

Portland State University, April 11, 2006

Final report on Peter Moeck's NWACC project "Nanocrystallography Visualizations"

Summary of Completed Work

The project web site has been established at <http://nanocrystallography.research.pdx.edu/> and the NWACC logo is displayed at this site prominently

At <http://nanocrystallography.research.pdx.edu/CIF-searchable/> we provide access to a local version of the free Crystallography Open Database (COD), which contains the records of approximately 11,000 structure determinations. Queries of this database can be downloaded in the standard Crystallographic Information File (CIF) format and displayed by the free java based program Jmol. For details see the attached manuscripts of a paper in the peer reviewed international Journal of Materials Education (appendix A) and of a paper that is going to be published on the website of Symposium KK: Education in Nanoscience and Engineering, http://www.mrs.org/s_mrs/doc.asp?CID=3336&DID=167381 (appendix B) and to be presented orally at that symposium on April 19, 2006.

Between December 5 to 16, 2005, a field test of the educational value of the project during a lecture series on Materials Science and Engineering by Peter Moeck at the Technical University Chemnitz, Germany, has been successfully performed.

Now our websites are ready for widespread use throughout the community of Materials Science Educators, see URL <http://nanocrystallography.research.pdx.edu>.

Crystal structure visualizations in three dimensions with support from the open access Nano-Crystallography Database

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ABSTRACT

Crystallographic databases for inorganic materials that are freely accessible over the internet are reviewed. The Nano-Crystallography Database project is described. Instructions are given on how to visualize in three dimensions the atomic arrangements of several thousand entries of the Crystallography Open Database.

Keywords: Open Access, Crystallography, Databases

1. INTRODUCTION

Courses in materials science and engineering, crystal physics, crystal chemistry, and mineralogy typically employ two-dimensional sketches of the atomic arrangement in crystal structures and unit cells. The chapter on ideal crystal structures of the widely used introductory materials science and engineering text by Schaffer et al.¹ contains for example 14 such sketches. Textbooks on mineralogy contain a much larger number of such sketches (e.g. Hibbard's text² features a picture with more than ten ball-and-stick models on the dedication page and approximately one hundred sketches of atomic arrangements in crystal structures and unit cells in the body of the text). Physical three-dimensional models of crystal structures and unit cells are also popular. While academic departments in the developed part of the world may possess some tens of such three-dimensional models and allow their students to explore those hands on, their counterparts in the developing part of the world may consider such models too expensive and fragile for class room usages.

To help remedying this situation we made a survey on crystallographic databases that are freely accessible on the internet and also started our own nano-crystallography database project with on line three-dimensional (3D) visualizations of ideal and real structures. This paper reports on both the results of the survey and our ongoing project.

2. FREE INTERNET ACCESSIBLE CRYSTALLOGRAPHIC DATABASES

Fifteen years after the development of the World Wide Web, there is already a variety of internet based free-access crystallographic databases. We discuss in this paper the subset of free databases that includes or primarily deals with inorganic crystals.

The free database MINCRYST³ is maintained and hosted by the Russian Academy of Sciences and contains more than 6,000 entries for minerals from which X-ray powder diffractograms can be calculated on the fly. 3D visualization of the entries are provided by means of the java-based freeware program “Jmol”⁴. The Naval Research Laboratory’s Center for Computational Materials Science provides a free on-line database for education and research support under the name “Crystal Lattice Structures”⁵. Currently this database contains 254 entries in 90 space groups. Visualizations of the entries are also provided by Jmol applets. The “Reciprocal Net” is a distributed database of molecular structure information and its main web site is hosted at Indiana University at Bloomington⁶. Information from approximately 400 common molecules (and crystal structures) can be downloaded in the standard Crystallographic Information File (CIF)^{7,8} format (file extension *.CIF). 3D visualizations of these common molecules (and crystal structures) are provided by a range of Java based applets.

Since its adoption in 1990 by the International Union of Crystallography as the standard file format and syntax for communicating crystallographic information between both human beings and computers and between different kinds of software programs and computers, CIF has become a crystallographic entity in its own right of such a significance that a volume of the latest edition of the International Tables for Crystallography⁸ is dedicated to describing it comprehensively. A free on-line check of the syntax of CIFs is provided by the International Union of Crystallography at the URL given in ref.⁹.

The free on-line American Mineralogist Crystal Structure Database (AMCSD) was erected in 2003 and contains more than 8,000 critically evaluated entries^{10,11}. Files can be downloaded from this database in CIF and the American Mineralogist Crystal data format (file extension *.amc). A range of PC based freeware programs, for e.g. the visualization of crystal structures (XtalDraw) and for the calculation of powder X-ray and neutron diffractograms (XPow), is available for downloading from the AMCSD site at ref.¹². The database is maintained under the care of both the Mineralogical Society of America and the Mineralogical Association of Canada. Ref.¹⁰ states that approximately 75 % of the submitted manuscripts to the journals “American Mineralogist” and the “Canadian Mineralogist” possess errors of one sort or another. (For comparison, ref.¹³ states that about 40 % of the CIFs received for inclusion into the commercial Cambridge Structural Database contain errors that arise mainly from the manual editing of these files by their authors.) The critical evaluation of data to be included in a crystallographic database is, therefore, a major concern for both commercial and free databases.

