Electron Microscopy

4. TEM

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

Image formation: contrasts,

Types of electron microscopes

Transmission Electron Microscope

Scanning Electron Microscope

What you see is what the detector sees !!!
Typical TEM

Electron Source
Electron Beam
Sample
Projector Lenses
Viewing Screen
Condenser Lenses
Objective Lens
Objective Aperture

Signals from a thin sample

Backscattered electrons (BSE)  secondary electrons (SE)
Auger electrons
Visible light
Characteristic X-rays
1-100 nm
Specimen

electron-hole pairs
“absorbed” electrons

elastically scattered electrons
Bremstrahlung X-rays
inelastically scattered electrons

Autumn 2009
Experimental Methods in Physics
Marco Cantoni
Interaction of high energetic electrons with matter

- Elastic scattering in amorphous specimens
- Elastic scattering in crystalline specimens
- Inelastic scattering at specimen atoms

- 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)
- Dark field image of differently ordered domains: Diffraction contrast
- High-resolution image: Image contrast due to interference between transmitted and diffracted beam

- STEM-DF
- EDS, element maps
- STEM-DF

Element distribution maps of Nb3Sn superconductor
Two basic operation modes
**Diffraction <-> Image**

**Diffraction Mode**
- Specimen
- Remove aperture
- SAD aperture
- Intermediate image 1
- Change strength
- Second intermediate image
- Fixed strength
- Diffraction pattern
- Screen

**Image Mode**
- Objective lens
- Objective aperture (back focal plane)
- Intermediate lens
- Projector lens
- Final image

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**Projector lens system, TEM**

- **TEM:**
- Intermediate and projector lenses
  - Projection of the back focal plane to the screen “diffraction” mode
  - Projection of the image plane to the screen “image” mode (haute resolution)
Not to forget....!
the specimen preparation
electron transparency: sample thickness < 100nm
standard sample holders: disc shaped samples with 3mm diameter

Cross-section preparation

- Mechanical polishing down to a thickness of 30 mm
- Ion milling (4kV Ar ions) until perforation

1 – 1.5 days

- Gluing face-to-face
- Cutting a slice
- Polishing down to 30mm
- Copper washer for mechanical stability
Plane-view preparation (also bulk)

Thick film of PZT (Pt bottom electrode)

- cutting a disk of 3mm (ultrasonic cutter)
- polishing down to 30mm (copper washer for mechanical stability)
- Ion milling until perforation

Lucky if you have powders!
preparation time: 15-30Min.

Optical microscope
reflected light

Cupper grid covered with carbon film

Optical microscope
transmitted light
preparation time: 15-30Min.

(K,Nb)TaO$_3$
Nano-rods

Shape, lattice parameters, defects, lattice planes

(K,Nb)O$_3$
Nano-rods

Bright field image

Dark field image

Diffraction pattern

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
  \[ \Rightarrow \text{diffraction from atomic planes (e.g. } 200 \text{ kV } e^-, \lambda = 0.0025 \text{ nm)} \]

• electrons interact very strongly with matter \( \Rightarrow \) strong diffraction intensity
  (can take patterns in seconds, unlike X-ray diffraction)

  • spatially-localized information
  \( (\geq 200 \text{ nm for selected-area diffraction; } \text{2 nm possible with convergent-beam electron diffraction}) \)

  • 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

BaTiO$_3$ nanocrystals (Psaltis lab)
Insert selected area aperture to choose region of interest

Take selected-area diffraction pattern

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
Scattering theory - Atomic scattering factor

Consider coherent elastic scattering of electrons from atom

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

Atomic scattering factor

\[ f(\theta) = \left(1 + \frac{E_0}{m_0 c^2}\right) \left(\frac{\lambda}{\sin \frac{\theta}{2}}\right)^2 (Z - f_x) \]

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: ½,½,½
Structure = lattice +motif => Start applying motif to each lattice point
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>(\beta, \gamma = 90^\circ)</td>
<td>(a \neq b \neq c)</td>
<td>(a \neq c)</td>
<td>(a, \beta, \gamma \neq 90^\circ)</td>
</tr>
</tbody>
</table>

Diagrams from 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 x 4 = 28) possibilities

