NEW techniques for TEM nanoanalysis
precession electron diffraction for organic – inorganic nanostructures

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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. algorithms) we find directly crystal structure: atomic positions
- Smallest crystals for str. determination 1-5 micron: Synchrotron solution

Courtesy I. Margiolaki ESRF Grenoble
X-ray Crystallography

X-ray crystallography is the science of determining the arrangement of atoms within a crystal from the manner in which a beam of X-rays is scattered from the electrons within the crystal. The method produces a three-dimensional picture of the density of electrons within the crystal, from which the mean atomic positions, their chemical bonds, their disorder and sundry other information can be derived.
Many small single crystals make a powder

- Spots cover spheres in 3D reciprocal space
- 2D area detector takes a slice
  - (on Ewald sphere)
- 1D powder scan measures distance from origin

Courtesy I. Margiolaki ESRF Grenoble
X-Ray powder diffraction: limitations

- Overlapping of reflections
- Stacking intergrowth
- Preferential orientation
- Nanocrystals
- Impurities
- Light atoms (Li, Be)
X- Ray powder diffraction limitations

overlapping

Preferential orientation

Modification III sulphathiazole

Fig. 4.21. The influence of preferred orientation on the experimental X-ray powder diffraction pattern of modification III of sulphathiazole. Upper, expected pattern calculated from the single crystal structure; lower, experimental powder pattern. (Adapted from Threiffall 1999, with permission.)

From book J.Bernstein Polym in molecular crystals
X- Ray powder diffraction limitations

overlapping

Stacking intergrowth

Preferential orientation

Impurities

Light atoms (Li, Be)
Electron diffraction in transmission electron microscope (TEM)

Powder patterns: sum of individual nanocrystals

Cell parameter and symmetry determination from nm single crystals
Image formation in TEM

Sample

Objective Lens

Back Focal Plane

Image Plane

Point resolution

Electron diffraction

Information limit

High resolution image

NanoMEGAS
Advanced Tools for electron diffraction
With TEM we can analyze nm size crystals.

Data extracted from JCPDS-ICDD Database 1997.
Characterization for new unknown compound

Find crystal cell parameters
Find atomic crystal structure
Texture – (multi) phase analysis
High resolution TEM: only 2D projected atomic structure

NOT possible to get 3D atomic model

a = 5.70 Å, b = 13.18 Å, c = 19.92 Å
S.G. Cmca(64)

Courtesy K Boulahya Univ Madrid
Find crystal cell parameters

TEM: manual tilt series acquisition

Problem: “missing cone” = lost data

Courtesy: Prof. U Kolb UMainz
Hexagonal cell parameters:
- $a = 5.05 \text{ Å}$
- $c = 32.5^\circ$

Li Ni$_{0.5}$Ti$_{1.5}$O$_4$

Find crystal cell parameters by combining several ZA ED patterns from same crystal.

Courtesy M.Gemmi IIT Pisa
ORGANIC crystals: beam sensitive

Only possible to collect several (non ZA oriented ED patterns) from different crystals

Penicillin G, courtesy Dr. D. Gueorguieva, Leiden Univ NL
Find and index ANY 3d CELL from RANDOM diffraction patterns from same or several crystals.

Courtesy JP Abrahams, D.Georgieva Univ Leiden
Characterization
for new unknown compound

Find crystal cell parameters
Find atomic crystal structure
Texture – (multi) phase analysis
Electron diffraction is highly dynamical.

Electron diffraction intensities cannot be used for solving or refining the structure in a straightforward way as X-ray data.

