Structural fingerprinting of nanocrystals from HRTEM images and precession electron diffraction patterns

Peter Moeck, Nano-Crystallography Group, Department of Physics



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 & Structure-Factor (amplitude and phase) Fingerprinting of nanocrystals, experimental demonstrations for HRTEM and Precession Electron Diffraction
- 4. Developments in 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

B

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 λ 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 a₀ 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











 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,^{1,*} P. Y. Zavalij,² S. Lutta,² M. S. Whittingham,² V. Parvanov,¹ and S. Shastri³ ¹Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859, USA
 ²Chemistry Department, State University of New York at Binghamton, Binghamton, New York 13902, USA ³Advanced 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-O₆ octahedral (light green) and V-O₄ 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. Vol. 222 (11) 634-645 (2007), special issue on "Nanocrystallography", expanded version available at arXiv:0706.2021, June 14, 2007

either electron diffraction patterns or structure images can be employed if combined with either spectroscopic or prior information on the elements present and/or absent within the unknown, but one does not 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>Alternative:</u> utilize established electron crystallography procedures and combine with new developments in open-access crystallographic databases – as you only want to recognize a nanocrystal structure after it has been solved and became part of a database

Довлады Академии Наук СССР 1949. Ton LXIV. N 1

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

ФИЗИКА

4 = 9,02 Å-

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 плотность 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 получен-ные из эксперимента значения модуля структурной амплитуды | F_{hkl} и определяя косвенным путем фазу*, можно суммированием ряда (1) получить 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 can 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 l = 0 - 1004, R = 20 %





FROM MACROMOLECULES TO BIOLOGICAL ASSEMBLIES

Nobel lecture, 8 December, 1982

by AARC

AARON KLUG

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





"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



electrostatic Structure factors and "wave scatterer" are Fourier mates ! potential energy $elec_density(x_jy_j, z_j) = \frac{1}{\Omega} \sum_{hkl} |F(h, k, l)| \cdot e^{i\phi} \cdot \exp(-2\pi i (hx_j + ky_j + lz_j))$ distribution

 $electro_stat_pot(x_j y_j, z_j) = \frac{h^2}{2\pi \cdot m \cdot e \cdot \Omega} \sum_{hkl} |F(h, k, l)| \cdot e^{i\phi} \cdot \exp(-2\pi i (hx_j + ky_j + lz_j))$



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



(-)

magnetite



Fe₃O₄, F d -3 m (center at 3m) Cell parameter: a = 8.4 Å gamma-Fe₂O₃, P 4₁ 3 2 **Cell parameter:** a = 8.33 Å

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

Similar structures may be distinguished on the basis of the projected symmetry alone

Copyright © Calidris, Manhemsvägen 4, SE-191 45 Sollentuna, Sweden Tel & Fax: +46 8 6250041 http://www.calidris-em.com Email: info@calidris.em se CIP ELD PhIDO Statistics Calculate Options Window Held FFT Filt FFT 1K 2K 4K 🗔 ₩ Phase origin map (• p1 map v= 90.0 a=2.95Å b=2.95Å Shift h=71.0 Shift k=117.1 Edit HK Create Img Try All Refine Ready (982 200) Y=164

Example: Iron oxide nano-crystals may have maghemite (γ -Fe₂O₃, S.G. P4₁32, a = 0.833 nm) or magnetite (Fe₃O₄, S.G. Fd-3m, a = 0.832 nm) structures, projected symmetries are different for [001] zone axes ! software CRISP from Calidris

