# Structural fingerprinting in the TEM and open access crystallographic databases



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financial support: Oregon Nanoscience and Microtechnologies Institute, Army Research Laboratory, Research Corporation, North-West Academic Computing Consortium, National Science Foundation, Portland State University, National Center for Electron Microscopy Berkeley

# Outline

- 1. Motivation: Conventional structural fingerprinting only for micro-crystalline powders
- 2. From electron crystallography to structural fingerprinting of nanocrystals in the TEM
- 3. Lattice-Fringe, Projected Symmetry & Structure-Factor (amplitude and phase) Fingerprinting of nanocrystals from HRTEM images and PED patterns (single and polycrystalline)
- 4. Open-access crystallographic databases
- **5. Summary and Conclusions**



Figure 3. Identification of white powder from the threatening letter (from the "anthrax" period), picctura ture from optical microscope.

21-255

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Z. Kristallogr. Suppl. 23 (2006) 35-40 © by Oldenbourg Wissenschaftsverlag, Münche Application of X-ray diffraction in forensic science

© Joint Committee on Powder Diffraction Standards 197 2.97 2.47 3,47 CoCr2S4 1.75  $I/I_1$ 100 80 70 20 Cobalt Chromium Sulfide hkl d A 1/11 hkl  $1/l_1$ d A Rad. CrKa  $\lambda$  2,2909 Filter Cut off  $I/I_1$  Microphotometer Dia. 5.47 20 80 10 220 2.966 311 222 Ref. \* 2.836 70 30 400 422 2.466 Sys. Cubic a<sub>0</sub> 9.91 Fd3m (227) 2.015 9.91 1,897 60 333,511 Dx 3.97 a Ref. Ibid. 1.745 100 440 ¥ 973.24 1.564 10 620 1.508 20 10 533 €a 2V Ref. 622 1.491 1.427 20 444 1.385 10 551,711 1.323 20 642 \*L.C.D. Bok, Chemistry and Structure of Double Metal 1.289 50 553,731 1.239 Sulfides, Thesis, Dipl. Imperial College, London (1955) 60 800 Synthetic, by fusion of elements. 1.212 10 20 733 660,822 Spinel structure. FORM T-2

Marek Kotrlý

8 d-spacing comparison of an unknown with reference materials, red highlights show matches 🚟 ICDD DDView+ - PDF-4+ 2006 RDB - Ja | File Edit Tools Window Help Goodness of Fit for the reference pattern, sorted 🗵 🚷 💱 🗳 🥁 **\_** 6 × (Untitled) Matches Phases Lines Help 1 🛛 🖉 🔊 🔊 🍤 👗 Rot. PDF # Compound Name Chemical Formula D1 D2 D3 D4 DS D6 D7 D8 I/Ic Pat 04-007-4784 Lutetium Chromium Aluminum 1116 Cr6 76 0140 24 9.3972 4.6986 4.13 1566 3.1843 2.4598 2.3755 2.3493 2.2989 1.92 486 -083-1768 Magnesium Hydro 3,489 2,4984 1629 -073-0147 Magnesium Silicate Hydroxide Mg3 (Si2 O5)2 (OH)2 4.5394 4.3279 4.1368 3543 3.8961 3 1181 2.5911 2 4985 446 1810 -008-5439 Lutetium Chromium Aluminum Lu6 Cr4 Al43 9.3695 4.6848 4.1302 3.1977 2.4762 2.3738 2.3424 2.3007 2.29 437 1769 4-008-1752 Ytterbium Manganese Aluminun Yb6 Mn4 Al43 .3453 4.6726 4.1274 3.2042 2.4853 2.371 2.3363 2.3002 2.13 433 1645 01-075-0857 Aluminum Silicate Hydroxide A12 SI4 O10 ( O H 9.3473 4.6737 4.4174 4.3391 4.2383 4.1246 3.5432 3.1158 1.37 428 1568 91-987-9564 Lead Zirconium Oxid Pb (Zr O3) 4.1614 2.9461 2.939 2.9214 2.0807 2.0511 1.6962 1.6934 13.33 382 Experiment Lines (65 of 66) Search Line: 9.354 D1 Range: 9.176 - 9.531 Rotation: All Ex d(Â) ▼ Ex I PI d(Å) P1 I P2 d(Å) P2I P3 d(Å) P3I Preferences 3.1189 369 3.1171 45 3.112 Search Window: 0.18 3.0404 4575 .0387 100 3.0564 Match Window: 0.18 2.92692 217 2.923 Search Method: Fink wable GOM: 1500 2.88629 468 2.882 25 Cu Kal 1. 4056Å Wavelength: 2.84415 272 2.856 2.8468 2.80084 374 2.799 20 Phases (3) 2.74812 243 2.742 10 2.7484 PDF a Int. Ratio Int. % # Accepted Compound Name I/Ic 2.71364 203 2.711 01-072-19 Calcium Carbonate 63.17 47 3.240... 2.68265 243 10 2.677 00-024-197 2.5754 2 Sucrose 18,285 13 0.7 199 2.574 2.5015 847 .497 2.504 2.4984 23 2.43173 229 2.4312 2.43 2,40859 289 2,406 2.34841 402 2.349 2.3378 d-spacings rotated and sorted by Goodness of Merit, 2.29 1217 2.2868 2.291 118 2,2932 2,25777 310 2.258 14 2.23576 290 2.234 2.2355 available for Hanawalt, Fink and Long 8 searches 2.1873 227 2.189 2.1959 2.17235 212 2.171 2.1711 2.0963 2.09996 1069 14 2.101 2.101 Larger data files can be imported Unlimited phase matches Display for the program SIeve + 2006 demonstrating a three phase search and index solution for an experimental unknown. New features in this year's release are highlighted. Software support only for The International Centre for Diffraction Data® EBSD/SEM, not much interests in