Records of approximately 24,000 full crystal structure determinations in the form of CIFs are freely accessible on-line at the Crystallography Open Database (COD)^{14,15}. This database was also started in 2003 and is rapidly growing as more and more crystallographers and scientific institutes/societies/academies donate their collections of CIFs and upload them over the internet so that anybody with access to the World Wide Web can access them for free. The COD also contains all the data sets that are in the AMCSD. An approximately 2,000 entry subset of the COD is named PCOD for Predicted Crystallography Open Database^{14,15} and allows 3D displays of structural polyhedra and wire frames in the so called Virtual Reality Modeling Language (VRML)¹⁶ format by using common (HTML based) web browsers (if necessary with plug-ins such as COSMO¹⁷ player).

The long term objectives of the COD initiators are summarized on the COD web page¹⁵ as: (i) providing free access to comprehensive crystallographic data (including the atomic coordinates) on all known inorganic, metallic, organometallic and organic crystalline compounds and (ii) complementing the existing commercial databases (which typically specialize on only one or two classes of crystals and contain in addition to crystallographic information a range of physical properties). Another major concern of the COD initiators is supporting crystallographers in emerging countries. By providing the opportunity to check rapidly and early on in an investigation (i.e. already after the cell parameters have been determined) if the structure of the particular crystal under investigation has already been solved, the COD also helps increasing the productivity of structure determinations world wide. To insure a high quality of the data entries, the policy of the COD is that only those CIFs that result from structure refinement software can be uploaded by the general public.

3. THE NANO-CRYSTALLOGRAPHY DATABASE PROJECT AND VISUALIZATION OF CRYSTAL STRUCTURES IN THREE DIMENSIONS

As a complementary project with a similar philosophy to both the COD and the AMCSD, the nanocrystallography group at Portland State University started in 2005 the Nano-Crystallography Database (NCD) project¹⁸. Since structure and morphology of nanocrystals are crucial to their physical properties, the NCD is collecting entries on both the full structure (including atomic coordinates) and the typical morphology (tracht and habit) of inorganic nanocrystals in the form of CIFs. The experimental morphological information that is collected in the "Bestimmungstabellen für Kristalle"¹⁹ will be the first to be included in the NCD. Since we consider the surface of nanocrystals and the possible presence of single or multiple twins as important real structure, the NCD project will collect and later on display such information as well (together with visualizations of other important crystal defects).

As many electron microscopist work on rather simple inorganic structures, we are writing and uploading CIFs to support their work. A good starting point for this are the descriptions of the about 150 full structure determinations in the second edition of Wyckoff's classical reference book "Structure of Crystals"²⁰. To insure a high quality of the data entries, we provide a comprehensive on-line syntax check for CIFs²¹. Only those CIFs that pass both this test and the test that is available at the IUCr web site⁹ will be uploaded to the NCD.

Since the NCD is being developed to support not only materials science education but also image-based nanocrystallography in general (i.e. methods that determine both structure and morphology of nanocrystals from images²²⁻²⁶ taken in transmission electron microscopes), visualizations in 3D of the entries in this database are crucial. For a start, we provide 3D visualizations²¹ by means of Jmol applets for the structural information that is contained in the entries of the COD, Figs. 1 to 5. Next we will work on providing visualizations of the morphological information that will be contained in the entries of the NCD by means of the program "XMorph"²⁷. Fig. 1 shows the opening screen of the website that hosts our local version of the COD. The menu entries are self explanatory and read from top to bottom: *Search the Database, Upload Data, Check syntax errors* and *Insert symmetry equivalent positions*.

Fig. 2 shows the search screen that is accessible from the opening screen, Fig. 1. The elements Au and K were entered into this screen to conduct a search for all the entries that contain these two elements together in one crystal phase. Fig. 3 shows the result screen for the search for the simultaneous presence of Au and K. By clicking on *CIF file* for the second entry in this list, the

respective CIF is displayed on the user's computer with the program he or she may select for this purpose. The text editor "Notepad" can be employed to display (and edit) CIFs, but the free program "enCIFer" was specifically designed for the display, editing, and for syntax checks of CIFs. This program can be downloaded for all common platforms at ref.²⁸. Using enCIFer, Fig. 4 shows the CIF for As_2AuK_5 .

Fig. 5 finally shows the 3D visualization of the As_2AuK_5 structure in Jmol. Alternatively, the *asymmetric unit* (which is typically just one molecule in molecule crystals) can be displayed. By clicking on *3 x 3 x 3 unit cells*, the content of nine unit cells can be displayed at once. There are options to display only the atoms or the atoms together with a sketch of the unit cell superimposed on the atoms. The unit cell parameters are listed in addition when a structure is displayed with the latter option. As with any Jmol applet, one can zoom into the display of the atomic arrangement by using the Shift key together with the mouse. A range of tools that allow, for example, for the measurement of distances between atoms or the bond angles between three atoms are accessible by a left mouse click directly onto the Jmol structure display. (To display the 3D visualizations with Jmol, the internet browser must support Java 1.4. If not already installed within the browser, the JAVA™ 2 platform is available for free at ref.²⁹.)

The actual visualization of a COD database entry in three dimensions is obtained by turning the displayed atomic arrangement, e.g. Fig. 5, around three mutually perpendicular axes by clicking on *Rot X*, *Rot Y*, and *Rot Z*. Rotations by 45 degrees are default, but arbitrary rotations (with a negative or positive sign) can be realized by either entering the desired rotations in the respective boxes of the rotation menu or by moving the mouse. The option to *Reset to (the) original orientation* also exist.

