IDENTIFICATION – FINGERPRINTING – SOLVING \textit{ab-intio} NANOSTRUCTURES

BY \textit{PRECESSION ELECTRON DIFFRACTION}
PRECESSION ELECTRON DIFFRACTION

NEW analysis technique

> 25 articles in 2 years!

Ultramicroscopy Special Issue vol.107 issue 6-7 June 2007
Unknown nanostructures...... HOW analyze them ??

- Single crystal > 5 microns X-ray diffraction
- Powder X-ray diffraction
- TEM microscopy

NanoMEGAS
Advanced tools for electron diffraction
X-Ray powder diffraction: limitations

Nanocrystals: peak broadening

< 10nm

> 1μm

overlapping
Electron diffraction: advantages

Every TEM (electron microscope) may produce ED patterns from individual single nanocrystals

ED information: Cell parameter and symmetry determination

Measuring intensity values leads to structure determination
**Electron diffraction: challenges for structure analysis**

... electron diffraction data can be strongly distorted by dynamical scattering.

**Dynamical scattering**  
(thickness > 10 nm)

**Kinematical scattering**  
(very thin crystals)

\[ I(k) = |F(k)|^2 \]

**CORRECT MODEL**

Light atoms do not appear  
Atomic positions displaced

**WRONG MODEL**

NanoMEGAS  
Advanced Tools for electron diffraction
Solution: Precession Electron Diffraction (Vincent-Midgley)

Beam precesses about exact zone axis direction; reduces extent of dynamical scattering in on-axis condition.

Precession Reflections
More kinematical (like X-ray case)

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
SPINNING STAR

UNIVERSAL INTERFACE FOR PRECESSION ELECTRON DIFFRACTION FOR ANY TEM

- JEOL 200 kv, JEOL 120 KV, 2010, 2100, 2000, 2010 FEG
- FEI Tecnai 30 FEG, Tecnai 12 (120 kv), Tecnai 20 (200 kv), Tecnai 10
- Philips EMXXX, CM10, CM20, CM30, STWIN, UTWIN

Topcon 200 KV (Japan demo facility)

- Zeiss 912
- Hitachi 200 KV

- Can be easily installed to any TEM 100-400 KV (LaB6-FEG)
- Precession is possible for a parallel or convergent beam

- Precession spot size (5-50 nm)
- Precession angle can vary continuously from 0° to 4°, to observe true crystallographic symmetry variation

NanoMEGAS
Advanced Tools for electron diffraction
Ab-initio structure solution with precession of ……

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

Proteins
APPLICATION: FIND TRUE CRYSTAL SYMMETRY – SOLVING CRYSTAL STRUCTURES

Dynamical interactions due to thickness effects may deform intensities in a way that crystal symmetry cannot be recognized; by applying precession true crystal symmetry can be revealed and dynamical scattering is greatly reduced.

PRECESSION ED INTENSITIES (PED) ARE CLOSE TO (IDEAL) KINEMATICAL INTENSITIES: WE CAN USE PED TO SOLVE DIRECTLY CRYSTAL STRUCTURES OF NANOCRYSTALS LIKE IN X-RAY DIFFRACTION

Garnet cubic Ia3d  a=1.2 nm

UVAROVITE  Ca₃Cr₂(SiO₄)₃

Courtesy M.Gemmi  Univ of Milano
Is possible from simple ZOLZ/FOLZ symmetry comparison to deduce point and space group nanocrystal symmetry.

HOW?

by simply increasing precession angle. FOLZ/ZOLZ reflections and their relative symmetry becomes visible in ED patterns.

J.P. Mornirolli, JW Steeds
Ultramicroscopy 1992, 45, 219

From J.P. Mornirolli and J.W. Steeds, Ultramicroscopy, 1992, 45, 219
SiC

Space group determination by
PRECESSION ELECTRON DIFFRACTION

SiC 4H hexagonal  \( P6_3mc \)

Courtesy JP Mornirolli Univ of Lille France
AUTOMATIC crystal symmetry determination by analysis of ZOLZ @ FOLZ precession patterns
Precession electron diffraction: 
*ab initio* determination of nanostructures

TEM crystal experiment

ED intensities collection from several zone axis (ELD – Triple) 
semi-automatic (off-line)

