is spreading on the internet that week combined with how often people look at the newsgroups via an internet news reader

Mailing lists

Same type of thing as the newsgroup but more specialized.

Rietveld users mailing list

To subscribe, send mail to sympa@ill.fr with the command: subscribe rietveld_l
Rietveld web archive of messages at http://www.mail-archive.com/rietveld_l@ill.fr/

Clay Minerals Mailing list

http://cms.lanl.gov/listserv.html

SDPD (Structure Determination from Powder Diffractometry)

http://www.cristal.org/sdpd/

Rietveld Mailing list

Don't use the mailing list to regularly ask for crystal structures - too frequent requests may get ignored.

Very often you will not be given the structure but a reference (which may be more useful)

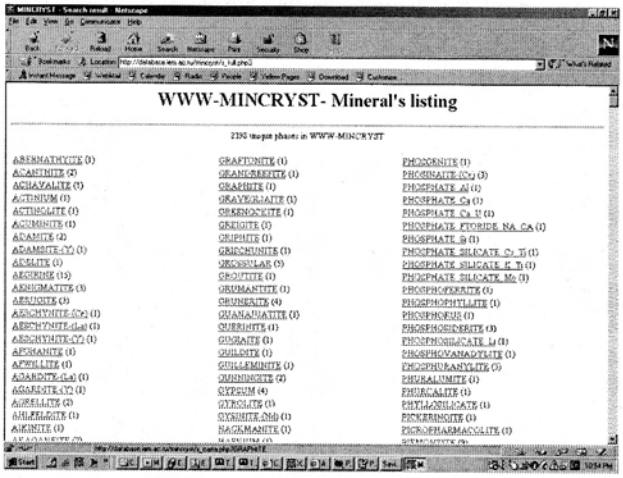
Politeness costs nothing - it can help by explaining what you are trying to achieve.

The list can be a great resource for more fundamental questions on Rietveld refinement - be warned a lot (but not all) of the discussion is in the context of GSAS-based refinement

Don't bother asking HighScore-specific questions - they will probably remain unanswered. ***Such questions should be directed to PANalytical***

