Electron Microscopy

4. TEM

Basics: interactions, basic modes,
Diffraction: elastic scattering theory, reciprocal space, diffraction pattern,
Laue zones
Diffraction phenomena

Image formation: contrasts,
Signals from a thin sample

Interaction of high energetic electrons with matter

- **Auger electrons**
- **Backscattered electrons (BSE)**
- **Secondary electrons (SE)**
- **Characteristic X-rays**
- **Bremsstrahlung X-rays**
- **Inelastically scattered electrons**
- **Elastic scattering** in crystalline specimens
- **Elastic scattering** in amorphous specimens
- **Inelastic scattering** at specimen atoms

**Sample Applications:**
- Biological samples, polymers
- Crystalline structure, defect analysis, high-resolution TEM
- Chemical analysis, spectroscopy
Interaction -> contrast

Thin section of mouse brain: mass contrast of stained membrane structures (G. Knott)

Two basic operation modes

**Diffraction <-> Image**

Diffraction Mode

Image Mode
(K,Nb)TaO₃ Nano-rods

**SEM**

TEM
holey Carbon film

**Diffraction pattern**

Shape, lattice parameters, defects, lattice planes

(K,Nb)O₃ Nano-rods

**Bright field image**

**Dark field image**

**High-resolution image**
Diffraction theory

- Introduction to electron diffraction
- Elastic scattering theory
- Basic crystallography & symmetry
- Electron diffraction theory
- Intensity in the electron diffraction pattern

Thanks to Dr. Duncan Alexander for slides

Why use electron diffraction?

Diffraction: constructive and destructive interference of waves

- Wavelength of fast moving electrons much smaller than spacing of atomic planes ⇒ diffraction from atomic planes (e.g. 200 kV $e^-$, $\lambda = 0.0025$ nm)
- Electrons interact very strongly with matter ⇒ strong diffraction intensity (can take patterns in seconds, unlike X-ray diffraction)
  
  - Spatially-localized information
    (≥ 200 nm for selected-area diffraction; 2 nm possible with convergent-beam electron diffraction)
  - Close relationship to diffraction contrast in imaging
    - Orientation information
    - Immediate in the TEM!

  (Diffraction from only selected set of planes in one pattern - e.g. only 2D information)

  (Limited accuracy of measurement - e.g. 2-3%)

  (Intensity of reflections difficult to interpret because of dynamical effects)
Image formation

BaTiO₃ nanocrystals (Psaltis lab)

Area selection

BaTiO₃ nanocrystals (Psaltis lab)

Insert selected area aperture to choose region of interest
Press "D" for diffraction on microscope console - alter strength of intermediate lens and focus diffraction pattern on to screen.

Find cubic BaTiO$_3$ aligned on [0 0 1] zone axis.

Autumn 2011 Experimental Methods in Physics Marco Cantoni 4-13

Scatter range of electrons, neutrons and X-rays

(99% of intensity lost)

<table>
<thead>
<tr>
<th>Élément (masse spécifique)</th>
<th>4-Be 1.84 g/cm$^3$</th>
<th>13-Al 2.7 g/cm$^3$</th>
<th>29-Cu 8.93 g/cm$^3$</th>
<th>82-Pb 11.3 g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayons X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-K$\alpha$ $\lambda=1.54$ Å</td>
<td>16 mm 83 mm</td>
<td>0.35 mm 3.3 mm</td>
<td>0.10 mm 0.10 mm</td>
<td>0.017 mm 0.034 mm</td>
</tr>
<tr>
<td>Mo-K$\alpha$ $\lambda=0.71$ Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutrons thermiques $\lambda=1.08$ Å</td>
<td>89 m 6 m</td>
<td>0.26 m 14 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>électrons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda=0.037$ Å à 100 kV</td>
<td>39 µm 42 µm ~330 µm</td>
<td>11 µm 0.6 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda=0.020$ Å à 300 kV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Consider coherent elastic scattering of electrons from atom

Differential elastic scattering cross section:

\[ \frac{d\sigma(\theta)}{d\Omega} = |f(\theta)|^2 \]

Atomic scattering factor for electrons

The Mott-Bethe formula is used to calculate electron form factors from X-ray form factors \( f_x \)
Scattering theory - Huygen’s principle

Periodic array of scattering centres (atoms)
Plane electron wave generates secondary wavelets

Secondary wavelets interfere =>
strong direct beam and multiple orders of diffracted beams from constructive interference

Atoms closer together => scattering angles greater

=> Reciprocity!