www.icdd.com

ICDD.

dealing with nanocrystals







 $V_7O_{16}$ 

Let's use smaller wavelengths, let's go to a synchrotron !



FIG. 2. Experimental powder diffraction patterns for  $V_2O_5$  nanotubes (a) and crystalline  $V_2O_5$  (b). The high-Q portion of the patterns is given in the insets on an enlarged scale.



Figure 2. (a) TEM image of a typical nanotube (C12-VOx-NT),

PHYSICAL REVIEW B 69, 085410 (2004)

### Structure beyond Bragg: Study of V2O5 nanotubes

 V. Petkov,<sup>1,\*</sup> P. Y. Zavalij,<sup>2</sup> S. Lutta,<sup>2</sup> M. S. Whittingham,<sup>2</sup> V. Parvanov,<sup>1</sup> and S. Shastri<sup>3</sup> <sup>1</sup>Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859, USA
 <sup>2</sup>Chemistry Department, State University of New York at Binghamton, Binghamton, New York 13902, USA <sup>3</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA (Received 5 November 2003; published 25 February 2004)

The structure of  $V_2O_5$  nanotubes has been experimentally determined. The approach of the atomic pair distribution function technique was employed because of the limited structural coherence in this nanophase material. It has been found that even a nanocrystal with the complex morphology of vanadium pentoxide nanotubes possesses an atomic arrangement very well defined on the nanometer length scale and well described in terms of a unit cell and symmetry. Using refined structural parameters a real-size model for the nanotubes has been constructed and used to explain their peculiar morphology.



FIG. 7. (Color) Structure description of  $V_2O_5$  nanotubes. Double layers of V-O<sub>6</sub> octahedral (light green) and V-O<sub>4</sub> tetrahedral (red) units are undistorted and stacked in perfect registry with crystalline  $BaV_7O_{16}$ ,  $nH_2O$  (a). When bent (b) such layers may form nanoscrolls (c) or closed nanotubes (d). Double layers of such complexity may sustain only a limited deformation. As a result,  $V_2O_5$  nanotubes occur with inner diameters not less than 5 nm. The real-size models shown in (c) and (d) have an inner diameter of approximately 10 nm and involve 33 000 atoms. The bending of vanadium oxide layers into nanotubes can be explained by the presence of an anisotropy in the distribution of vanadium 4+ and 5+ ions as discussed in Ref. 24.

F. Krumeich et al., Morphology and Topochemical Reactions of Novel Vanadium Oxide Nanotubes, *J. Am. Chem. Soc.* **1999**, *121*, 8324-8331



Figure 4. (a) Typical selected area electron diffraction pattern of a nanotube. (b) Schematic representation. The reflections 00l (symbolized by +) are caused by the regular interlayer distance while the square arrangement of spots hk0 (symbolized by  $\spadesuit$ ) corresponds to a square lattice ( $a \approx 0.62$  nm) within the layers.





**Figure 30.** Theoretical diffraction patterns of 4 nm diameter ZnS crystallite calculated for a model with (a) a perfect sphalerite lattice, and (b) with a relaxed structure as simulated by Molecular Dynamics calculations [59].

Projection into 2D by TEM's small angle approximation "circumvents" this problem, because the 80 diperiodic space groups (E. A. Wood, Bell System Techn. Journ. 43 (1964) 541-559) project into the same plane groups as their 230 triperiodic counterparts. There can be (and frequently is), however, changes in the lattice parameters due to the nanometer size of crystals, possibly also in structure factors.