Assuming 0.19 nm poin resolution of HRTEM	^t magneti	cubic maghemite No. 213			
structure factor/{hkl} multiplicity	Fe₃O₄ F in nm,	$Fe_3O_4 \phi$ in degrees if center at 3m	γ -Fe₂O₃ F in nm	γ -Fe ₂ O ₃ ϕ in degrees	
011 12	法では認		0.78	90 (-90)	
111 8	1.55	0 (180)	0.55	45 (-45, ±135)	
012 24			0.90	90 (-90, 180)	
112 24		-100	0.60	0 (180)	
022 12	3.29	0 (180)	3.25	0	
013 24			0.50	90 (-90)	
113 24	4.85	0 (180)	4.41	-45 (45, ±135)	
222 8	1.11	0	0.15	90 (-90)	
023 24			0.63	0 (± 90, 180)	
123 48			0.43	0 (180)	
004 6	6.47	0	5.65	0	
033 12		t- north of the	0.38	90 (-90)	
114 24			0.38	90 (-90)	
133 24	0.37	0 (180)	0.28	45 (-45, ±135)	

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 also plane symmetry group and structure factor phase and amplitude fingerprinting!

no 7.05 nm -1 "systematic 153 absences" for H + K = odd(0.1)(3,0) (both H and K 022 \neq 0) in FT of 5.33 nm HRTEM \bigcirc 131 (1.0)image, plane 222 240 group cannot 111be centered. 000240also (H,0) or 4.13 nm -(2.-1)(0K) for H or K odd not 222 very weak, 333 13 plane group 022 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⁻¹ is marked by the dotted large circle

two-fold astigmatism visible in FT of image, can be corrected for by Crystallographic Image Processing

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

53

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° or 180°, average deviation of phase angles from theoretical values about ± 30° (< 20 % of total phase angle range)

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

31 systems installed in Europe, one in South Korea, two in US, first US demo site at Portland State University !

40

30

10

1990

number 20

TEM: Jeol 2000FX **Precession angle:** 2° Correction: OFF Magnification: 8000 Beam diameter: 1212 nm

TEM: Jeol 2000FX 2° **Precession angle: Correction:** ON Magnification: 8000 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

9.2 - 18

• 0.3 - 0.6

· 0.1 - 0.3

0.0 - 0.

Si [110], 10 nm thick, 200 kV, 2º precession angle, left: kinematic intensities I ~ F², **right:** two-beam dynamic intensities in asymptotic limit, I ~ F, 2nd order Laue zone becomes clearly visible

· 3-5

0-3

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 1st order Laue zone are kinematically forbidden

Figure 4: Double diffraction.

a - Schematic description of a double diffraction path.

b - Conventional ZAP. Several double diffraction paths to a kinematical forbidden reflection are available.

c - PED pattern. A double diffraction path to a kinematical forbidden reflection is only available when the three involved reflections $h_1k_1l_1$, $h_2k_2l_2$ and $h_3k_3l_3$ are simultaneously located within the Laue area.

Figure 5: Silicon [110] ZAPs

a to c - PED patterns obtained at three different precession angles. The double circled spots are kinematical forbidden reflections due to the d glide planes. The circled spots are kinematical forbidden reflections due to 8a Wyckoff positions.

d - Bright-field and Dark-field LACBED patterns of the kinematical forbidden reflections.

Double diffraction significantly reduced due to precession of primary electron beam, compare with SAED, left

Alternative view: Precession electron diffraction patterns are dark field Large Angle Convergent Beam Electron diffraction patterns, right one can extract structure factor amplitudes reliably from precession electron diffraction spots, use them for either electron crystallography (direct methods, charge flipping algorithm, ..., some 30 groups worldwide) or **structural fingerprinting**, the crystal thickness can be up to about 50 nm (with correction of primary extinction effects according to the the two-beam dynamical theory), *further benefits: it's experimentally not demanding* $I_{RES} = \frac{\sum_{H,K} |I(H,K) - \frac{1}{2} \{I(H,K) + I(-H,-K)\}|}{\sum_{i} I(H,K)}$

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 ($\overline{111}$) and that of the other two symmetry equivalent ±($1\overline{11}$) reflections in the SAED (a), the intensities of all four {111} reflections are very similar for the PED patterns (b), (c) and (d).

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 typically gets more electron diffraction spots, intensities are quasi-kinematic, with higher precession angles: double 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.