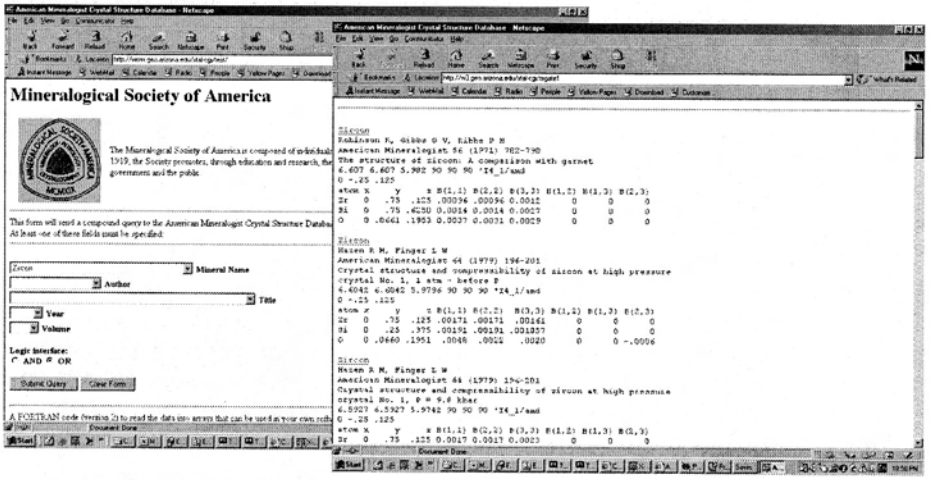
Mincryst - 2398 mineral phases

http://database.iem.ac.ru/mincryst/ - with atomic coordinates



American Mineralogist mineral structures

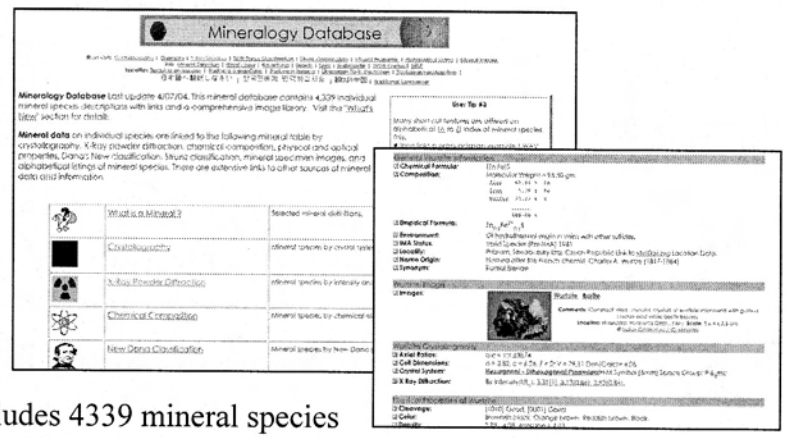
http://www.geo.arizona.edu/xtal-cgi/test/



UT-BATTELLE

David Bathelmy's mineral database

http://www.webmineral.com/

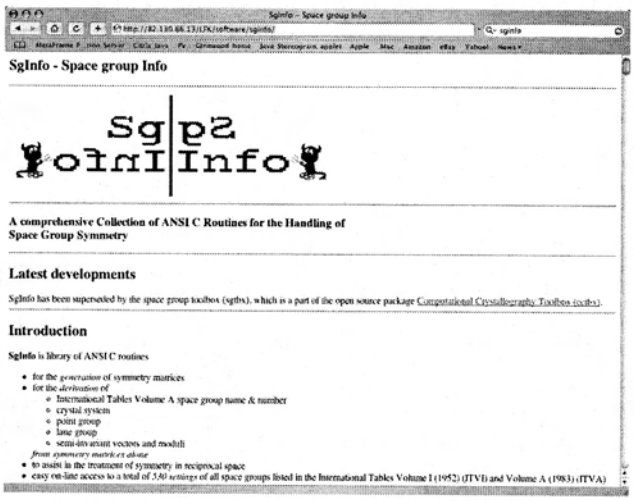


Includes 4339 mineral species

UT-BATTELLE

SgInfo - Spacegroup information

http://82.130.66.13/LFK/software/sginfo/



SgInfo - Space group Info

A comprehensive Collection of ANSI C Routines for the Handling of Space Group Symmetry

Latest developments

SgInfo has been superseded by the space group toolbox (sgtbx), which is a part of the open source package Computational Crystallography Toolbox (cctbx).

Introduction

SgInfo is library of ANSI C routines

- for the *generation* of symmetry matrices
- for the *derivation* of
  - International Tables Volume A space group name & number
  - crystal system
  - point group
  - lattice group
  - semi-invariant vectors and moduli

  from symmetry matrices above
- to assist in the treatment of symmetry in reciprocal space
- easy on-line access to a total of *530 settings* of all space groups listed in the International Tables Volume I (1952) (ITVI) and Volume A (1983) (ITVA)

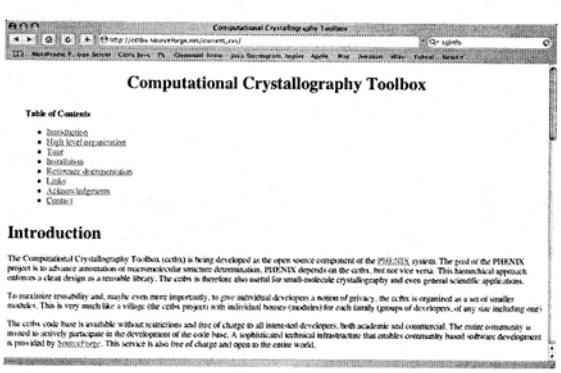
Superceded by cctbx (Computational Crystallography Toolbox) at http://cctbx.sourceforge.net/ but still very useful

Computational Crystallography Toolbox

http://cctbx.sourceforge.net/

Can be installed on Windows, Unix, MacOSX, etc.

Includes the ability to get spacegroup symbols from symmetry operators



Computational Crystallography Toolbox

Table of Contents

- Introduction
- High level organization
- Tour
- Installation
- Reference documentation
- Links
- Acknowledgements
- Contact

Introduction

The Computational Crystallography Toolbox (cctbx) is being developed as the open source component of the PHENIX system. The goal of the PHENIX project is to advance automation of macromolecular structure determination. PHENIX depends on the cctbx, but not vice versa. This hierarchical approach enforces a clear design as a reusable library. The cctbx is therefore also useful for small-molecule crystallography and even general scientific applications.

