NEW techniques for TEM nano - analysis : precession electron diffraction and high resolution crystallite orientation-phase mapping



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PRECESSION ELECTRON DIFFRACTION

NEW analysis technique

> 40 articles in 5 years

Reference book Williams and Carter Transmission Electron Microscopy

Ultramicroscopy Special Issue vol.107 issue 6-7 June 2007

X-ray Diffraction (single crystal): all info in reciprocal space

Bragg law $n\lambda = 2dsin\theta$



• Single X-Ray diffractometer collects set of 3d HKL reflections

single crystal dim. about 0.3 mm

- We measure HKL intensities
- From direct methods (mathem. algoritms) we find directly crystal structure : atomic positions
- Smallest cystals for str.determination
 <u>5 micron : Synchrotron solution</u>

X-rays in

X-Ray diffraction : advantages and limitations



X-Ray diffraction structure analysis can be applied for single crystals and powder diffraction

ALL structure information is in reciprocal space: we collect and measure HKL intensities , then solve and refine a crystal structure



however not always possible to have single crystals 0.3 mm (std size)



On the other hand , in powder X-Ray pattern, many reflections ovelap because of crystal symmetry

Even worst, X-Ray powder peaks are broadened when crystal is badly crystallized or nanocrystals are studied







Courtesy P.Moeck PSU Oregon

Electron diffraction

> Electron diffraction is highly dynamical



 $I_{exp} \approx F(\vec{h})^2$

(200) forbidden

(111) allowed The electron diffraction intensities cannot be used for solving or refining the structure in a straightforward way as Xray data

Si [011] spg Fd3m (h00) allowed only if h=4n



Electron diffraction : many advantages but



Electron diffraction is the ideal technique for studying single nanocrystals



Crystal cell symmetry, cell parameters can be easily extracted from electron diffraction patterns

BUT



Electron diffraction scattering interactions are 10 exp4 stronger than X-Ray: there is strong dynamical interactions for crystal thickness > 10 nm



in practice , that means that electron diffraction HKL intensities do not behave

like X-Ray (kinematical scattering) where: $I_{exp} \approx F(\vec{h})$

Moreover, (kinematical) space group <u>extinction rules</u> are no longer valid for electron diffraction patterns



• Ð

Normal electron diffraction pattern (dynamical) thickness > 10 nm Ideal kinematic diffraction pattern (like X-Ray)

Melilite: tetragonal a=b=7.8A c=5.0A $P - 4 2_1 m$ Space group extinction rules :(h00) e (0k0) h=2n, k=2n

Courtesy M.Gemmi Univ Milano

Solution: Precession Electron Diffraction (Vincent-Midgley)



Electron (precession) diffraction : the right way to solve nanostructures in TEM



Electron diffraction intensities (usually dynamical) cannot be used (like X-Ray) to solve structures, as they lead in wrong structural models



Precession electron diffraction in TEM has been discovered in Bristol, UK by Vincent and Midgley (1994, Ultramicroscopy 53, 271)



During beam precession, the beam is tilted and precessed at high frequency though the optical axis on a conical surface : crystal is not moving, but Ewald sphere is precessing aroung the optical axis



Due to precession many HKL intensities far out in reciprocal space appear with intensities integrated over the excitation error



Precession intensities behave much closer to ideal (kinematical) intensities, therore can be used to solve crystal nanostructures (Ultramicroscopy, vol.107, issue 6-7, July 2007)



Advantages of precession in single exposure data collection



with beam precession, Ewald sphere also precess though the reciprocal space

- More fully recorded reflections
- More spots per image
- Reduced dynamic effect



Precession electron diffraction : novel TEM dedicated device



To perform TEM beam precession , diffraction coils (usually beam tilt and image shift or others) need to be controled to perform beam precession





Effective Spot size increases with precession angle (Cs dependent) but can be small (5 nm) for FEG TEMs (1° precession angle) and 25 nm for LaB6 TEMs (CM30 at 1° precession angle)

Precession angle may vary from 0-5° continuously (max. angle value TEM dependent)





SPINNING STAR

UNIVERSAL INTERFASE FOR PRECESSION ELECTRON DIFFRACTION FOR ANY TEM



S NanoMEGAS

• Precession angle can vary continuously from 0° to 5°, to observe true crystallographic symmetry variation

DigiStar Digital precession unit



With "DigiSTAR" is possible to visualize directly and rapidly modify precession angle using (memory saved) TEM alignements