# So what to do to fingerprint nanocrystals structurally?

There is also structural fingerprinting in the Transmission Electron Microscope, recent review: P. Moeck and P. Fraundorf, *Zeits. Kristallogr.* 222 (2007) 634-645, *special issue on "Nanocrystallography"*, expanded version in open access arXiv:0706.2021

either electron diffraction patterns or high resolution "structure images" can be employed combined with either spectroscopic or prior information on the elements present and/or absent within the unknown, but does one really want to focus the electron beam to get an EDX spectrum from a nanocrystal? e.g. H. V. Hart, J. Appl. Cryst. 35 (2002) 552-555.

<u>Our research program:</u> utilize established electron crystallography procedures and combine them with new developments in open-access crystallographic databases – we only want to recognize a nanocrystal structure after it has been solved and became part of a database

### Довлады Академии Наук СССР 1949. Том LXIV, № 1

B. K. Vainshtein, Z. G. Pinsker, Application of Harmonic Analysis in Electron Diffraction, Doklady Akademii Nauk SSSR 64 (1949) 49-52

### ФИЗИКА

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Б. К. ВАЙНШТЕЙН и З. Г. ПИНСКЕР

### ПРИМЕНЕНИЕ ГАРМОНИЧЕСКОГО АНАЛИЗА В ЭЛЕКТРОНОГРАФИИ

(Представлено академиком А. А. Лебедевым 9 XI 1948)

В современном рентгеноструктурном анализе широко используется представление кристаллической решетки по Фурье. Электронная илотность кристалла  $\rho(xyz)$  разлагается в трехмерный ряд Фурье

$$\rho(xyz) = \frac{1}{v} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \dot{F}_{hkl} e^{-2\pi i \, (\bar{r}\,\bar{H})}. \tag{1}$$

Интенсивность (*hkl*) отражения рентгеновских лучей пропорциональна квадрату структурной амплитуды  $|F_{hkl}|^2$ . Используя полученные из эксперимента значения модуля структурной амплитуды  $|F_{hkl}|$  и определяя косвенным путем фазу \*, можно суммированием ряда (1) волучить полное представление о строении кристалла, которому отвечает картина распределения электронной плотности.

Дифракция электронов в кристаллической решетке также может быть использована для построения синтеза Фурье.

# *"Electron diffraction at crystalline lattices may also be use for the creation of Fourier syntheses."*

≈ 60 kV, polycrystalline material, averaging over mm sized beam and many orientations, spotty ring and oblique texture patterns, 105 reflections I = 0 - 4, R = 20 %



$r_{son}(x, y, z) = 1/V \sum_{\substack{hkl \\ y = 45/k}}  F ^2 \exp(-2x)$ $cell_length_a = 4.51(1)$ $cell_length_c = 11.28(3)$ $cell_angle_alpha = 90$ $cell_angle_gamma = 90$ $cell_angle_gamma = 90$ $cell_angle_gamma = 90$	$\frac{1}{2\pi}(hx+ky+lz)$
loop_	mcn
_atom_site_taben _atom_site_type_symbol _atom_site_symmetry_multiplicity _atom_site_Wyckoff_symbol _atom_site_fract_x _atom_site_fract_y _atom_site_fract_z Ba1 Ba2+ 4 c 0.25 0.115(5) 0.18(1) O1 O2- 4 c 0.25 0.61(1) 0.18(1)	$BaCl_2$ $H_2O$ , now precession electron
CI1 CI1- 4 c $0.25 0.11(1) -0.12(1)$ CI2 CI1- 4 c $0.25 0.645(10) -0.11(1)$	diffraction !

### FROM MACROMOLECULES TO BIOLOGICAL ASSEMBLIES

Nobel lecture, 8 December, 1982

by

AARON KLUG

MRC Laboratory of Molecular Biology, Cambridge CB2 2QH, U.K.



"for his development of crystallographic electron microscopy and ..."





"The approach is similar to conventional X-ray crystallography, except that **the phases** of the X-ray diffraction pattern cannot be measured directly, whereas here they **can be computed from a digitised image** ... In order to produce a "true" image, the **electron image must be processed to correct for the phase contrast transfer of the microscope** so that all spatial frequencies contribute with the same sign of contrast."

$$F_{one\_image / zone\_axis}(h,k,l) = \left| F(H,K,0) \right| \cdot e^{i\phi} \approx \frac{\Omega}{2\lambda t} \cdot \frac{FT[I_{image}(X,Y,0)]}{CTF(\vec{s})}$$

Zone axis of image [uvw] or [001] contains reflection (hkl) or (HK0), obtainable by Fourier transform, so that  $u\cdot h+v\cdot k+l\cdot w = 0$  or  $u\cdot H+v\cdot K+1\cdot 0 = 0$ , Weiss zone law

# To know an object (reasonably well) is to know all (or most) of its Fourier coefficients,

to recognize an unknown crystal at the atomic level is to extract and compare structure factor information with that of candidates from a database



Recording of diffraction patterns results in loss of structure factor phases, well known phase problem of diffraction based crystallography



(-)



Fe<sub>3</sub>O<sub>4</sub>, F d 3 m (origin at  $\overline{4}$ 3m for display) Cell parameter:  $a \approx 8.2$  Å

gamma-Fe<sub>2</sub>O<sub>3</sub>, P 4<sub>1</sub> 3 2 Cell parameter:  $a \approx 8.3$  Å

essential differences only in occupation of tetrahedral and octahedral intersites within cubic densest packing of oxygen, but significantly different physical properties !