Basic crystallography
Crystals: translational periodicity & symmetry

Repetition of translated structure to infinity
Crystallography: the unit cell

Unit cell is the smallest repeating unit of the crystal lattice
Has a lattice point on each corner (and perhaps more elsewhere)
Defined by lattice parameters $a$, $b$, $c$ along axes $x$, $y$, $z$
and angles between crystallographic axes: $\alpha = b^c$; $\beta = a^c$; $\gamma = a^b$

Building a crystal structure

Use example of CuZn brass
Choose the unit cell - for CuZn: primitive cubic (lattice point on each corner)
Choose the motif - Cu: 0, 0, 0; Zn: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
Structure = lattice +motif => Start applying motif to each lattice point
Building a crystal structure

Use example of CuZn brass

Choose the unit cell - for CuZn: primitive cubic (lattice point on each corner)

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Structure = lattice + motif => Start applying motif to each lattice point

Extend lattice further in to space

The seven crystal systems

7 possible unit cell shapes with different symmetries that can be repeated by translation in 3 dimensions

=> 7 crystal systems each defined by symmetry

<table>
<thead>
<tr>
<th>Triclinic</th>
<th>Monoclinic</th>
<th>Orthorhombic</th>
<th>Tetragonal</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha, \beta, \gamma \neq 90^\circ )</td>
<td>( \alpha \neq 90^\circ ), ( \beta, \gamma = 90^\circ )</td>
<td>( a \neq b \neq c )</td>
<td>( a \neq c )</td>
<td>( \alpha, \beta, \gamma \neq 90^\circ )</td>
</tr>
</tbody>
</table>

Hexagonal

Cubic

Diagrams from [www.Wikipedia.org](http://www.Wikipedia.org)
Four possible lattice centerings

P: Primitive - lattice points on cell corners

I: Body-centred - additional lattice point at cell centre

F: Face-centred - one additional lattice point at centre of each face

A/B/C: Centred on a single face - one additional lattice point centred on A, B or C face

Diagrams from www.Wikipedia.org

14 Bravais lattices

Combinations of crystal systems and lattice point centring that describe all possible crystals - Equivalent system/centring combinations eliminated => 14 (not $7 \times 4 = 28$) possibilities

Diagrams from www.Wikipedia.org
**Crystallography - lattice vectors**

A lattice vector is a vector joining any two lattice points
Written as linear combination of unit cell vectors \( a, b, c \):
\[ t = Ua + Vb + Wc \]
Also written as: \( t = [U \ V \ W] \)

Examples:

- \([1 \ 0 \ 0]\)
- \([0 \ 3 \ 2]\)
- \([1 \ 2 \ 1]\)

Important in diffraction because we “look” down the lattice vectors (“zone axes”)

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**Crystallography - lattice planes**

Lattice plane is a plane which passes through any 3 lattice points which are not in a straight line

Lattice planes are described using Miller indices \((h \ k \ l)\) where the first plane away from the origin intersects the \(x, y, z\) axes at distances:

- \(a/h\) on the \(x\) axis
- \(b/k\) on the \(y\) axis
- \(c/l\) on the \(z\) axis
Crystallography - lattice planes

Sets of planes intersecting the unit cell - examples:

\( \frac{a}{h} \) on the \( x \) axis
\( b/k \) on the \( y \) axis
\( c/l \) on the \( z \) axis

Diffraction theory - Bragg law

Path difference between reflection from planes distance \( d_{hkl} \) apart = \( 2d_{hkl}\sin\theta \)

\[ n\lambda = 2d_{hkl}\sin\theta \]

Electron diffraction: \( \lambda \sim 0.001 \text{ nm} \)

therefore: \( \lambda \ll d_{hkl} \)

\[ n\lambda \approx 2d_{hkl}\theta \]

Reciprocity: scattering angle \( \theta \sim d_{hkl}^{-1} \)
Bragg’s law

\[ 2 \sin \theta \, d_{hkl} = n \lambda \]

\[ d_{hkl} = n \lambda / 2 \sin \theta \]

Elastic diffraction

\[ |k| = |k'| \]

Periodic arrangement of lattice planes:
\( g \): reciprocal lattice vector

Diffraction theory - 2-beam condition

2-beam condition: strong scattering from single set of planes
Multi-beam scattering condition

Electron beam parallel to low-index crystal orientation \([U \ V \ W]\) = zone axis
Crystal “viewed down” zone axis is like diffraction grating with planes parallel to e-beam
In diffraction pattern obtain spots perpendicular to plane orientation
Example: primitive cubic with e-beam parallel to \([0 \ 0 \ 1]\) zone axis