STRUCTURE DETERMINATION
(Direct methods) 
semi-automatic (SIR software)

Refinement crystal structure
Electron diffraction intensities are measured automatically (ELD software) from:

- Image plates
- Photo film
- CCD camera
  - 1k x 1k
  - 2k x 2k
  - 4k x 4k
  - 8k x 8k

or from electron diffractometer.
3D structure solution examples

Mauro Gemmi and Stavros Nicolopoulos

Structure solution with three-dimensional sets of precessed electron diffraction intensities

Ultramicroscopy, Volume 107, Issues 6-7, June-July 2007, Pages 483-494

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>Space Group</th>
<th>Cations</th>
<th>Oxygens</th>
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<td>Åkermanite</td>
<td>(Ca$_2$MgSi$_2$O$_7$)</td>
<td>P-42$_1$m</td>
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<td>Uvarovite</td>
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<td>I a –3 d</td>
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Structure solution with precession diffraction: Åkermanite

Three-dimensional set of precession electron diffraction intensities obtained merging [1 0 0] [0 0 1] [1 0 1] [1 0 2] zone axes.

All atoms found, correctly labelled, <Distance> = 0.1262 from published coordinates.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X(Sir)</th>
<th>Y(Sir)</th>
<th>Z(Sir)</th>
<th>X(Pub)</th>
<th>Y(Pub)</th>
<th>Z(Pub)</th>
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<tr>
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</table>
PRECESSION RESOLUTION - X RAY RESOLUTION

0.24 nm
STWIN

0.19 nm
UTWIN

0.12 nm
CONVENTIONAL X-RAY

> 17,000 REFLECTIONS OBSERVED

0.05 nm
SYNCHROTRON X RAY

CS-Nb-W-0 oxide, ALL heavy atoms revealed by precession diffraction

Weirich et al. Ultramicroscopy 2006

TVIPS F224 HD

NanoMEGAS
Advanced tools for electron diffraction
PRECESSION on POLYMERS

Melon

\([\text{C}_6\text{N}_7(\text{NH}_2)(\text{NH})]_n\), plane group \(p2gg\)

\(a = 16.7 \, \text{Å}, \; b = 12.4 \, \text{Å}, \; g = 90^\circ, \; Z = 4\)

Courtesy M. Doblinger  Univ of Munich Germany
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.

**amoxyccillin**

**penicillin G-potassium**

Samples C.Giacovazzo CNR Bari  
Courtesy JP Abrahams, D.Georgieva Univ Leiden
Precession ED from 3d protein lysozyme nanocrystals

protein crystals show much better quality PED patterns (suitable for symmetry and structure determination) than conventional SAED patterns
ZEOLITES

ITQ-29 *ab initio* structure determination

Is possible to determine complete structure from a single ED obtained at 100 kV

Different methods: direct methods (FOCUS), maximum entropy (MICE), real space (FOX), ...

\[ I_{hkl} \text{ proportional to } |F_{hkl}|^2 \]

Pm\(\bar{3}\)m, \(a=11.87\) Å
ZEOLITES : 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)
PRECESSION ON old TEM...... works well!

SOLUTION: ENHANCE NEW TEM

OR UPGRADE OLDER TEM

TO POWERFUL STRUCTURE DETERMINATION

> 36 installations world-wide
NanoMEGAS INSTALLATIONS WORLDWIDE

**PHILIPS TEM**
CM30, CM 20, CM12, CM10, EM 400

**JEOL TEM**
JEOL 2000, JEOL 2100, JEOL 2010, JEOL 2010 FEG, JEOL 1400

**FEI TEM**
TECNAI 10, TECNAI 12, TECNAI 20, TECNAI 20 FEG STEM, TEM 30 FEG STEM

**ZEISS TEM**
912 OMEGA FILTER

**DEMO SITES**
PARIS Philips CM12
JAPAN Tokyo Topcon EM 002B 200 kv
TVIPS Munich JEOL 2010, Tecnai12

TOTAL
> 36 INSTALLATIONS
1st precession electron diffraction user meeting

Martina Franca 8-9 May, 2008

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PRECESSION UNIT

EDS

EELS

STEM

CCD

HAADF

ELECTRON DIFRACTOMETER

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