To maximize reusability and, maybe even more importantly, to give individual developers a notion of privacy, the cctbx is organized as a set of smaller modules. This is very much like a village (the cctbx project) with individual houses (modules) for each family (groups of developers, of any size including one).

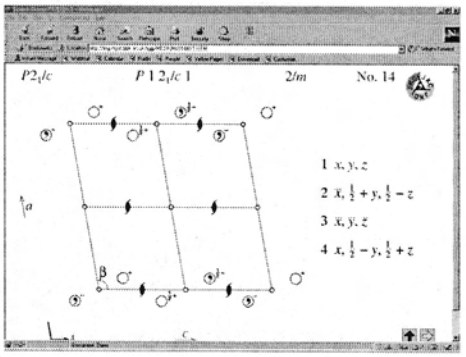
The cctbx code base is available without restrictions and free of charge to all interested developers, both academic and commercial. The entire community is invited to actively participate in the development of the code base. A sophisticated technical infrastructure that enables community based software development is provided by SourceForge. This service is also free of charge and open to the entire world.

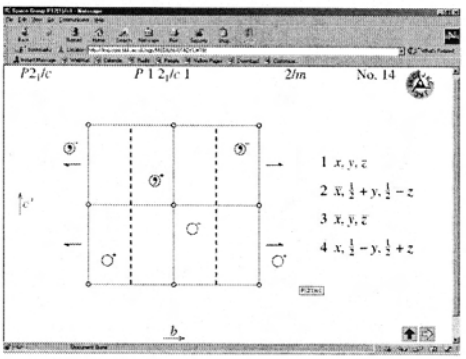
Hypertext Book of Crystallographic Space Group Diagrams and Tables on CD-ROM

http://img.cryst.bbk.ac.uk/sgp/mainmenu.htm

The CD-ROM is a fraction of the price of the IUCr International Tables and includes non-standard space groups and settings. (£9.95 plus postage)

Can purchase an intranet site license for £100.00



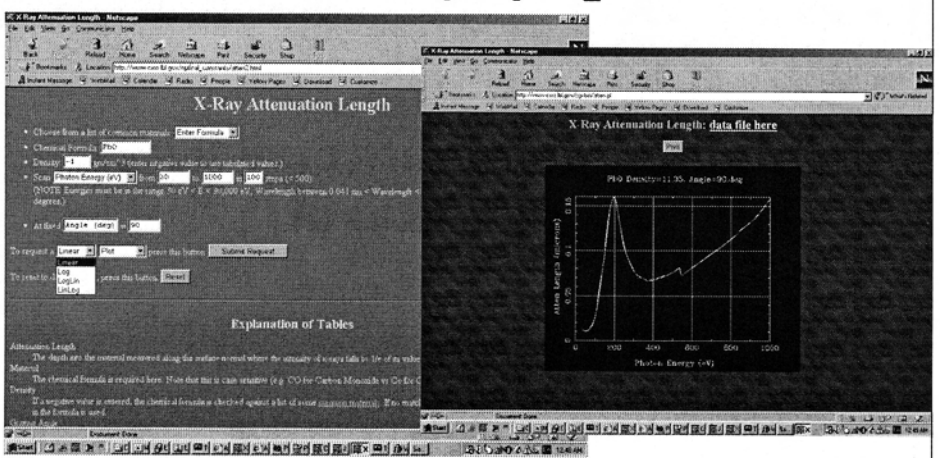


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Atomic Scattering Factors and X-Ray Attenuation Lengths