Our new method: Lattice-fringe -ingerprinting with Projected Symmetry and Structure Factor Phase (and Amplitude) Extraction from HRTEM data

Au-nanocrystats in aberration-corrected HRTEM, courtesy U Kaiser, Univ. Ulm/Germany 0.19 nm point resolution, Philips EM 430 ST (300 kV) at U of Missouri at St Louis, no objective aperture R. Bjoerge, MSc thesis, 2007

nano-powder mixture: magnetite & maghemite



Image of unknown ironoxide nanocrystal HRTEM image plus Hanning window and their FFT (contrast inverted for clearness, spatial frequencies up to 0.14 nm due to double diffraction, non-linear imaging, not explored further



same crystal in 5 images, which were recorded with  $\pm 2^{\circ}$  maximal tilt around eucentric axis, foreshortening effects negligible for projected reciprocal-lattice geometry plots

... get the indices of the observed zone axis by the cross products, then it is checked that all reflections that belong to this zone axis (up to the limit that is set by the objective aperture) are really present, that all the reciprocal spacings and angles match and give combined a high figure of merit, that there are no other reflections (due to moiré effects or Fresnel fringes),

### utilizing crystallographic image processing, there is, in addition, plane symmetry group and structure factor phase (and amplitude) fingerprinting!

no "systematic absences" for H + K = odd(both H and K  $\neq$  0) in FT of HRTEM image, plane group cannot be centered. also (H,0) or (0K) for H or K odd not very weak, plane group cannot have glide planes along these directions



e.g. [211] zone axis of magnetite, Fourier transform of our HRTEM image is indexed for a right-handed coordinate system, the microscope's point resolution, 0.526 nm<sup>-1</sup> is marked by the dotted large circle

> when two-fold astigmatism visible in FT of image, correction by **Crystallographic Image Processing**

e. g.: H + K = odd are present, no centered plane group reasonable

Determination of plane group for a magnetite crystal in [211] orientation (pmm), all 2D projections have to be centro-symmetric, i.e. have to contain at least a two-fold axis, all structure factor phases must be either  $0^{\circ}$  or  $180^{\circ}$ , average deviation of phase angles from theoretical values about ±  $30^{\circ}$  (< 20 % of total phase angle range)



P: phase between symmetry related reflections differs by more than  $45^{\circ}$ ; U: phase relation between reflection and its symmetry restricted value differs by more than  $45^{\circ}$ ; A: amplitude of one member of a symmetry related set is zero while the other member is observed. Deviation from  $0^{\circ}$  or  $180^{\circ}$  know as "centric phase error", for random data:  $\pm 45^{\circ}$  (V. M. Unger, Acta Cryst. D56 (2000) 1259-1269).



Resolution [nm]	Number and type of visible net-plane families (lattice fringe types)	Number and type of visible zone axes (lattice fringe crossings)
0.2	2, i.e. {111}, {200}	<b>2</b> <sup>1</sup> , i.e. [001], [011]
0.15	3, i.e. {111}, {200}, {220}	<b>2</b> <sup>2</sup> , i.e. [001], [011], [111], [112]
0.1	<b>2</b> <sup>2</sup> , i.e. {111}, {200}, {220}, {311}	<b>2</b> <sup>3</sup> , i.e. [001], [011], [111], [112], [013], [114], [125], [233]
≤ 0.05	$\geq 18, \text{ i.e. } \{111\}, \{200\}, \{220\}, \{311\}, \{331\}, \{420\}, \{422\}, \{511\}, \{531\}, \{442\}, \\ \{620\}, \{622\}, \{551\}, \{711\}, \{640\}, \{642\}, \{731\}, \{820\}$	2 <sup>5</sup> , e.g. [001], [011], [111], [012], [112], [013], [122], [113], [114], [123], [015], [133], [125], [233], [116], [134], [035],

Relationship between point-to-point resolution of a TEM and the principle visibility of net-plane families and zone axes within one stereographic triangle [001]-[011]-[111] for a hypothetical cubic AB-compound with 0.425 nm lattice constant and space group Fm3m, i.e. halite structural prototype.