Si [011] spg Fd3m
(h00) allowed only if \( h = 4n \)
Normal electron diffraction pattern (dynamical) thickness > 10 nm

Ideal kinematic diffraction pattern (like X-Ray)

Melilite: tetragonal a=b=7.8Å c=5.0Å

\[ P - 4 \ 2_1 \ m \]

Space group extinction rules: (h00) e (0k0) h=2n, k=2n

Courtesy M. Gemmi Univ Milano
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 around 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, therefore can be used to solve crystal nanostructures (Ultramicroscopy, vol.107, issue 6-7, July 2007).
Scan lens

De-scan lens

(Diffracted amplitudes)

Reference: C.Own PhD thesis

Non-

Precessed

Precession...
DigiSTAR digital precession unit

PRECESSION: DISCOVERED IN UK 1996 R. Vincent- P. Midgley

NanoMEGAS: FIRST TEM commercial device

- MORE THAN 50 ARTICLES SINCE 2004
- MORE THAN 60 INSTALLATIONS WORLD-WIDE
Digital precession interface for advanced TEM

Zeiss Libra 200F Cs corrected  Jeol 2200 FS  Jeol 2010F
Tecnai 20F  Tecnai 30F
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.
Advantages of precession in single exposure data collection

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

with beam precession, Ewald sphere also precess though the reciprocal space
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.Georgieva Univ Leidenc
Precession electron diffraction (PED) from penicillin G – potassium oriented PED patterns show Laue class symmetry.

Easier to find crystal cell parameters from “randomly oriented” PED patterns.

Orthorombic  \( a = 6.4 \text{ Å} \quad b = 9.4 \text{ Å} \quad c = 30 \text{ Å} \)

Samples C. Giacovazzo CNR Bari

Courtesy JP Abrahams, D. Georgieva Univ Leiden
Obtaining « randomly oriented » PED in PHARMACEUTICALS

ASPIRIN

Potential Polymorphs of Aspirin

The Polymorph Predictor was used to examine the potential for additional polymorphs of aspirin.

Aspirin, also known as acetylsalicylic acid, has numerous pharmaceutical applications. First synthesized in 1897, aspirin is only found experimentally in

Courtesy JP Morniroli, samples T.Weirich RWTH Aachen

NanoMEGAS

Advanced Tools for electron diffraction
Data collection: precession electron diffraction from lysozyme nanocrystals

P43212 \(a=b=79.2\) A, \(c=38.0\) A

Courtesy JP Abrahams, D. Georgieva Univ Leiden
Combine 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 polycrystalline materials**
- **useful for solving structures of complex organic and inorganic materials**
- **useful in presence of unknown phases in X-Ray powder pattern**

one of the **most complex known zeolites TNU-9 (Si$_{19}$O$_{234}$)** has been solved by combining Synchrotron X-Ray powder results and data from 5 ZA PED patterns from 300 kV TEM
Precession electron diffraction: \textit{ab initio} determination of nanostructures

**Step 1**
- TEM crystal experiment
- PED patterns collection

**Step 2**
- ED intensities collection and merging from several zone axis (ELD – Triple)
- Semi-automatic (off-line)

**Step 3**
- STRUCTURE DETERMINATION
  - (Direct methods)
  - Semi-automatic (SIR software)
- Refinement crystal structure
**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, input HKL and intensities at direct methods software using electron 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 (e.g., 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%
Electron diffraction intensities are measured automatically

FROM

Image plates
Photo film

OR

CCD camera
1k x 1k
2k x 2k
4k x 4k
Use Direct methods, charge flipping (like X-Ray) to solve crystal structures

DIRECT METHODS (electron scattering)

SIR 96, SIR 2007, SIR 2008, FOX, ....

Structure solution with direct methods: SIR2008

http://www.ic.cnr.it/registration_form.php

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.

\[ P \ 6_3/mmc, \ a=0.867 \text{ nm} \ c=0.816 \text{ nm} \]

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 Ia-3d \( a=1.2 \text{ nm} \) 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 \( \text{~Mg₃Si₂O₆(OH)₄} \) and solving with direct methods (SIR2008), most of the atomic positions are revealed
Ab initio determination of MCM-22 (ITQ-1) zeolite framework

3D frameworks can be revealed by collecting and combining quasi-kinematical precession electron diffraction intensities from different zone axis to one 3D electron diffraction data set (image courtesy Douglas Dorset USA)
3D precession electron diffraction tomography (ADT)
3D visualization - Detection of disorder