In the future, we will add to the NCD both interactive 2D fringe fingerprint plots^{25,26} and more crystallographic functionality to the 3D display of structures in order to provide on-line support for image-based nanocrystallography²²⁻²⁶. The NCD shall then become a free internet based research support tool for electron microscopists in addition to providing world wide support for materials science and engineering, crystal physics, crystal chemistry, and mineralogy education.

SUMMARY

Crystallographic databases for inorganic materials that are freely accessible over the internet were reviewed. The objectives, current state of the affair, and future directions of the Nano-Crystallography Database project were described. Instructions were provided on how to visualize the atomic arrangements in three dimensions for several thousand crystals for which entries exist in the Crystallography Open Database.

ACKNOWLEDGMENTS

This project is supported by the NorthWest Academic Computing Consortium. Additional support was provided by both an award from Research Corporation and a Scholarship of Teaching Resources Team Incentive Grant from Portland State University.

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27. Courtesy of Dr. Dedong Wu, AstraZeneca Pharmaceuticals LP, 1800 Concord Pike, Wilmington, DE 19850.
28. http://www.ccdc.cam.ac.uk/free_services/encifer/
29. <http://www.java.com/en/download/index.jsp>

About the authors

Peter Moeck is a German-British crystallographer (with more than 20 years of experience in the structural characterization of semiconductors by complementary methods) and currently an Assistant Professor at Portland State University (PSU). In the late 90s he and Phil Fraundorf (a Full Professor at the University of Missouri at Saint Louis) laid the foundations of image-based nanocrystallography and transmission electron goniometry, i.e. methodologies that can be used with the current generation of high resolution (HR) transmission electron microscopes (HRTEMs), but become much more viable with the wider availability of aberration-corrected TEMs. Peter also volunteers some of his time to services on the international Advisory Board of the Crystallography Open Database. Ondrej Certík is a Czech undergraduate physics student, worked over the summer of 2005 in Peter's research group, and wrote the parser that allows the 3D visualization of CIFs with Jmol. Girish Upreti is a Nepalese graduate physics student in Peter's research group and writes CIFs of simple inorganic structures for uploads to both the COD and the NCD. Bjoern Seipel is a German powder X-ray crystallographer, Adjunct Assistant Professor at PSU, and member of Peter's research group. He writes the software to calculate fringe fingerprint plots from CIFs. Will Garrick heads PSU's Office of Academic & Research Computing for Instruction and Research Services, which kindly provides the infrastructure for this project. Morgan Harvey is an undergraduate student of Computer Science at PSU and works for Will's office. Morgan and Will were instrumental in designing the web pages for this project and provide high level programming support.

Nanocrystallography Visualizations : Crystallography Open Database - Mozilla Firefox

File Edit View Go Bookmarks Tools Help

http://nanocrystallography.research.pdx.edu/cod/

DSPAM v3 Control C... JMOL Ondřej Čertík slovník.cz - Multilingu... JMOL Python Library Refer... CIF file checker

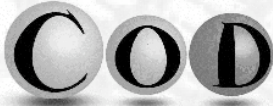
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USA ondra@dell: /home/ondra

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Fig. 1

Nanocrystallography Visualizations - Mozilla Firefox

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http://nanocrystallography.research.pdx.edu/cod/search.php

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Search

Output limited to 300 entries maximum, see the [hints and tips](#)

Search by physical properties:

Text (1 or 2 words)

With these elements

Without these elements

Minimum and Maximum volume

Strict number of elements

Search by cell parameters:

a (min - max)

b (min - max)

c (min - max)

α (min - max)

β (min - max)

USA ondra@dell: /home/ondra Nanocrystallography Vis... Mon Aug 29, 12:29

Fig. 2

Nanocrystallography Visualizations : Open Crystallography Database : Search Results - Mozilla Firefox

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http://nanocrystallography.research.pdx.edu/cod/result.php

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Result : There are 6 entries in the selection Searching elements including Au K

[CIF file](#) Formula : - P 1.00 Au 1.00 K 2.00 -
 Comments : Eisenmann, B Klein, J Somer, M Crystal structure of dipotassium catena-phosphidoaurate Zeitschrift fuer Kristallographie (149,1979-) 197 (1991) 277 278
 Space group : C m c m
 Cell volume: 446.40
 Cell parameters: 9.7870 ; 7.3950 ; 6.1680 ; 90.000 ; 90.000 ; 90.000

[show](#)

[CIF file](#) Formula : - As 2.00 Au 1.00 K 5.00 -
 Comments : Eisenmann, B Klein, J Somer, M Linear anions (CuAs₂)₅- (AuP/2)₅- and (AuAs₂)₅- in potassium compounds Journal of Alloys Compd. 178 (1992) 431 439
 Space group : P 63/m m c
 Cell volume: 546.40
 Cell parameters: 5.7300 ; 5.7300 ; 19.2160 ; 90.000 ; 90.000 ; 120.000

[show](#)

[CIF file](#) Formula : - P 2.00 Au 1.00 K 5.00 -
 Comments : Eisenmann, B Klein, J Somer, M Linear anions (CuAs₂)₅- (AuP/2)₅- and (AuAs₂)₅in potassium compounds Journal of Alloys Compd. 178 (1992) 431 439
 Space group : P 63/m m c
 Cell volume: 514.90
 Cell parameters: 5.6360 ; 5.6360 ; 18.7160 ; 90.000 ; 90.000 ; 120.000

[show](#)