Digital precession interface for advanced TEM







Zeiss Libra 200F Cs corrected Jeol 2200 FS Jeol 2010F Tecnai 30F



Digital Version: DigiStar with galvanic isolation Block



« DigiSTAR » can avoid excessive central diffraction spot diameter increase with precession angle by <u>correcting diffraction aberration effects by dedicated software</u>

(Patent pending technique)

Before correction







TEM: Jeol 2000FX Precession angle: 2° Correction: Off Magnification: 8000 Circle diameter 1212 nn



TEM: Jeol 2000FX Precession angle: 2° Correction: Off Magnification: 8000 Circle diametel 226 nm

ろ NanoMEGAS Advanced Tools for electron diffraction

Examples of structure solution with precession

FOR

Catalysts (zeolites) Oxides (perovskites) Complex oxides (Cs-Nb-O) Minerals Polymers Pharmaceuticals

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Proteins

PRECESSION : QUASI – KINEMATICAL INTENSITIES



UVAROVITE cubic mineral (111)

When applying precession, dynamical conventional SAED patterns (left) they become very close to kinematical (right); compare with simulated kinematical intensities pattern (center).

Observe the film of cubic mayenite mineral along 111 ZA, ED pattern how it changes from dynamical to very kinematical at increasing precession angle (http://drop.io/precession, password = precession)



Courtesy M.Gemmi Univ of Milano



<mark>3</mark>°

2°

Precession electron diffraction : Space and point group symmetry determination



By increasing precession angle, FOLZ and SOLZ rings are inceasing in size and as a result, more FOLZ spots are visible; at the same time ZOLZ ring is also increasing in size at higher precession angles, and at some (quite small) precession angle, ZOLZ and FOLZ ring reflection begin to overlap



ZOLZ and FOLZ reflections clearly visible at quite small (0.5°) precession angles allow (like in Buerger precession technique in X-Ray) to clearly compare periodicity in ZOLZ/ FOLZ reflections, observe extinctions in ZOLZ/FOLZ reflections and clearly establish Space / point group suymmetry ab-initio using just a few PED patterns



See Morniroli et al . Ultramicroscopy 107 (2007) 514-522







SiC

Space group determination by

PRECESSION ELECTRON DIFFRACTION

SiC 4H hexagonal P63mc

Courtesy JP Mornirolli Univ of Lille France



70

reflections

reflections

 $\alpha = 2.1^{\circ}$

<u>AUTOMATIC</u> crystal symmetry determination by software analysis of ZOLZ @ FOLZ precession patterns



INFLUENCE OF ENERGY FILTER

Mayenite mineral Libra 200 FEG, 200 KV, ZL Omega filter



DigiSTAR 0.5 deg precession (Left) unfiltered (right) filtered Omega filter : 100 mrad acceptance angle at $\Delta E = 10 \text{ eV}$



Precession from pharmaceutical nanocrystals

PED patterns in pharmaceutical crystals allow to work with close or with ZA oriented patterns, revealing true crystal symmetry and kinematical intensities good for structure determinations

amoxycillin



penicillin G-potassium



without precession

without precession

with precession



Samples C.Giacovazzo CNR Bari

Courtesy JP Abrahams, D.Georguieva Univ Leidenc

Precession electron diffraction :

ab initio determination of nanostructures



Precession electron diffraction : steps to solve crystal structure

STEP 1 : collect precession diffraction patterns from oriented ZA; for symmetrical crystals (cubic, tetragonal) a few 3-4 patterns may be enough ; collection can be done with films (less precise method as films are easily saturated in intensity , image plates , CCD or our electron diffraction dedicated electron diffractometer)

STEP 2: extract electron diffraction intensities automatically by software; merging intensities from different ZA by comparing and establish scale factor between common row intensities

STEP 3 : after reducing intensities , considering possible space group symmetry , imput HKL and intensities at direct methods software using electrion diffraction scattering factors (example SIR2008 , SHELX etc..) to solve structure

STEP 4 : all atomic positions and atomic type will appear as one of the most probable solutions; heavy atoms are usually all placed in correct positions, while lighter atoms (eg oxygen appear displaced from ideal positions).