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

Example: Analysis of Mayenite [111], p3m1 Ca₁₂Al₁₄O₃₃, *I-43d*, using precession electron diffraction and employing crystallographic SOftware Space Group Determinator from Calidris

ZOLZ		1	HOLZ	Suggestions from intensities		
Symm 2 2mm 4 4mm 6 5mm	RA% 4.95 6.46 6.65	Symm 1 2 m(x) m(y) 2mm 4 4mm 3 31m 6 6 6mm	RA% 0.00 97.48 11.22 12.93 99.11 99.05 99.28	Trigonal -3m [0001] Cubic m-3m [111]	*	
Partial R(ZOLZ) R(HOLZ) Trigonal Cubic <1	space group)= 0.9%, h-k)= 1.5%, h-k 	o symbol from -l=3n -l=3n	m extinctions		-	
					-	

point symmetry in ZOLZ is 6mm (due to Friedel's law) while it is only 3m1 in FOLZ – this demonstrates that there is no two-fold axis in this direction, so hexagonal space groups are ruled out, the possibility of a cubic I-lattice centering is correctly inferred from the systematic absences

PRECESSION I_{hkl}

 $\Omega \cdot (ha^* + kb^* + lc^*) \cdot \sqrt{1 - \left(\frac{ha^* + kb^* + lc^*}{2|\vec{k}|\sin\varepsilon}\right)^2}$ $Ca_{12}AI_{14}O_{33}$ I-43d

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

17-08-2008 22:40:42

 $\lambda \cdot |F_{hkl}|$

courtesy: Yves Maniette, NanoMEGAS

 $2 \cdot \lambda^2 \cdot \left| F_{hkl} \right|^2 \cdot t$ PRECESSION I_{hkl} I_0S $I_0 S$ 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)

Advantages of precession electron diffraction beneficial to powder XRD as well

Fig. 6: Electron diffraction ring patterns from the same (μ m²-sized) area of a fine-grained crystal-powder of Ni-doped cassiterite (SnO₂) 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 (left) and PED (right) patterns of Zeolite Socony Mobil #5 (ZSM-5), 100 kV

Powder PED fingerprinting on crystallographically challenged materials

111 C

110

Depending on the desired orientation resolution, a stack of diffraction templates is calculated for a known crystal structure, experimental diffraction patterns are compared to these templates to determine most probably orientation by means of the maximum of the "correlation index"

Experimental studies on severely deformed Cu show that the correlation index increases significantly when primary electron beam precesses

magnetite/maghemite nanocrystals

precession on

correlation index

orientation & crystal phase magnetite

0.2 μm

correlation index

orientation magnetite

pseudo-STEM bright field, (red dots stand for some of the position where PEDs were taken), microscope does not need to possess STEM unit CTEM bright field

crystallite sizes 3 to 200 nm, the majority of the nanocrystals belongs to the magnetite phase

precession off

Automated assessment of projected reciprocal lattice geometry

Processing of HRTEM images of PbSe ($a \approx 0.61$ nm) nanocrystals with software that complements the ASTAR system.

Resolution of the TEM becomes crucial for success of the automated procedure, best with C, corrected machines

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}	2, i.e. [001], [011]
0.15	3, i.e. {111}, {200}, {220}	4, i.e. [001], [011], [111], [112]
0.1	<mark>2</mark> ² , i.e. {111}, {200}, {220}, {311}	2 ³ , 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 ⁵ , 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.

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

http://nanocrystallography.org http://www.crystallography.net http://cod.ensicaen.fr/

more than 80,500 entries and 50,000 hits per month

IMAGES Starring The Cell

Chromosomes caress, tangle then get wrenched apart as a French torch song plays in "Twisted Sisters," probably the most touching movie ever made about the first division of meio sis. 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 researchers 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)

DATABA SE

Free the Crystals!