Cell parameter determination on single nanoparticle

Conference by Dr. Gorelik

Courtesy: Prof. U Kolb UMainz
Characterization for new unknown compound

Find crystal cell parameters
Find atomic crystal structure
Texture – (multi) phase analysis
NEW precession application  
“EBSD” – TEM
Comparison SEM-(EBSD) vs TEM spatial resolution

SEM orientation map
deformed Ta6V alloy

TEM orientation map
(1-10 nm stepsize)

EBSD-SEM map (50 nm resolution)

Electron Backscattering Diffraction (EBSD) orientation maps in SEM have usually poor resolution in comparison with TEM maps showing detailed nanostructure.
ASTAR: diffraction pattern acquisition

Example: Severely deformed 7075 Aluminium Alloy

Any TEM – FEG/LaB6 may work with ASTAR

NanoMEGAS
Advanced Tools for electron diffraction
ASTAR (EBSD-TEM like procedure)

Using precession diffraction the number of ED spots observed increases (almost double); correlation index map becomes much more reliable when compared with templates.

In this example (right) a metal particle gives wrong correlation index without precession due to presence of Kikuchi lines; after applying precession (right lower image), index gets correct value as ED quality improves and Kikuchi lines disappear.

Orientation map

NanoMEGAS
Advanced Tools for electron diffraction
ASTAR phase –orientation mapping for advanced TEM

Zeiss   LiIBRA 200F Cs corr   TECNAI 20F   TECNAI 30F
JEOL 2200 FS     JEOL 2010F
DiffGen: Template generator

Features:
- Any crystallographic structure
- Laue class adapted to the space group
- Structure generator (space group, structure factor equ.)
- Input from ICDD database

input from ICDD database
**ASTAR: crystallographic orientation identification**

Pre-calculated templates

\[ Q(i) \sim \sum_{j=1}^{m} P(x_j,y_j) T_i(x_j,y_j) \]

Correlation index

Acquired pattern

Degree of matching between experimental patterns and simulated templates is given by a correlation index; highest value corresponds to the adequate orientation/phase

Template generation of all possible simulated orientations (every 1°) within stereographic triangle for given crystal lattice(s) and symmetry

Stereographic projection

(example, cubic) ~ 2000 simulated patterns
ASTAR identification example: nanocrystalline Cu

For a given ED pattern, the correlation index map is calculated for all possible template orientations and plotted on a map that represents a portion of the stereographic projection (reduced to a double standard triangle). That resulting map reveals the most probable orientation for every experimental spot ED pattern (in this case ED pattern is found to be close to 110 ZA orientation)
ASTAR: ultra-fast TEM orientation map

Sample: severely deformed copper

Orientation map

250 x 200 pixel data acquisition

5-10 min

Typical software data analysis time (for cubic)

5-15 min (hexagonal, tetragonal)

x 3-4 more time

Map resolution equals beam size resolution
NBD step 20 nm (LaB6)
**Power of the ASTAR Technique:** nanoparticles

**ASTAR**: Orientation analysis from Pt ~100 particles ~ 6 nm in size

1 nm resolution for orientation map

Data courtesy Prof. P. Ferreira, J. Ganesh, Univ Texas at Austin USA  
JEOL 2010 FEG
This 8 nm bar is most clearly visible in (b) and divided into 20 sections of 0.4 nm each (that represent the utilized scanning-precession increments of the primary electron beam) in (d). Note that there are jumps in the local mis-orientation profile along the 8 nm bar of almost 60° between sections 3 and 4, 8 and 9, as well as 10 and 11.
texture analysis of several areas (combined)

→ 20 nm to 40 nm step size in LaB6-TEM scans sufficient to capture morphology of microstructure with high fidelity (ASTAR)