More than 30 systems installed in Europe?, 2 in Asia?, 4 in USA? first USA demo site at Portland State University



40

30

10

1990

number 20



**TEM: JEOL JEM 2000FX** Precession angle: 2° Correction: OFF Magnification: 8,000 Beam diameter: 1,212 nm



**TEM: JEOL JEM 2000FX** Precession angle: 2° **Correction:** ON Magnification: 8,000 Beam diameter: 226 nm All settings can be saved, can be moved easily between microscopes, no major realignment required

1995

2005

2010

HRTEM

2000

year

50

25

ED = Electron Diffraction

PED = Precession Elecron Diffraction

ED



PRECESSION  $\lambda \cdot |F_{hkl}|$  $I_0S$  $\Omega \cdot (ha^* + kb^* + lc^*) \cdot \sqrt{1 - \left(\frac{ha^* + kb^* + lc^*}{2|\vec{k}|\sin\varepsilon}\right)^2}$ 

# Mayenite [111] $Ca_{12}AI_{14}O_{33}$ 143d

 $I_{hkl}$ 

Alternative I: multislice calculations for some 360 individual beam orientations for the same precession angle (out to very high resolution) and incoherent addition of all "off zone axis" diffraction patterns; known problem: overestimation of effect of excitation errors

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courtesy: Yves Maniette, NanoMEGAS

 $2 \cdot \lambda^2 \cdot \left|F_{hkl}\right|^2 \cdot t$ PRECESSION I<sub>hkl</sub>  $I_0S$ Kinematic  $\Omega^2 \cdot (ha^* + kb^* + lc^*) \cdot \sqrt{1 - \left(\frac{ha^* + kb^* + lc^*}{2|\vec{k}|\sin\varepsilon}\right)^2}$ 

## Two-beam dynamic

Alternative II: phase grating calculations for some 360 individual beam orientation for the same precession angle (out to very high resolution) and incoherent addition of all "off zone axis" diffraction patterns (assumes a flat Ewald sphere)

Alternative III: Bloch wave calculations JEMS ....



Si [110], 10 nm thick, left: intensity 200 kV, **3 degrees precession angle**, red ring signifies 0.035 nm, i.e. extend of zero order Laue zone without overlap from 2nd order Laue zone, e.g. reflection (7-5 13) at 0.0348 nm, all reflections in 1<sup>st</sup> order Laue zone are kinematically forbidden (due to F-centered Bravais lattice), software eMap of AnaliTeX

### one can extract structure factor amplitudes reliably from precession electron diffraction spots, use them for structural fingerprinting,

 $\frac{|F_{hkl}|}{|F_{h'k'l'}|} = \frac{\sqrt{I_{hkl}^{\text{int}T}} \cdot \sqrt{L_{h'k'l'}}}{\sqrt{I_{h'k'l'}} \cdot \sqrt{L_{hkl}}} = \frac{\sqrt{A_{hkl}^2 + B_{hkl}^2}}{\sqrt{A_{h'k'l'}^2 + B_{h'k'l'}^2}}$  A and B tabulated in International Tables

all depends on combination of structure factor modulus (small), unit cell volume (large), wavelength (small) and crystal thickness (small, but possibly up to about 50 nm (only if really necessary, correction of primary extinction effects according to the the two-beam (Blackman) or three-beam (Bethe potentials) models)

further benefits: it's experimentally not demanding, crystallite does not need to  $I_{RES} = \frac{\sum_{H,K} \left| I(H,K) - \frac{1}{2} \{ I(H,K) + I(-H,-K) \} \right|}{1}$ be in exact zone axis orientation



Fig. 2: Experimental diffraction patterns from a silicon crystal, approximately 60 nm thickness, orientation close to [110], 200 kV. (a) SAED pattern (zero precession), (b), (c) and (d) PED patterns from the same area with increasing precession angle. Note that while the intensity of the  $(1\overline{11})$  reflection, marked by arrows, is much higher than that of its Friedel pair ( $\overline{1}11$ ) and that of the other two symmetry equivalent  $\pm(1\overline{1}1)$  reflections in the SAED (a), the intensities of all four {111} reflections are very similar for the PED patterns (b), (c) and (d).

## 2D Laue class - point group combinations can be determined from ZOLZ – HOLZ reflections

Example: Analysis of mayenite [111], Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, *I43d*, plane group p3m1, using precession electron diffraction and employing *crystallographic software* **Space Group Determinator** / **ELD** / **CRISP**  $\exists_{a}$  Calidric

Copyright © *Calidris*, Manhemsvägen 4, SE-191 45 Sollentuna, Sweden Tel & Fax: +46 8 6250041 <u>http://www.calidris-em.com</u>

Calidris





point symmetry in ZOLZ is 6mm (due to Friedel's law) while it is only 3m in HOLZ – this demonstrates that there is no two-fold axis in this direction, so hexagonal space groups are ruled out, the possibility of a cubic llattice centering is correctly inferred from the systematic absences