[CIF file](#) Formula : - H 4.00 O 2.00 Au 1.00 Br 4.00 K 1.00 -
 Comments : Cox, E G Webster, K C The Stereochemistry of Quadricovalent Atoms: Tervalent Gold Journal of the Chemical Society 1936 (1936) 1635 1637
 Space group : P 1 21/a 1
 Cell volume: 479.90
 Cell parameters: 9.5100 ; 11.9300 ; 4.2300 ; 90.000 ; 90.000 ; 90.000

[show](#)

No CIF Formula : - Au 5.00 K 3.00 Pb 1.00 -
 Comments : Zachwieja U; Wlodarski J - K₃Au₅Pb: Layers of (2)(infinity)[AuAu₃/2] gold tetrahedra and (1)(infinity)[Pb-2/2] lead chains - ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE 624 (1998) 1569-1572
 Space group : Imma

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Fig. 3

1008878.cif - enCIFer

File Edit Search Tools Help

Blocks: 1

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1 |data_1008878
2 |_chemical_name_systematic      'Pentapotassium diarsenidoaurate'
3 |_chemical_formula_structural   'K5 (Au As2)'
4 |_chemical_formula_sum         'As2 Au K5'
5 |_publ_section_title
6 |
7 |Linear anions (CuAs2)5-, (AuP2)5- and (AuAs2)5- in potassium compounds
8 |
9 |loop_
10|_publ_author_name
11| 'Eisenmann, B'
12| 'Klein, J'
13| 'Somer, M'
14|_journal_name_full            'Journal of Alloys Compd.'
15|_journal_codens ASTM         JALCEU
16|_journal_volume              178
17|_journal_year                 1992
18|_journal_page_first          431
19|_journal_page_last           439
20|_cell_length_a                5.730(2)
21|_cell_length_b                5.730(2)
22|_cell_length_c                19.21599(400)
23|_cell_angle_alpha            90
24|_cell_angle_beta              90
25|_cell_angle_gamma            120
26|_cell_volume                  546.4
27|_cell_formula_units_Z         2

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Errors - none
Warnings - none
Remarks - none

Loaded dictionary: /home/ondra/encifer/encifer_1.1/dict/cif_rho.dic
Starting new file "untitled1.cif"
Reading CIF "1008878.cif"
Read 80 lines.
No errors, warnings or remarks.

Line 1, Column 1

USA 1008878.cif - enCIFer Sun Aug 28, 14:26

Fig. 4

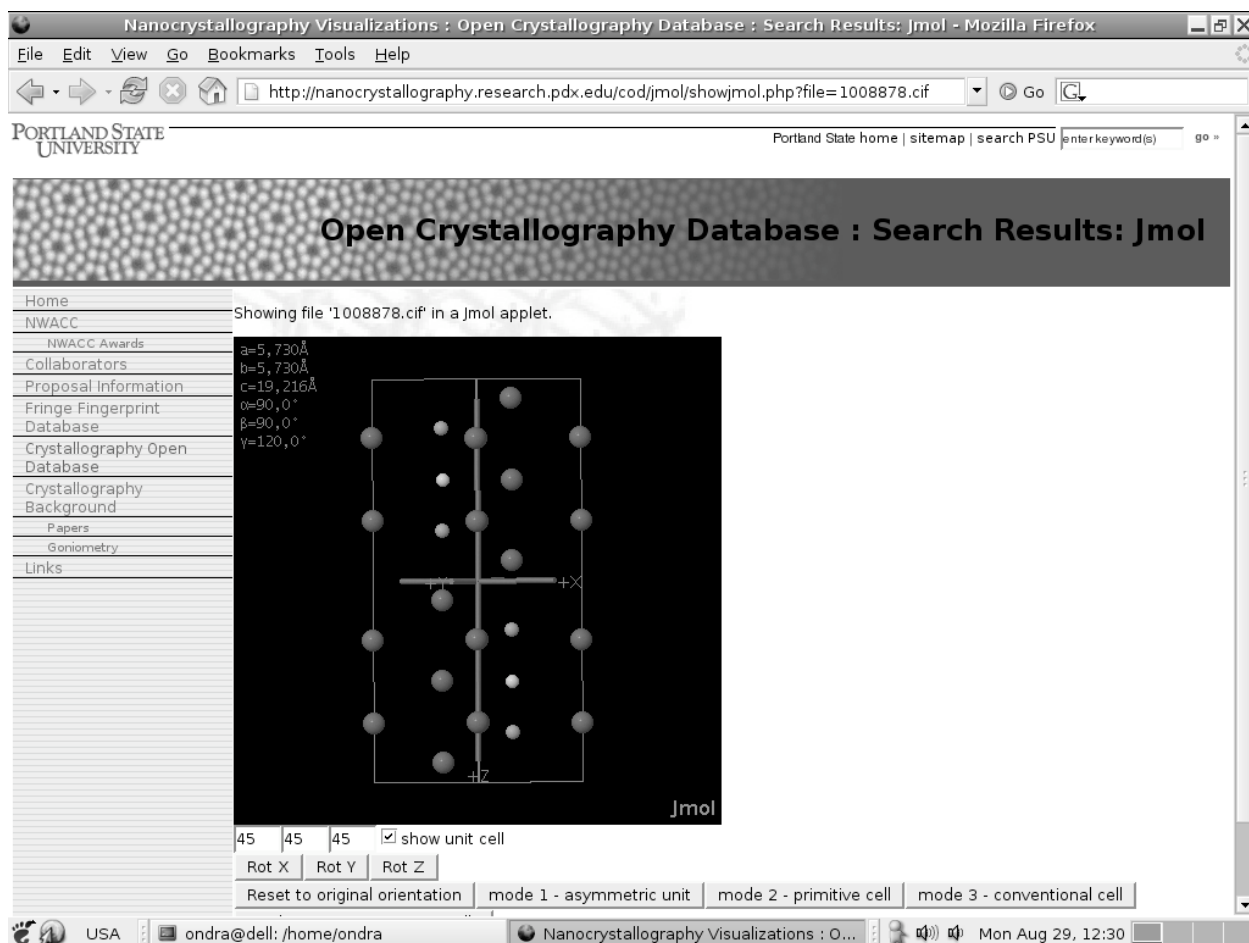


Fig. 5

Fig. 1: Screenshot of the opening screen of the website that hosts our local version of the COD.