→ ASTAR orientation data can be read/analyzed by TSL – HKL software

Data courtesy A. Kulovits, G. Facco, H. Kotan, Jörg M.K. Wiezorek
University of Pittsburgh USA
Problem: distinguish nanoparticles rutile - anatase (TiO$_2$) texture

Rutile $P4_2_1/mnm$  $a = 4.59$ Å,  $c = 2.95$ Å

 Courtesy Dr. Bakardieva REZ Prague

Jeol 3010 – ASTAR
**PROBLEM**: distinguish between goethite (alpha-FeO(OH)) 300x40x10nm and brookite (TiO2) platelets of 48nm diameter
Libra 200-ASTAR: sub-nanometer (< 1 nm) phase map

Replica with TiN, Fe$_2$B, MnS and Fe$_6$Cr$_6$

Phase map can distinguish between 3 phases:

TiN, Fe$_2$B, MnS and Fe$_6$Cr$_6$

< 1 nm resolution phase map
INDEX and create virtual dark and bright field maps

Diffraction Pattern viewer with virtual aperure

Virtual dark field image
Polycrystalline Electron diffraction

“X-Ray amorphous” OR nanocrystalline?
Orientation mapping on Nanocrystallized polycrystalline Ni-Fe sample

Polycrystalline thin film of Ni-Fe nanocrystals (average size 5-20 nm)

Data taken with JEOL JEM 2200F operating at 200 kV spot size 1-8 nm

ASTAR can index even overlapping diffraction patterns from polycrystalline sample

Results courtesy Prof. Dr. E. Rauch CNRS Grenoble
As for EBSD equipments, the orientation of one particular axis (usually the z axis) is given through a colour code. This enables the individual crystals to be recognized and/or their size to be estimated (step size 4 nm)

JEOL 2200 FS  200 KV, Humboldt  Univ Berlin
A STEM type image is reconstructed from the collection of diffraction patterns. Virtual Dark Field images (VDF) may be reconstructed as well by selecting a particular reflection placing a virtual aperture on that selected spot on a diffraction pattern.

JEOL 2200 FS  200 KV, Humboldt Univ Berlin
Nanoparticle (50 nm) phase identification

Magnetite or maghemite??

\[ P4_1 32 \gamma-\text{Fe}_2\text{O}_3 \]

\[ \text{Fe}_3\text{O}_4 \]

cubic 8.32 Å

\[ Fd\bar{3}m \]

ALL Nanoparticles REVEALED AS magnetite (RED)

Orientation map precession 0.3°

PHASE map precession 0.3°
New application: ASTAR on organic structures

TRIS structure $\text{C}_{16}\text{H}_{48}\text{N}_{4}\text{O}_{12}$

Pna2$_1$ cell $0.7768 \times 0.8725 \times 0.8855$ nm
ASTAR texture – (multi) phase analysis from different sample areas

What is the % of each phase?

% amorphous phase?
detection limit?
“Random 3D tomography” - ASTAR
Cell determination & basic structure model building - INORGANIC CRYSTALS
"Random 3D tomography" - ASTAR
Cell determination & basic structure model building – ORGANIC CRYSTALS
TEM advanced ELECTRON DIFFRACTION SOLUTIONS for pharma-organic crystals

AUTOMATIC ORIENTATION / PHASE MAPPING

ASTAR

ADT -3D diffraction tomography

PRECESSION « SpinningStar- DigiSTAR »

NanoMEGAS
Advanced Tools for electron diffraction
ASTAR combinations (examples)

Laurence Livermore Lab (Berkley –California) USA
CM300 FEG – Jeol 2000

Portland State Univ –Oregon USA
Tecnai 20F - Jeol 2000

Alabama Univ USA Tecnai 30F

Univ of Texas –Austin USA Jeol 2010 F

Humboldt Univ Berlin Jeol 2200 FS

KBSI Korea Jeol 2100F

Osaka Gas, Japan Jeol 2100F

Zeiss Application Lab (Germany) Libra 200 FE Cs – Libra 120
NATO summer school in Erice, Sicily
www.crystalerice.org
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Thanks for your attention!!