# utilizing ideas from robotics/computer vision communities for probability based decisions: e.g.

H. Zabrodsky, S. Peleg, and D. Avnir, "Symmetry of Fuzzy Data", Proc. 12th IAPR Intern. Conf. on Pattern Recognition, Conference A: Computer Vision & Image Processing, vol. 1 (1994) 499-504; *possibly in combination with geometric AIC* 



Fig. 5: Experimental diffraction patterns from a thicker part of a wedged shaped silicon crystal that was prepared in a focused ion beam microscope. The thickness was approximately 56 nm. (a) SAED pattern (zero precession). Note the slight mis-alignment of the primary electron beam in (a). (b) and (c) PED patterns (with the same primary electron beam-tilt mis-alignment with respect to the optical axis of the TEM) from the same sample area with increasing precession angle. One member of the kinematically forbidden  $\pm(002)$  reflections is marked by an arrow in each diffraction pattern and also shown magnified in the insets.

one gets more electron diffraction spots, one also does not need to align very carefully (both the incident beam and the crystal), intensities are "quasi-kinematic", with **higher precession angles:** double and multiple scattering is suppressed effectively so that intensity of kinematically forbidden reflections is significantly reduced



Effect of increasing precession angle on intensity of kinematically forbidden (002) reflections of silicon crystals with thicknesses between about 22 and 50 nm.

# Advantages of precession electron diffraction beneficial to powder diffraction as well



**Fig. 6:** Electron diffraction ring patterns from the same ( $\mu$ m<sup>2</sup>-sized) area of a fine-grained crystal-powder of Ni-doped cassiterite (SnO<sub>2</sub>) nanocrystals (deposited from toluene). (a) Powder SAED pattern, zero precession; (b) and (c) powder PED patterns with increasing precession angle. These nanocrystals possess an average size of approximately 3 nm, are paramagnetic, stable as colloids in non-polar solvents, and become ferromagnetic at room temperature when capped by trioctylphosphine oxide, spin coated into thin films on fused silica substrates, and calcined [19].







Powder SAED (top) and PED (bottom) patterns of Au, 50 nm size, 200 kV



Powder SAED (left) and PED (right) patterns of Zeolite Socony Mobil #5 (ZSM-5), 100 kV

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Crystallographic database

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From Wikipedia, the free encyclopedia (Redirected from Crystallographic databases) A crystallographic database is a database specifically designed to store information about crystals and crystal structures. Crystals are solids having, in all three dimensions of space, a regularly repeating arrangement of atoms, ions, or molecules. They are characterized by symmetry, morphology, and directionally dependent physical properties. A crystal structure describes the arrangement of atoms, ions, or molecules in a crystal. Crystal structures of crystalline material are typically determined from X-ray or neutron single-crystal diffraction data and stored in crystal structure databases. They are routinely identified by comparing reflection intensities and lattice spacings from X-ray powder diffraction data with entries in powder-diffraction fingerprinting databases. Crystal structures of nanometer sized crystalline samples can be determined via structure factor amplitude information from single-crystal electron diffraction data or structure factor amplitude and phase angle information from Fourier transforms of HRTEM images of crystallites. They are stored in crystal structure databases specializing in nanocrystals and can be identified by comparing zone axis subsets in lattice-fringe fingerprint plots with entries in a lattice-fringe fingerprinting database. Crystallographic databases can be categorized as crystallographic information from supersets or subsets of inorganics, metals/alloys, organics, and biological macromolecules. They differ in access and usage rights and offer varying degrees of search and analysis capacity. Many provide structure visualization capabilities. They can be browser based or installed locally. Newer versions are built on the relational database model and support the Crystallographic Information File (CIF) as a universal data exchange format. S - S - 🖹 🖆 🏠 🔎 📩 😔 😂 - 🛬 🗷 🎥 - ð > Contents [hide] External links onon accase [edit]