This site is som crystallographers' answer to open-source software, providing an alternative for chemists

and other researchers who can't afford the fees charged by suppliers of crystall ographic data. Supervised by an international team of scientists, The Crystallography Open Database houses measurements for some 18,000 molecules, from superconducting materials to antibiotics. Visitors can scan the data, which were contributed by

site users, for molecules sporting a specific combination of elements. The results appear as a standard "Crystallographic Infor-mation 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

Researchers can then parse the records, plotting counts for a particular area or species. For instance, you can chart the number of ospreys seen in each week of the year and map the fish-eaters' favorite haunts. www.eb.int.org COMMUNITY SITE

RESO URCES

Where Birds Count

Schizophrenia Symposium

Find out the conclusions of the latest study comparing different antipsychotic drugs, track down a potential collaborator in Italy, or discover what leading schizophrenia researchers have on their minds. You can do all this and more at the Schizophrenia Research Forum, which officially opened this week. Sponsored by the nonprofit National Alliance for Research on Schizophre-

NETWATCH

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, 3 June,

p. 1402), eBird lets visitors submit their sightings to a

database that already has entries from 15,000 people.

nia and Depression and the U.S. National Institute of Mental Health, the diverse site is modeled on a meeting place for Alzheimer's researchers (www.alzforum.org). Features include 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 as premature birth boost the risk of schizophrenia. Visitors to the Idea Lab can bat around novel notions. Live chats with experts start next month, and a gene database is in the works.

www.schizophreniaforum.org

DATABASE **Dinosaur Name Game**

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

597

COD Subset Sear File Edit View History COD COD COD COD Netscape.com Codettin COD Subset Search	ch - Netscape Navigat <u>B</u> ookmarks <u>T</u> ools <u>H</u> elp //nanocrystallography.researc ng Started Market Market Market Market Market Market Market Market Market Market Market Market Mark	or h.pdx.edu/search.py/sea	rch?database=	=cod ▼ ► G• Googl	e <u> </u>	work popu brow	ks for ular w vsers	all eb and
Interactive Databases COD Subset Nano-Crystallography Database Crystal Morphology Database	Search by physical propert Text (1 or 2 words) With these elements	des:	magnetite			syste	ems	
Tools Login Crystallography Background Papers Goniometry	Without these elements Minimum and Maximum volume Strict number of elements		Search Resul Edit ⊻iew Hig → → · @ ⊗ û Setting Started S	t - Mozilla Firefox story <u>B</u> ookmarks <u>T</u> ools http://nanocrystallog Latest Headlines	Help raphy.research.pdx.edu/search.	py/result?text=magne	titel • 🕨 🕞 Goog	_ म 🗙
Links Links Constructure Visualisation - Constructure Visualisation - Constructure Visualisation Constructure Visualisation Home	Search keset (Help. Search by morphology (tra Symmetry cell setting Windows Internet Explorer research.pdx.edu/view.py/jmol?database=co	<u></u> (Dack) cht): Horr Inter od&entry=4076 ▼ ↔ × Goog ⓐ ▼	ie ractive Databases Le P · lage • © Tools • "	Found 59 results (Search again) (Interac Formula: FegO4 Source: Bragg, W H N Space group: F d-3 m Cell volume: 575.93 Cell parameters: a = 8 User comments: None CIF View Download	tive Databases) (Help) ature (London) The Structure of Magner S 3200A, b = 8.3200A, c = 8.3200A; α = 3D Model View (old) View Structure (new window)	tite and the Spinels Nature = 90.000°, β = 90.000°, γ = Lattice-Fringe Fingerprint Kinematic Dynamic	(London) 95 (1915) 56 90.000° Edit Comment Deletion Mark	Search Result
Interactive Databases COD Subset Nano-Crystallography Database Crystallography Database Wiki Crystallography Database Tools Login Crystallography Background Pages	-300 3200 3200 0.0*	Display Mode: Shaves unit cells_isSpin Names of elements Stereo: None Rotate: 45 X Y Z Rese Configurations metric unit Select (1,884) View Style	t conventional c	Source: Magnetite We MT100-1350 American Space group: F d 3 m Cell volume: 591.82 Cell parameters: a = 8 User comments: None CIF View Download Formula: Fe2.7504Tig: Source: Titanomagnetii USP25-1350 American Space group: E d 3 m	achsler B A Lindsley D H Prewitt C 1 Mineralogist 69 (1984) 754 770 3958A, <i>b</i> = 8.3958A, <i>c</i> = 8.3958A; <i>α</i> : 3 D Model View (old) View Structure (new window) 25 te Wechsler B A Lindsley D H Prewitt 0 Mineralogist 69 (1984) 754 770	Crystal structure and call = 90.000°, β = 90.000°, γ = Lattice-Fringe Fingerprint Kinematic Dynamic C T Crystal structure and c	ion distribution in titan 90.000° Edit Comment Deletion Mark ation distribution in titar	omagnetites (Fe3-xTixO4)
Coniometry NWACC Links	U 4	Color Surfaces Do Surfaces Symmetry Von der Waals Surface Spin Sobert Accessible Surfa Spin Sobert Accessible Surfa Spin Sobert Surface (1-Assisted Surface) Molecular Surface (1-Assisted Surface) Surface (1-Assisted Surface) Molecular Surface (1-Assisted Surface) Surface (1	ace (VDW + 1.4 Angstrom) strom probe) otential	Temi Temi	Advanced Tools for ek	S setron diffraction A	e P	Proper materialised by <u>consultants filter and</u> © Perciland State University 2008 Units since January 1 ¹⁵ 2008-0411 « 📚 🗘 10:17 PM
Done Bart Note: Start Remov	/ab] 🗀 power p 🛛 🖳 30 min A 🗍	About Jmol	₹125% ▼ 2010:22 PM					