Diagrams from www.Wikipedia.org

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Defining Symmetry (rotation or inversion)</th>
<th>Conventional Unit Cell</th>
<th>Conventional Lattice Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>4 triads</td>
<td>$a = b = c$</td>
<td>P, I, F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1 hexad</td>
<td>$a = b \neq c$</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>Trigonal</td>
<td>1 triad</td>
<td>$a = b \neq c$</td>
<td>P, R</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>1 tetrad</td>
<td>$a = b \neq c$</td>
<td>P, I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3 diads</td>
<td>$a \neq b \neq c$</td>
<td>P, C, I, F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>1 diad</td>
<td>$a \neq b \neq c$</td>
<td>P, C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = \gamma = 90^\circ, \beta \geq 90^\circ$</td>
<td></td>
</tr>
<tr>
<td>Triclinic</td>
<td>-</td>
<td>$a \neq b \neq c$</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha \neq \beta \neq \gamma$</td>
<td></td>
</tr>
</tbody>
</table>
**Crystallography - lattice vectors**

A lattice vector is a vector joining any two lattice points.
Written as linear combination of unit cell vectors \( a, b, c \):

\[ \mathbf{t} = U \mathbf{a} + V \mathbf{b} + W \mathbf{c} \]

Also written as: \( \mathbf{t} = [U \ V \ W] \)

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:

- \( (1 \ 0 \ 0) \)
- \( (0 \ 2 \ 2) \)
- \( (1 \ 1 \ 1) \)

**Lattice planes and symmetry**

Lattice planes in a crystal related by the crystal symmetry

For example, in cubic lattices the 3-fold rotation axis on the \([1 \ 1 \ 1]\) body diagonal relates the planes \((1 \ 0 \ 0), (0 \ 1 \ 0), (0 \ 0 \ 1)\):

Set of planes \(\{1 \ 0 \ 0\} = (1 \ 0 \ 0), (0 \ 1 \ 0), (0 \ 0 \ 1), (-1 \ 0 \ 0), (0 \ -1 \ 0), (0 \ 0 \ -1)\)
**Diffraction theory - Bragg law**

Path difference between reflection from planes distance $d_{hkli}$ apart = $2d_{hkli}\sin\theta$

$\Rightarrow$ Bragg law:

$n\lambda = 2d_{hkli}\sin\theta$

Electron diffraction: $\lambda \sim 0.001$ nm

therefore: $\lambda << d_{hkli}$

$\Rightarrow$ small angle approximation: $n\lambda \approx 2d_{hkli}\sin\theta$

Reciprocity: scattering angle $\theta \sim d_{hkli}^{-1}$

**Loi de Bragg**

- $2\sin\theta \ d_{hkli} = n \ \lambda$
- $d_{hkli} = n \ \lambda/2 \ \sin\theta$

**Diffraction élastique**

$|k| = |k'|$

Arrangement périodique d’atomes dans l’espace (réelle): $g$ : vecteur dans l’espace réciproque
**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

2 x 2 unit cells

Note reciprocal relationship: smaller plane spacing \(\Rightarrow\) larger indices \((h k l)\)

& greater scattering angle on diffraction pattern from (0 0 0) direct beam
The reciprocal lattice

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

Real lattice vector: \( \mathbf{r}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \)

Reciprocal lattice vector: \( \mathbf{r}^* = m_1 \mathbf{a}^* + m_2 \mathbf{b}^* + m_3 \mathbf{c}^* \)

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

For scattering from plane \((h k l)\) the diffraction vector:
\[
\mathbf{g}_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*
\]
Plane spacing:
\[
d_{hkl} = \frac{1}{|\mathbf{g}_{hkl}|}
\]

Ewald Sphere

- A vector in reciprocal space:
- \( \mathbf{g}_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \)
- diffraction if:
  \( k_0 - k' = g \) and \( |k| = |k'| \)
- Bragg and elastic scattering

Bragg: \( d_{hkl} = \lambda / 2 \sin \theta = 1/|g| \)

Construction of EWALD sphere:
Intersection of two geometric locations:
Reciprocal space AND Ewald sphere
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
$\Rightarrow$ sphere circumference almost flat

Elastic scattering:
$$|k| = |k'|$$

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

Assume reciprocal lattice points are infinitely small

With crystal oriented on zone axis, Ewald sphere may not intersect reciprocal lattice points

However, we see strong diffraction from many planes in this condition

Because reciprocal lattice points have size and shape!