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3 Search	=	American Mineralogist Crystal Structure Database (AMCSD) (contents: crystal structures of minerals, access: free, size: medium)     Cambridge Structural Database (CSD) (contents: crystal structures of organics and metal-organics, access: restricted, size: large)
4 Crystal phase identification	109,000 =	Crystal Lattice Structures (contents: a selection of common crystal structures, access: free, size: small)     Crystal Lattice Structures (contents: a selection of common crystal structures, access: free, size: small)     Crystal Lattice Structures (contents: a selection of common crystal structures, access: free, size: small)
4.1 Powder diffraction fingerprinting (1D)		intermetallics, access: free, size: medium - large)
4.2 Lattice-fringe fingerprinting (2D)	entries =	Database of Zeolite Structures (contents: crystal structures of zeolites, access: free, size: small)
4.9 Membelogical fingerprinting (9D)	=	Incommensurate Structures Database (contents: incommensurate structures, access: free, size: small)
4.3 Morphological ingerprinting (3D)		<ul> <li>Inorganic Crystal Structure Database (ICSD) (contents: crystal structures of minerals and inorganics, access: restricted, size: large)</li> </ul>
4.4 Lattice matching (3D)	_	Metals Structure Database (CRYSTMET) (contents: crystal structures of metals, alloys, and intermetallics, access: restricted, size: large)
5 Visualization		Mineraiogy Database (contents: crystal structures of minerals, access: free, size: medium)     MinCryst (contents: crystal structures of minerals, access: free, size: medium)
5.1 Crystal structures		Nano-Crystallography Database (NCD) (contents: crystal structures of nanometer sized crystallites, access: free, size: small)
5.2 Morphology and physical properties		<ul> <li>NIST Structural Database NIST Structural Database (contents: crystal structures of metals, alloys, and intermetallics, access: restricted, size: large)</li> </ul>
and physical properties		<ul> <li>NIST Surface Structure Database (contents; surface and interface structures, access; restricted, size; small.medium)</li> </ul>
6 References	_	Nucleic Acid Database (contents: crystal and molecular structures of nucleic acids, access: free, size: medium)
7 See also		Pearson's Crystal Data (contents: crystal structures of organics, metalorganics, minerals, inorganics, metals, alloys, and intermetallics, access:
8 External links		restricted, size: large)
6 External links		Protein Data Bank (PDB) (contents: crystal and molecular structures of biological macromolecules, access: free, size: medium-large)
8.1 Crystal structures	-	<ul> <li>Wiki Crystallography Database (WCD) (contents: crystal structures of organics, metalorganics, minerals, inorganics, metals, alloys, and intermediate the product of the produ</li></ul>
		intermetatics, access. tree, size: medium)

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# **Crystallography Open Database**



### **Advisory Board**

Daniel Chateigner, Xiaolong Chen, Marco Ciriotti, Robert T. Downs, Saulius Gražulis, Armel Le Bail, Luca Lutterotti, Yoshitaka Matsushita, Peter Moeck, Miguel Quirós Olozábal, Hareesh Rajan, Alexandre F.T. Yokochi

# http://cod.ibt.lt

## mirrors worldwide

www.crystallography.net cod.ensicaen.fr 20 nanocrystallography.org jcod.nanocrystallography.net cod.nanocrystallography.net/cod

### web portal http://nanocrystallography.net

### IMAGES Starring The Cel

Chromosomes caress, tangle then get wrenched apart as a French torch song plays in "Twisted Sisters." most touching movie ever made about the first division of melosis. It's also one of the standouts at the Web site of the Bioclips proj

ect, sponsored by the French government. The virtual multi-plex displays entrants from the last four rounds of the Cinema of the Cell festival. Held annually at the European Life Scientist Organization meeting, the contest lets res and students present their educational Web films, which use techniques from traditional animation to stop-motion with Lego blocks. The more than 30 shorts range from "A Day in the Life of a Social Amoeba" to a work about the establishment of cell polarity in nematodes from auteurs at the University of Wisconsin, Madison (above).

### DATABASE Free the Crystals!

This site is som crystallographers' answer to open-source software, providing an alternative for and other researchers who an afford the fees charged by the sof crystall ographic international team vstallography Open of scientis es measurements for some ecules, from superconducting to antibiotics. Visitors can scan the which were contributed by e users, for molecules sport ing a specific combination of elements. The results appear as a standard Crystallographic Information File" that includes atomic coordinates and the source of the measurements. A linked site furnishes predicted structures for more than 1500 compounds, such as boron-containing nanotubes (top image) and fluoroaluminate crystals.

www.crystallography.net

# **NETWATCH**

edited by Mitch Leslie

#### **RESOURCES**

#### Where Birds Count

The careful observations of birdwatchers are invaluable to scientists studying avian distribution and abundance.eBird, a recently revamped site from Cornell University's Lab of Ornithology and the National Audubon Society, helps researchers access and analyze birders' tallies. One of the lab's collaborations with birdwatchers (Science as lune, p. 1402), eBird lets visitors submit their state people. database that already has entries from 15 of people. Researchers can then parse the record, and chounts for a particular area or species. For usal re, yo can chart the number of ospreys seen in each week of the year and map the

fish-eaters' favorite haunts.

#### COMMUNITY en a Symposium

ons of the latest study comparing different ugs, track down a potential collaborator in Italy, what leading schizophrenia researchers have on their u can do all this and more at the Schizophrenia eserch Forum, which officially opened this week. Sponsored the nonprofit National Alliance for Research on Schizophreand the U.S. National Institute of Mental Health, the diverse site a meeting place for Alzheimer's researchers (www.alzforum.org). oclude a news section and interviews with scientists such as Robin Murray of the Institute of Psychiatry in London, who helped show that "obstetric events" such

premature birth boost the risk of schizophrenia. Visitors to the Idea Lab can bat round novel notions. Live chats with experts start next month, and a gene database is in the works.

www.schizophreniaforum.org

#### DATABASE Dinosaur Name Game

Feature.