http://www-cxro.lbl.gov/optical_constants/

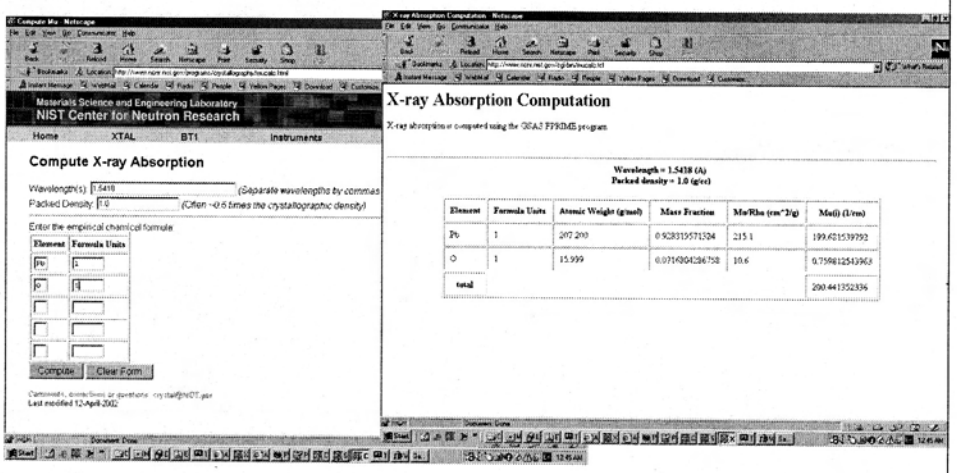


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

X-ray Absorption Computation

http://www.ncnr.nist.gov/programs/crystallography/mucalc.html

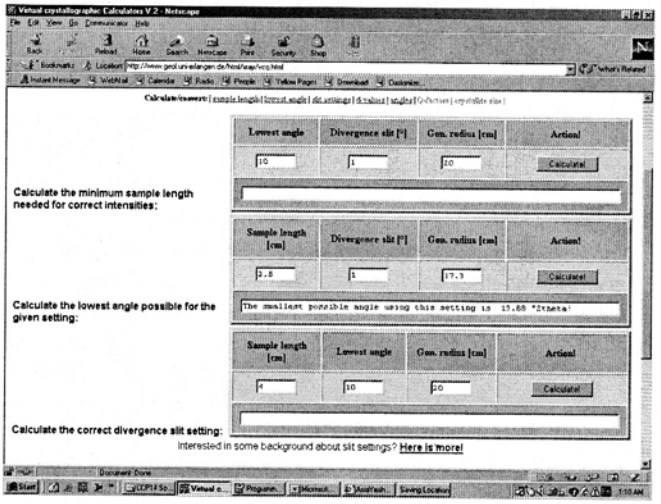


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Virtual Crystallographic Calculators V.2

http://www.geol.uni-erlangen.de/html/xray/vcc.html



OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

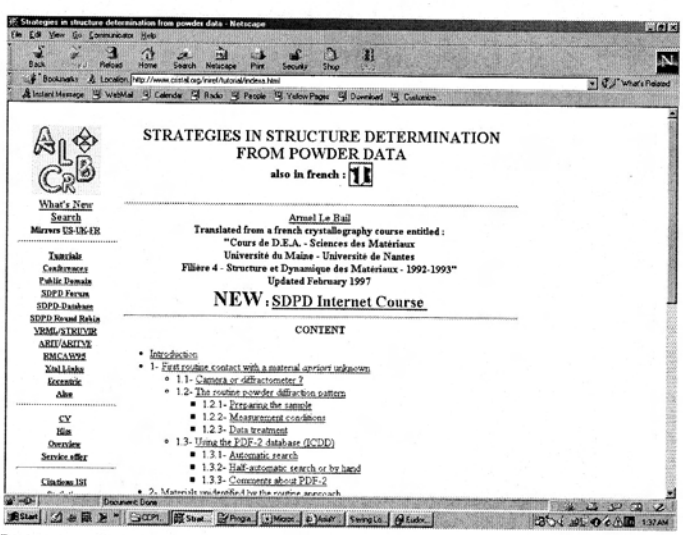
Some Web Teaching Resources

- List of resources: http://www.ccp14.ac.uk/educate.htm

- **Free on the web:**
  - Armel Le Bail's strategies for solving crystal structures from powder XRD tutorial
  - Interactive Tutorial about Diffraction - Proffen and Neder
  - Kevin Cowtan's Book of Fourier Transforms
- **Accredited University based courses:**
  - SDPD Internet Course - Le Mans, France - Armel Le Bail, Yvon Laligant and Alain Jouanneaux
  - Advanced Certificate in Powder Diffraction on the Web - Birkbeck University of London, UK - Jeremy Cockcroft