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.
**Intensity in the electron diffraction pattern**

**Structure factor**

Amplitude of a diffracted beam:

\[ A_{\text{cell}} = \frac{e^{2\pi i \mathbf{K} \cdot \mathbf{r}}}{r} \sum_{i} f_i(\theta) e^{2\pi i \mathbf{K} \cdot \mathbf{r}_i} \]

\( \mathbf{r}_i \): position of each atom \( \Rightarrow \mathbf{r}_i = x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c} \)

\( \mathbf{K} = \mathbf{g} \):

\[ \mathbf{K} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \]

Define structure factor:

\[ F_{hkl} = \sum_{i} f_i e^{2\pi i (hx_i + ky_i + lz_i)} \]

Intensity of reflection:

\[ I_{hkl} \propto |A_{\text{cell}}|^2 \propto F_{hkl} \cdot F_{hkl}^* \]

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** Forbidden reflections**

Consider FCC lattice with lattice point coordinates:

\(0,0,0; \quad \frac{1}{2},\frac{1}{2},0; \quad \frac{1}{2},0,\frac{1}{2}; \quad 0,\frac{1}{2},\frac{1}{2}\)

Calculate structure factor for (0 1 0) plane (assume single atom motif):

\[ F_{hkl} = \sum_{i} f_i e^{2\pi i (hx_i + ky_i + lz_i)} \]

\[ F_{010} = f \sum_{i} e^{2\pi i (hx_i + ky_i + lz_i)} \]

\( \Rightarrow F_{010} = f [e^0 + e^{2\pi} + e^0 + e^{2\pi}] = f [2 - 2] = 0 \)

\[ F_{020} = f [e^0 + e^{2\pi} + e^0 + e^{2\pi}] = f [2 + 2] = 4f \]
Forbidden reflections

Cu$_3$Au - like FCC Au but with Cu atoms on face-centred sites.
What happens to SADP if we gradually increase Z of Cu sites until that of Au (to obtain FCC Au)?

Diffraction pattern on [0 0 1] zone axis:

Patterns simulated using JEMS
Extinction rules

Face-centred cubic: reflections with mixed odd, even $h, k, l$ absent:

$$F_{hkl} = f_i \left[ 1 + e^{\pi i (h+k)} + e^{\pi i (h+l)} + e^{\pi i (k+l)} \right]$$

Body-centred cubic: reflections with mixed odd, even $h, k, l$ absent:

$$F_{hkl} = f_i \left[ 1 + e^{\pi i (h+k+l)} \right]$$

Reciprocal lattice of FCC is BCC and vice-versa

Selected-area diffraction phenomena
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]_{ZnO} // [0 -1 0]_{sapphire}

Planes:
c-plane_{ZnO} // c-plane_{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 MnZnO₃ - which XRD failed to observe!
**Ring diffraction patterns**

Larger crystals => more “spotty” patterns

Example: ZnO nanocrystals ~20 nm in diameter

**Kikuchi lines**

Inelastic scattering event scatters electrons in all directions inside crystal

Some scattered electrons in correct orientation for Bragg scattering => cone of scattering

Cones have very large diameters => intersect diffraction plane as ~straight lines
Kikuchi lines

Position of the Kikuchi line pairs of (excess and deficient) very sensitive to specimen orientation

Lower-index lattice planes => narrower pairs of lines

Convergent beam electron diffraction

A

Small $2\alpha$

Thin specimen

Kossel-Möllmann pattern

B

Medium $2\alpha$

C

Large $2\alpha$

Kossel pattern

D

E

F
Convergent beam electron diffraction

Instead of parallel illumination with selected-area aperture, CBED uses highly converged illumination to select a much smaller specimen region.

\[ 2\alpha \]

Small illuminated area =>
no thickness and orientation variations

There is dynamical scattering, but it is useful!

Can obtain disc and line patterns
“packed” with information:

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