Fig. 2: Screenshot of the search screen with entries for the elements Au and K.

Fig. 3: Screenshot of the results of the search for the simultaneous presence of the two elements Au and K.

Fig. 4: Screenshot of the CIF of the second entry in the result list of Fig. 3 displayed by the LINUX version of the free program “enCIFer”²⁸.

Fig. 5: Screenshot of the visualization screen for one unit cell of As_2AuK_5 displayed by Jmol.

Appendix B: Freely accessible Internet Resources for Nanoscience Education and Research at Portland State University's Research Server

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ABSTRACT

Because a great deal of nanoscience and nanotechnology relies on crystalline nanometer sized or nanometer structured materials, crystallographers have to provide their specific contributions to the National Nanotechnology Initiative. Here we review two open access internet-based crystallographic databases, the Crystallography Open Database (COD) and the Nano-Crystallography Database (NCD), that store information in the Crystallographic Information File (CIF) format. Having crystallographic data available on the internet in a standardized format allows for many kinds of internet-based crystallographic calculations and visualizations. Examples for this that are dealt with in this paper are interactive crystal structure visualizations in three dimensions (3D) and calculations of theoretical lattice-fringe fingerprints for the identification of unknown nanocrystals from their atomic-resolution transmission electron microscopy images.

Keywords: Open Access, Crystallography, Databases, Lattice Fringe Fingerprinting, Crystallographic Information File (CIF)

1. INTRODUCTION

In his LETTER FROM THE PRESIDENT (of the International Union for Crystallography), Yuji Ohashi, recently proposed to the community of crystallographers that: “*We must take steps to ensure that crystallography continues to flourish. To accomplish this I believe we need to promote the following two initiatives. The first is the development of new crystallographic techniques. ... The second is the wider expansion of crystallography to scientists in other scientific fields.... Moreover, crystallography should be expanded to include scientists in the developing countries. Because ... teaching systems are insufficient in the developing countries.*” [1].

The members of the Nanocrystallography Group at Portland State University and their collaborators are contributing to both of these initiatives. We develop image-based nanocrystallography in two and three dimensions for atomic resolution transmission electron microscopy [2-5]. This may be understood as both *development of new crystallographic techniques* and *wider expansion of crystallography to scientists in other scientific fields* (Yuji Ohashi). Our developments are for the transmission electron microscopy community and complement existing internet based free resources of that community [6-8].

We also develop a dedicated nanocrystallography website [9,10] for both educational and research support purposes. Over this website [10] free (open access) crystallographic databases (e.g. an approximately 11,500 entry subset of the Crystallographic Open Database (COD) [11,12] and the Nano-Crystallography Database (NCD) [13]) are accessible. Having more than ten thousand sets of crystallographic data (including atomic coordinates and space groups) available on the internet in the standardized Crystallographic Information File (CIF) format [14,15] allows for many kinds of web-based crystallographic calculations and visualizations. Two such examples, i.e. interactive crystal structure visualizations in three dimensions and calculations of theoretical lattice-fringe fingerprints for the identification of unknown nanocrystals from their atomic-resolution transmission electron microscopy images will be dealt with in this paper after a brief introduction to the crystallographic information that is

stored as CIFs in the COD and the NCD. Our developments and this paper may be understood as *to include scientists in the developing countries because ... teaching systems are insufficient in the developing countries* (Yuji Ohashi).

2. THE CRYSTALLOGRAPHIC INFORMATION FILE (CIF)

The standard Crystallographic Information File (CIF) format (file extension *.CIF) [14] has been adoption in 1990 by the International Union of Crystallography as the standard file format and syntax for communicating crystallographic information between both human beings and computers and between different kinds of software programs and computers. Since then CIF has become a crystallographic entity in its own right of such significance that a volume of the latest edition of the International Tables for Crystallography [15] is dedicated to describing it comprehensively. Table 2 displays CIFs for two structures from the COD where the first column one is for the rutile prototype and second column is for a structure that may be derived from this prototype.

Obviously, all the crystallographic (and bibliographic) information for many kinds of visualizations and calculations is contained in CIFs and a human being with a minimum of crystallographic training being can discern this information. The above mentioned volume of the International Tables [15] may serve as a “dictionary” if necessary. The two CIFs in Table 1 are from the Crystallography Open Database (COD) [11,12] and having such kind of data in open access at the internet opens up new opportunities to support Yuji Ohashi’s proposal above.