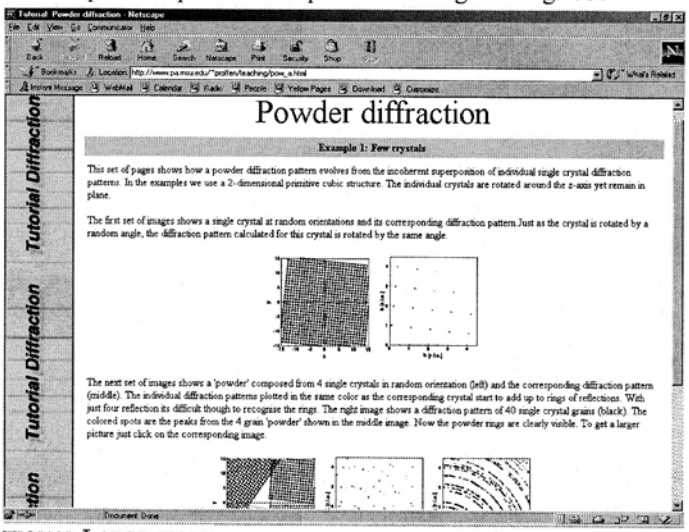
Strategies in Structure Determination

http://www.cristal.org/iniref/tutorial/indexa.html



Interactive Diffraction Tutorial

http://www.pa.msu.edu/~proffen/teaching/teaching.html

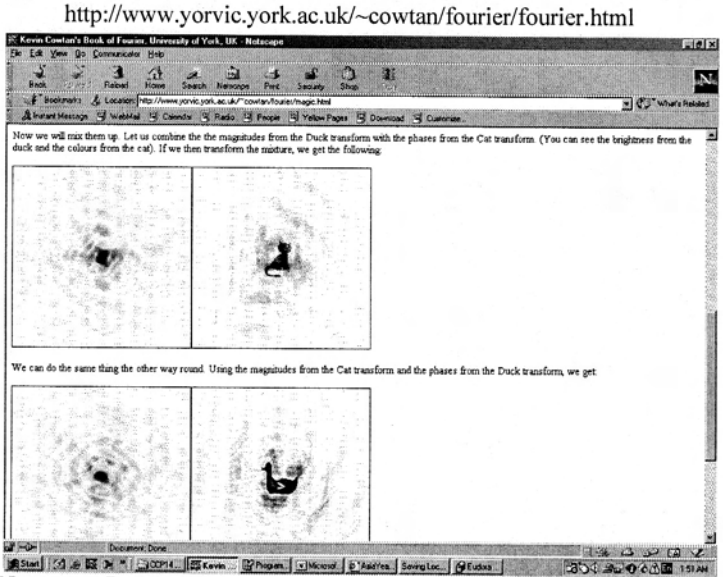


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

Kevin Cowtan's Book of Fourier Transforms

http://www.yorvic.york.ac.uk/~cowtan/fourier/fourier.html

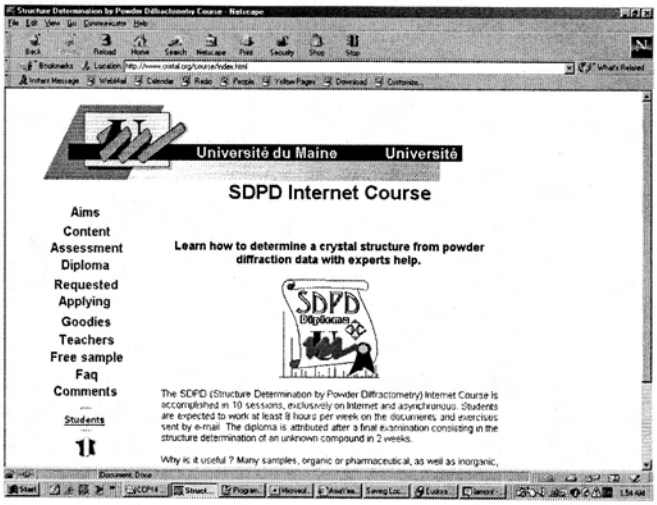


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

SDPD Internet Course - Le Mans, France

http://www.cristal.org/course/



Other Rietveld refinement codes

- **Free (non-commercial) codes:**
  - DBWS (a bit dated)
  - GSAS (Windows&Linux)(widely used)
  - EXPGUI/GSAS (Win, Linux, MacOSX)
  - Rietan (Win, Linux, MacOSX)(Japanese standard)
- **Commercial codes**
  - HighScore Plus (PANalytical)
  - Topas (Bruker)
  - RiQAS/Jade+Riet (MDI)
- **So what do you get for your money?**
  - ***Ease of use***
  - ***Tight integration***
  - ***Product support***