0.24 nm point resolution

modern analytical TEM

kinematic

brookite

dynamic

taking account of double and multiple diffraction within one nanocrystal

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

pseudo-brookite

Lattice-Fringe and Structure-Factor Fingerprinting result in novel types of characteristic data for crystallographic identification of unknown nanocrystals from HRTEM images and/or precession electron diffraction data, (three step procedure in each case, projected geometry, symmetry, structure factors)

Structural distinction between magnetite and maghemite from HRTEM images already demonstrated! (R. Bjoerge, MS thesis, 2007).

(On-line) support from comprehensive open-access databases, ~80,500 entry COD, <u>http://cod.ibt.lt</u> with 3 mirrors, our mainly inorganic subset of COD, <u>http://nanocrystallography.research.pdx.edu/CIF-</u> searchable (~20,000 entry subset of COD)

also Nano-Crystallography Database, Crystal Morphology Database, Wiki-Crystallography Database in progress

structure factor phase is with respect to the projected origin of the unit cell, more general with respect to the symmetry elements of the atomic arrangement.

Fig. 3. Relations between phases of the structure factor, F(h), the diffracted beams, $\Psi_{ex}(h)$, at the exit surface, the diffracted beams. $\Psi_{im}(h)$. on the image plane and the Fourier component, $I_{im}(h)$. of an HREM image. The phase of F(h) for a reflection is ϕ . the diffracted beam at the exit surface has a phase of $\phi - 90^{\circ}$. When passing through the objective lens, the phase of the diffracted beam of the back focal plane is shifted by $\chi(h)$ (here $\chi(h) < 0$). On the other hand, the phase of F (-h) is $-\phi$, and $\Psi_{ex}(-h)$ has the phase $-\phi - 90^{\circ}$. The complex

conjugate of $\Psi_{ex}(-\mathbf{h})$ then has the phase $-(-\phi - 90^\circ) = \phi + 90^\circ$, which is exactly 180° away from $\Psi_{ex}(\mathbf{h})$. The phase of $[\Psi_{ex}(-\mathbf{h})]^*$ on the back focal plane is shifted by $-\chi(\mathbf{h})$. For a WPO, the Fourier components are the vector sum of $\Psi_{im}(\mathbf{h})$ and $[\Psi_{im}(-\mathbf{h})]^*$. Thus, the Fourier components are equal to 2 sin $[\chi(\mathbf{h})]\Psi_{im}(\mathbf{h})$, which have the same phase as that of F(**h**) if sin $\chi(\mathbf{h}) > 0$ and the opposite phase if sin $\chi(\mathbf{h}) < 0$.

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.