R crystallographic residual from PED intensities is usually between 10-25 % as structure solution by electron diffraction is less precise than X-Ray solution where R is 3-5%

ced Tools for electron diffraction



Electron diffraction intensities are measured automatically







DIRECT METHODS (electron scattering)

SIR 96, SIR 2007, SIR 2008, FOX, charge flipping algorithms

Structure solution with direct methods: SIR2008 <u>http://www.ic.cnr.it/registration_form.php</u>

FullProf suite : http://www.ill.eu/sites/fullprof/

Use precession diffraction intensities to solve crystal structures

In this example PED intensities from 5 zone axis (ZA) from **Mg5Pd2 nanocrystal** have been collected with a 100 kV TEM. Use of **SIR2008** direct methods software allowed direct calculation of all the (Mg,Pd) atomic positions.



Collection of 3 ZA ([0 0 1], [1 0 1], [1 0 2]) PED intensities with a 200KV TEM from uvarovite mineral Ca₃Cr₂(SiO₄)₃ cubic la-3d a=1.2nm and the use of SIR2008 revealed precise atomic structure (see table) calculated atomic positions are very close to X-Ray 3D refined atomic model



Using set of simulated PED intensities from 2 ZA of complex commensurate structure of **antigorite mineral** ~Mg3Si2O5(OH)4 and solving with direct methods (SIR2008), most of the atomic positions are revealed









Combining precession electron diffraction - powder X-Ray diffraction to solve complex structures



Information from PED can be combined with *hkl reflections from X-Ray* powder diffraction to accurately solve and refine *ab-initio* structures using either *charge-flipping* algorithms or direct methods.

- technique is useful for poorly crystallized / nm size pollycrystalline materials
- useful for solving structures of complex organic and inorganic materials
- useful in presence of unknown phases in X-Ray powder pattern





Courtesy from PhD thesis C.Own Northwestern University 2005

Modern data collection

3D DATA COLLECTION





- No need for perfect ZA crystal orientationmore user friendly !!!
- 3D partial information about reciprocal space
- Automatic 3D unit cell determination and intensities extraction

Collecting complete 3D electron diffraction data using <u>rotation</u> or tomography

Courtesy Prof. Hovmoller Stockholm University

Rotation axis $\pm 0,5^{\circ}$ 10 +-Here are shown the integrated diffraction patterns from rotation.

3D (precession) diffraction tomography



Charoite : 90 atoms , 8495 total reflections2878 independent reflectionsP21/m32.08 A , 19.55 A7.16 AData courtesy Prof. U.Kolb Mainz University

Structures solved with 3D precession diffraction tomography

Natrolite zeolite: non-centrosymmetric space group **Fdd2**, unit cell volume 2246 **A³,10 atoms in the asymmetric unit, 4560 experimentally** collected reflections for structure solution.



Phthalocyanines and their derivative constitute the major part of all organic pigments. Structure of **Pigment Blue 15:3** (P.B.15:3 β -CuPc) was solved in P2₁/c, unit cell volume 1166A³, 41 non-H atoms in the asymmetric unit, 14094 reflections collected within a total tilt range of 120° and used for abinitio structure solution.



OPBA4 is a four-member oligomer of the *para*benzamide homologous row. The molecules are important building blocks for co-polymer supra molecular chemistry due to their H-bonds driven stiff geometry.

Structure of OPBA4 is solved in C2/c space group, volume of the unit cell is 4546 A³, 39 non-hydrogen atoms in the asymmetric unit. The structure was solved from a data set with 14719 collected reflections.



Data courtesy Prof. Ute Kolb Mainz University

Structures (inorganics) solved with 3D precession diffraction tomography

CaCO ₃	R-3c 4.96 A, 6.41 A
BaSO ₄	Pnma 8.89 A, 5.51 A 7.17 A
Zn ₁ Sb ₁	Pbca 6.46 A, 8.11 A 8.43 A
MFU-4I	Fm-3m 31.05 A , large pore structure Zn ₅ Cl ₄ (BTDD) ₃
Charoite	P21/m 32.08 A , 19.55 A 7.16 A

Structures (ORGANICS) solved with 3D precession diffraction tomography

	P.Y.213	P-1	7.0.	11.6	13.8 A	98.5	101.3	93.7
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NLO Pca21 28.15, 5.15, 11.09 A 2-(4-benzamido-cinnamoyl)-furane

NS3 P21/c 14.72, 9.98, 12.59 A 107.6 deg

ORBA2 Di-p-benzamide 5.66, 13.45, 15.09 A ORBA3 Tri-p-benzamide 13.38, 9.0, 11.56 A

Basolite Fm-3m 18.6 and many pharmaceuticals

Data courtesy Prof. Ute Kolb Mainz University