| | |
|--|--|
| <pre> data_1000094 _chemical_name_systematic 'Nickel divanadium oxide' _chemical_formula_structural 'Ni V2 O6' _chemical_formula_sum 'Ni O6 V2' _publ_section_title ; Structure determination of NiV~2~O~6~ from X-ray powder diffraction : a rutile-ramsdellite intergrowth ; loop_ _publ_author_name 'Le Bail, A' 'Lafontaine, M A' _journal_name_full ; European Journal of Solid State Inorganic Chemistry ; _journal_coden_ASTM EJSCE5 _journal_volume 27 _journal_year 1990 _journal_page_first 671 _journal_page_last 680 _cell_length_a 7.130(1) _cell_length_b 4.791(1) _cell_length_c 8.825(2) _cell_angle_alpha 90.16(1) _cell_angle_beta 102.13(1) _cell_angle_gamma 94.19(1) _cell_volume 293.9 _cell_formula_units_Z 3 _symmetry_space_group_name_H-M 'P -1' _symmetry_int_tables_number 2 _symmetry_cell_setting triclinic loop_ _symmetry_equiv_pos_as_xyz 'x,y,z' '-x,-y,-z' loop_ _atom_type_symbol _atom_type_oxidation_number Ni2+ 2.000 </pre> | <pre> data_9003520 _chemical_name Rutile loop_ _publ_author_name 'Meagher E P' 'Lager G A' _journal_name_full 'The Canadian Mineralogist' _journal_volume 17 _journal_year 1979 _journal_page_first 77 _journal_page_last 85 _publ_section_title ; Polyhedral thermal expansion in the TiO2 polymorphs: Refinement of the crystal structure of rutile and brookite at high temperature Sample at 25 degrees C ; _chemical_formula_sum 'Ti O2' _cell_length_a 4.593 _cell_length_b 4.593 _cell_length_c 2.959 _cell_angle_alpha 90 _cell_angle_beta 90 _cell_angle_gamma 90 _symmetry_cell_setting tetragonal _symmetry_space_group_name_H-M 'P 42/m n m' _symmetry_int_tables_number 136 loop_ _symmetry_equiv_pos_as_xyz x,y,z -y,-x,z y,x,-z 1/2+y,1/2-x,1/2-z 1/2-y,1/2+x,1/2+z 1/2+x,1/2-y,1/2+z 1/2-x,1/2+y,1/2-z x,y,-z -x,-y,z y,x,z -y,-x,-z 1/2-y,1/2+x,1/2-z </pre> |
|--|--|

| | |
|--|------------------------------------|
| V5+ 5.000 | 1/2+y,1/2-x,1/2+z |
| O2- -2.000 | 1/2-x,1/2+y,1/2+z |
| loop_ | 1/2+x,1/2-y,1/2-z |
| _atom_site_label | -x,-y,-z |
| _atom_site_type_symbol | loop_ |
| _atom_site_symmetry_multiplicity | _atom_site_label |
| _atom_site_Wyckoff_symbol | _atom_site_fract_x |
| _atom_site_fract_x | _atom_site_fract_y |
| _atom_site_fract_y | _atom_site_fract_z |
| _atom_site_fract_z | _atom_site_Uiso_or_equiv |
| _atom_site_occupancy | Ti 0.00000 0.00000 0.00000 0.00532 |
| _atom_site_attached_hydrogens | O 0.30510 0.30510 0.00000 0.00760 |
| _atom_site_calc_flag | |
| Ni1 Ni2+ 1 a 0. 0. 0. 1. 0 d | |
| Ni2 Ni2+ 2 i -0.0140(4) -0.0131(6) 0.3315(3) 1. 0 d | |
| V1 V5+ 2 i 0.4192(5) 0.8826(6) 0.2334(5) 0.88 0 d | |
| V2 V5+ 2 i 0.7217(36) 0.4257(51) 0.8044(27) 0.12 0 d | |
| V3 V5+ 2 i 0.7158(4) 0.4551(6) 0.4677(3) 1. 0 d | |
| V4 V5+ 2 i 0.7145(4) 0.4522(6) 0.1109(4) 1. 0 d | |
| O1 O2- 2 i 0.1678(12) 0.3478(15) -0.0022(9) 1. 0 d | |
| O2 O2- 2 i 0.1673(12) 0.3500(15) 0.3837(12) 1. 0 d | |
| O3 O2- 2 i 0.2050(12) 0.3706(16) 0.7020(11) 1. 0 d | |
| O4 O2- 2 i 0.1751(10) 0.8718(15) 0.2009(11) 1. 0 d | |
| O5 O2- 2 i 0.1580(11) 0.8247(15) 0.5219(10) 1. 0 d | |
| O6 O2- 2 i 0.1566(11) 0.8382(14) 0.8624(11) 1. 0 d | |
| O7 O2- 2 i 0.5263(11) 0.2192(16) 0.2486(12) 1. 0 d | |
| O8 O2- 2 i 0.5317(10) 0.2700(14) 0.5814(10) 1. 0 d | |
| O9 O2- 2 i 0.5176(11) 0.2822(14) 0.9256(11) 1. 0 d | |
| _refine_ls_R_factor_all 0.043 | |

Table 1: Two exemplary Crystallographic Information Files.

3. THE CRYSTALLOGRAPHY OPEN DATABASE

This database was started in March of 2003 in Europe and is rapidly growing as more and more crystallographers and scientific institutes/societies/academies donate their collections of CIFs and upload them over the internet so that anybody with access to the World Wide Web can access them for free. As of March 2006, the COD contained approximately 34,000 entries. An approximately 2,000 entry subset of the COD is named PCOD for Predicted Crystallography Open Database [11,12].

The long term objectives of the COD initiators are summarized on their web page [12] as: (i) providing free access to comprehensive crystallographic data (including the atomic coordinates) on all known inorganic, metallic, organometallic and organic crystalline compounds and (ii) complementing the existing commercial databases (which typically specialize on only one or two classes of crystals and contain in addition to crystallographic information a range of physical properties). Another major concern of the COD initiators is supporting crystallographers in emerging countries.