Note reciprocal relationship: smaller plane spacing => larger indices \((h \ k \ l)\)
& greater scattering angle on diffraction pattern from \((0 \ 0 \ 0)\) direct beam

\[2 \times 2\] unit cells

The reciprocal lattice

In diffraction we are working in “reciprocal space”; useful to transform the crystal lattice in to
a “reciprocal lattice” that represents the crystal in reciprocal space:

\[r_1 = n_1a + n_2b + n_3c\]

Real lattice vector:
\[r = m_1a^* + m_2b^* + m_3c^*\]
Reciprocal lattice vector:

\[a^*.b = a^*.c = b^*.c = b^*.a = c^*.a = c^*.b = 0\]
\[a^*.a = b^*.b = c^*.c = 1\]
\[\text{i.e. } a^* = (b \wedge c)/V_c \quad V_c: \text{ volume of unit cell}\]

For scattering from plane \((h \ k \ l)\) the diffraction vector:
\[g_{hkl} = ha^* + kb^* + lc^*\]
Plane spacing:
\[d_{hkl} = \frac{1}{|g_{hkl}|}\]
Ewald sphere

A vector in reciprocal space:
\[ \mathbf{g}_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \]

diffraction if:
\[ k_\mathbf{g} - k_\mathbf{0} = \mathbf{g} \quad \text{and} \quad |k| = |k_\mathbf{0}| \]
Bragg and elastic scattering

Reciprocal space: sphere radius \(1/\lambda\) represents possible scattering wave vectors intersecting reciprocal space

Electron diffraction: radius of sphere very large compared to reciprocal lattice
\[ \Rightarrow \text{sphere circumference almost flat} \]

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta} = \frac{1}{|\mathbf{g}|} \]
Ewald sphere in “2-beam” condition

2-beam condition with one strong Bragg reflection corresponds to Ewald sphere intersecting one reciprocal lattice point.

Laue Zones
• Laue zones

Ewald Sphere: Laue Zones (ZOLZ + FOLZ)

Source: P.A. Buffat
Ewald Sphere: Laue Zones (ZOLZ+FOLZ) tilted sample

\[ \alpha = 2.0 \text{ mrad} \]
\[ s = 0.2 \]

Dynamical scattering

For interpretation of intensities in diffraction pattern, single scattering would be ideal - i.e. "kinematical" scattering

However, in electron diffraction there is often multiple elastic scattering: i.e. "dynamical" behaviour

This dynamical scattering has a high probability because a Bragg-scattered beam is at the perfect angle to be Bragg-scattered again (and again...)

As a result, scattering of different beams is not independent from each other
Symmetry information

Zone axis SADPs have symmetry closely related to symmetry of crystal lattice

Example: FCC aluminium

- [0 0 1] 4-fold rotation axis
- [1 1 0] 2-fold rotation axis
- [1 1 1] 6-fold rotation axis - but [1 1 1] actually 3-fold axis

Need third dimension for true symmetry!

Twinning in diffraction

Example: Co-Ni-Al shape memory FCC twins observed on [1 1 0] zone axis

(1 1 1) close-packed twin planes overlap in SADP

Images provided by Barbora Bartová, CIME
Epitaxy and orientation relationships

SADP excellent tool for studying orientation relationships across interfaces

Example: Mn-doped ZnO on sapphire

Zone axes:
\([1 -1 0]_{\text{ZnO}} \parallel [0 -1 0]_{\text{sapphire}}\)

Planes:
\(c\)-plane\(_{\text{ZnO}}\) // \(c\)-plane\(_{\text{sapphire}}\)

Ring diffraction patterns

If selected area aperture selects numerous, randomly-oriented nanocrystals, SADP consists of rings sampling all possible diffracting planes - like powder X-ray diffraction

Example: “needles” of contaminant cubic MnZnO\(_3\) - which XRD failed to observe!
Ring diffraction patterns

Larger crystals => more “spotty” patterns

Example: ZnO nanocrystals ~20 nm in diameter

References

“Large-Angle Convergent-Beam Electron Diffraction Applications to Crystal Defects”, Morniroli, Taylor & Francis Publishing

http://escher.epfl.ch/eCrystallography
http://www.doitpoms.ac.uk
JEMS Electron Microscopy Software Java version
http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html
Web-based Electron Microscopy APplication Software (WebEMAPS)
http://emaps.mrl.uiuc.edu/

http://crystals.ethz.ch/icsd - access to crystal structure file database
Can download CIF file and import to JEMS