Like the ancient beasts themselves. most of the names scientists have coined for dinosaurs over the last 2 centuries are defunct. At the new database TaxonSearch from paleontologist Paul Sereno of the University of Chicago, researchers can uncover which handles have survived and which have gone extinct as experts have refined taxonomies. Unlike other narrower references, the site focuses on taxonomic levels above the genus, and it

will cover all archosaurs-the group that comprises dinosaurs and their kin-except for birds and crocodiles. Dig into the listings to find out who first named a group, its official definition, and its chronological range. For example, the name of the clade Ankylosauridae, to which the herbivore Ankylosaurus (above) belongs, dates back to 1908. And if a name has died out, you can learn why. Sereno has posted the first batch of 50 records and plans to add about 700 more within the next few weeks.

Send site suggestions to netwatch@aaas.org.Archive: www.sciencemag.org/netwatch



www.sciencemag.org SCIENCE VOL 310 28 OCTOBER 2005 Rublished by AAAS

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View the Petition for Open Data in Crystallography Call to Volunteers           Call to Volunteers           See also the PCOD : Predicted Crystallography Open Database More on the COD project : what's new           Recent open access paper regarding COD development was published in Journal of Applied Crystallography. PDF available.           COD Advisory Board thanks Crystal Impact GbR for their financial support of this paper public	journal_volume 146 journal_year 1999 journal_page_first 114 journal_page_last 123 _cell_length_a 4.9940(1) _cell_length_b 4.9940(1) _cell_length_c 11.3871(4)		
CIFs Donators - Advice to potential CIF Donators Statistics of access generated by http-analyze and visitors programs Currently there are 109214 entries in the COD All data on this site have been placed in the public domain by the contributors	_cell_angle_gamma 120 _cell_volume 245.9		
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### COD Subset Search

Home			
Nano-Crystallography Group	Search by these properties:		
Interactive Databases	Text (1 or 2 words)		
COD Subset	Include these elements		
EduCOD	Without these elements		
Nano-Crystallography Database	Strict number of elements		
Crystal Morphology Database		Clear all Hide table	
Wiki Crystallography Database	<u>1</u> 2 3 4 5 6 7 8 9 10 11 12 13 1	4 15 16 17 18	
LFFP Matching (coming soon)		He	
Tools	3 Na Mg transition metals		
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### 0.24 nm point resolution

modern analytical TEM

## kinematic

contains space group information in case of cubic crystals

# dynamic

taking account of double and multiple diffraction within one nanocrystal



downloadable from our web site as \*.png or Bitmap after search and calculations

projected reciprocal lattice geometry, projected symmetry, and structure factor fingerprinting result in highly characteristic data for crystallographic identification of *individual* unknown nanocrystals from HRTEM images and/or PED patterns

for ensembles of nanocrystals, better statistics with powder PED

Structural distinction between magnetite and maghemite from HRTEM images demonstrated, R. Bjoerge, *MS thesis*, 2007, http://www.scientificjournals.org/journals2007/j\_of\_dissertation.htm. Most recent paper: P. Moeck and S. Rouvimov, *Zeits. Kristallogr.* **225** (2010) 110-124, special issue on *"Precession electron diffraction"* 

(On-line) support from comprehensive open-access databases, ≈ 109,000 entry COD, <u>http://cod.ibt.lt</u>, with 4 mirrors and 1 web portal; our mainly inorganic subset of COD, <u>http://nanocrystallography.research.pdx.edu/CIF-searchable</u> ≈ 20,000 entries for lattice fringe fingerprint plots

also Wiki-Crystallography Database, educational subset of COD, Nano-Crystallography Database, Crystal Morphology Database, ...





Figure 5-15: The defocus values and astigmatism are determined from the black ring(s) in the FT background. The image was taken at underfocus, so -pi is chosen for the zero cross-over in both directions.



# Similar structures may in future be distinguished on the basis of the projected symmetry



Example: Iron oxide nano-crystals may have maghemite  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, <u>P</u>4<sub>1</sub>32, p4gm, a = 0.83 nm Or magnetite Fe<sub>3</sub>O<sub>4</sub>, <u>Fd3m</u>, p4mm, a  $\approx$  0.83(1) nm structures, projected symmetries are different for [001] zone axes, *software CRISP* 

### utilizing ideas from robotic/computer science communities for fully objective/quantitative decisions:

geometric Akaike Information Criteria, e.g. I. Triono, N. Ohta, and K. Kanatani, "Automatic Recognition of Regular Figures by Geometric AIC", *IEICE Trans. Inf. & Syst.* vol. E81-D (1998) 224-226



p4gm, [001] maghemite

p4mm, [001] magnetite