4. WHY NANOCRYSTALS NEED THEIR OWN CRYSTALLOGRAPHIC DATABASE

It is well known that the long-range ordered atomic arrangements and their two dimensional (2D) discontinuities (i.e. structures and morphologies) of nanocrystals determine their physical and chemical properties. Structural prototype, lattice constants, and morphologies of nanocrystals are frequently dependent on the size of the crystals in the nanometer range. Added to this size dependency of the lowest thermo-dynamical potential of a structure, there is in the nanoparticle regime a strong tendency to metastability and spatially inhomogeneous non-stoichiometry.

Moreover, many nanocrystals possess structural defects in three, two, and one dimension as well as point defects in excess of their thermodynamical equilibrium levels. The presences of these structural defects are dependent on the particulars of the nanocrystal synthesis and processing procedures and significantly affect the properties of the nanoparticles.

In short, a whole new “crystallographic world” is waiting to be discovered in the nanocrystal realm by both *new crystallographic techniques* and *the wider expansion of crystallography to ... other scientific fields* (Yuji Ohashi). Eventually core models of classical text book crystallography, e.g. ideal crystals being represented by the infinite translation of a unit cells, may have to be modified on the basis of such discoveries. For all of these reasons, nanocrystals need their own crystallographic database.

5. THE NANO-CRYSTALLOGRAPHY DATABASE

As a complementary project with a similar philosophy to the COD, the nanocrystallography group at Portland State University started in the summer of 2005 the Nano-Crystallography Database (NCD). Since structure and morphology of nanocrystals are crucial to their physical properties, the NCD is collecting entries on both the full structure (including atomic coordinates) and the typical morphology (tracht and habit) of inorganic nanocrystals in the form of CIFs. The experimental morphological information that is collected in the “Bestimmungstabellen für Kristalle” [16] will be the first to be included in the NCD. Since we consider the surface of nanocrystals and the possible presence of single or multiple twins as important real structure, the NCD project will collect and later on display such information as well together with visualizations of other important crystal defects.

As many electron microscopists and nanocrystal researchers work on rather simple inorganic structures, we are writing and uploading CIFs to support their work. Since the NCD is being developed to support not only nanomaterials science education but also image-based nanocrystallography in general (i.e. methods that determine both structure and morphology of nanocrystals from images [2-5] taken in transmission electron microscopes), visualizations in 3D of the entries in this database are crucial.

6. VISUALIZATION OF CRYSTAL STRUCTURES & LATTICE FRINGE FINGERPRINT PLOTS

Figure 1 shows the 3D visualization [9] of the two structures for which the CIFs that are given in Table 1 at our nanocrystallography visualization web site [10]. For comparison purposes, the displayed structures can be rotated independently around three mutually perpendicular axes. Rotations by 45 degrees are default, but arbitrary rotations (with a negative or positive sign) can be realized by either entering the desired rotations in the respective boxes of the rotation menu or by moving the mouse.

Over the same web site [10], 2D theoretical lattice-fringe fingerprint plots [2,4] can be calculated in both the kinematical and the dynamical scattering limits. The latter limit is synonymous with double and multiple diffraction within one nanocrystal. Figure 2 shows, for example, theoretical lattice fringe fingerprint plots for the titania phase Rutile (CIF in left column of Table 1) for 0.19 nm point-to-point resolution of a (parallel illumination of scanning probe) transmission electron microscope (TEM). Such theoretical plots can be compared with experimental plots that are derived from atomic resolution TEM images in order to identify an unknown nanocrystal phase.

Since fringe fingerprint plots contain *two* sets of “crystal characteristic” information, i.e. interfringe angles and (reciprocal) lattice fringe spacings, Fig. 2, that are both used as the ordering principle of comprehensive databases [17-19], they are more characteristic of a crystalline material than either classical crystallography (morphological crystallography) [17,18] or powder diffraction databases [19].

As with any kind of “finger print” one needs the support of a comprehensive database to identify an unknown. With support from our NCD, lattice fringe fingerprinting may become one of the realizations of Boldyrew’s and Doliwo-Dobrowolsky’s 70 years old prophecy [18]: “*In the further development of crystallography one will either adopt one of the goniometric methods of determining crystals or develop eventually a new one which, as far as this is possible, combines the advantages of all of the prior methods and avoids their disadvantages.*”

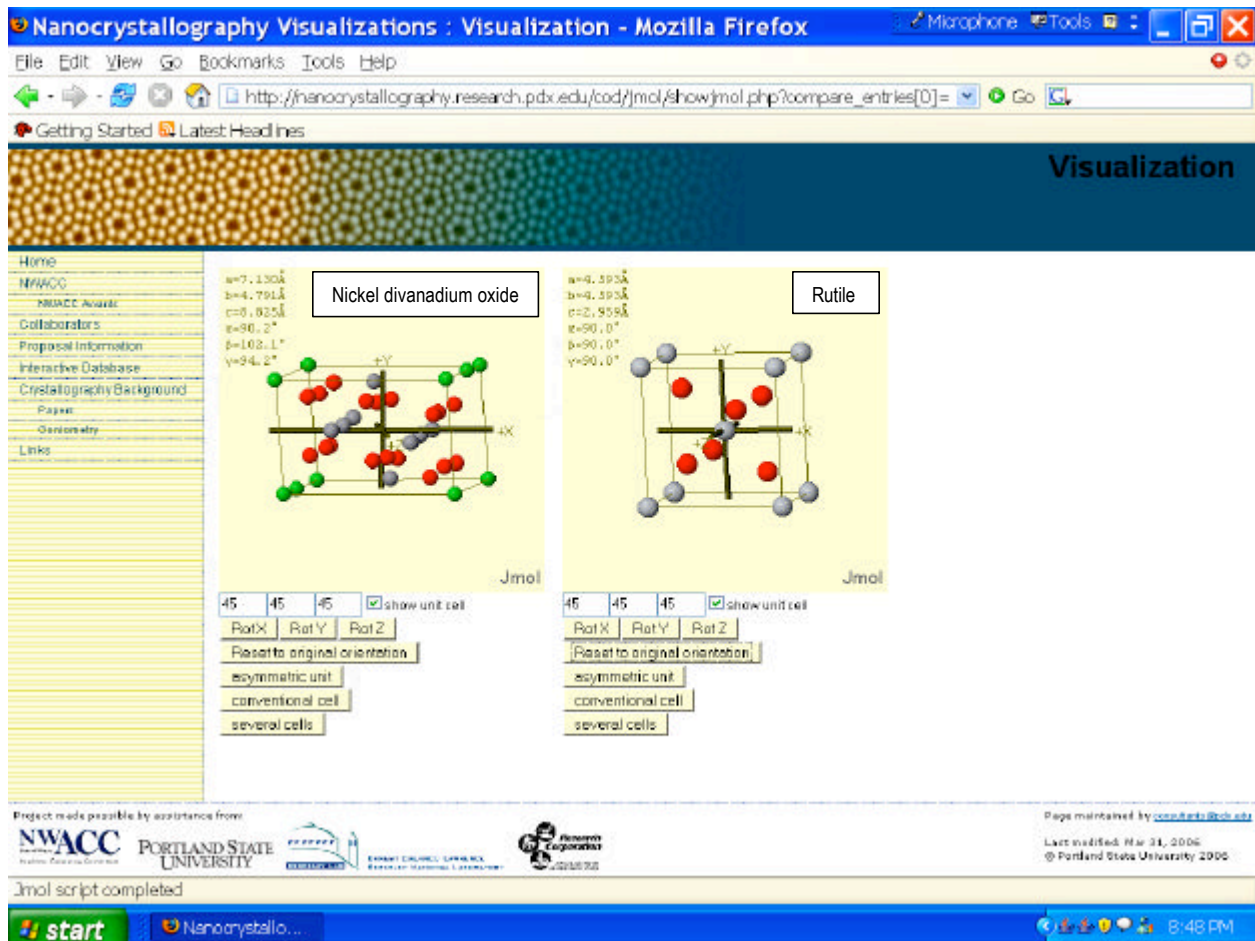


Fig. 1: Shot of the (3D) Visualization screen [11] for one unit cell of the two structures given in Table 1.

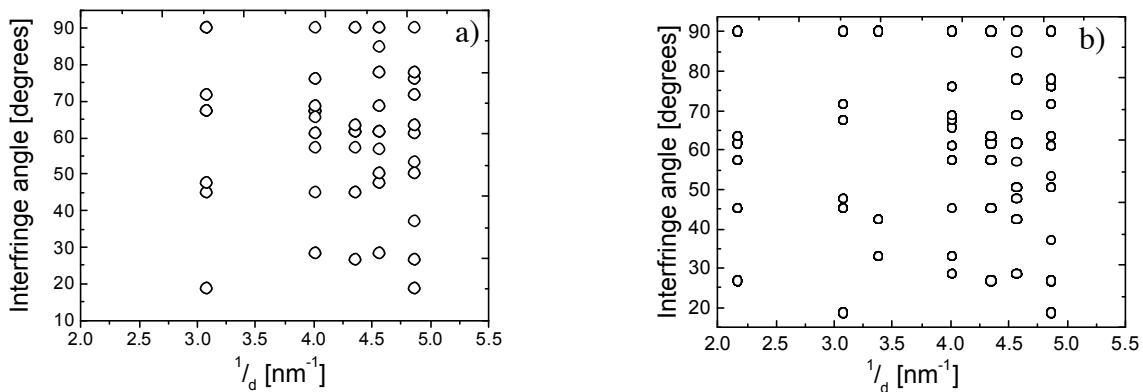


Fig. 2: Theoretical lattice fringe fingerprint plots for the titania phase Rutile (CIF in right column of table 1) for a 0.19 nm point-to-point resolution (S)TEM; **(a)** kinematical scattering limit, **(b)** dynamical (i.e. double and multiple diffraction within one nanocrystal) scattering limit.

SUMMARY

Two open access databases that are freely accessible over the internet and store crystallographic information in the so called Crystallographic Information File format were briefly reviewed. Having such

data available on the internet in a standardized format allows for many kinds of internet-based crystallographic calculations and visualizations. Interactive crystal structure visualizations in three dimensions are one such example. The other example we briefly dealt with in this paper is the calculations of theoretical lattice-fringe fingerprint plots for the identification of unknown nanocrystals from their atomic-resolution transmission electron microscopy images. More examples will be presented elsewhere.

ACKNOWLEDGMENTS

This project was supported by the NorthWest Academic Computing Consortium. Additional support was provided by an award from Research Corporation. Faculty Enhancement grants, Faculty Development grants, Scholarship of Teaching Resources Team Incentive grants, and one Internationalization grant from Portland State University and a visiting scientist award from the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, supported this project as well.

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