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Introduction to
electron diffraction

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
  (\( \approx 200 \) 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)
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
Basic crystallography & symmetry

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)
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
Extend lattice further in to space

Excerpt from Bruno Munari’s “Zoo”, First Chronical Books
Introduction to symmetry

As well as having translational symmetry, nearly all crystals obey other symmetries - i.e. can reflect or rotate crystal and obtain exactly the same structure.

Symmetry elements:

- Mirror planes:
- Rotation axes:
- Centre of symmetry or inversion centre:

Inversion axes: combination of rotation axis with centre of symmetry

Example - Tetragonal lattice: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$

Anatase TiO$_2$ (body-centred lattice) view down [0 0 1] (z-axis):

- Identify mirror planes
- Identify rotation axis: 4-fold = defining symmetry of tetragonal lattice!
More defining symmetry elements

Cubic crystal system: $a = b = c, \alpha = \beta = \gamma = 90^\circ$
View down body diagonal (i.e. $[1 1 1]$ axis)
Choose Primitive cell (lattice point on each corner)
Identify rotation axis: 3-fold (triad)
Defining symmetry of cube: four 3-fold rotation axes (not 4-fold rotation axes!)

More defining symmetry elements

Hexagonal crystal system: $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Primitive cell, lattice points on each corner; view down z-axis - i.e.$[1 0 0]$
Draw $2 \times 2$ unit cells
Identify rotation axis: 6-fold (hexad) - defining symmetry of hexagonal lattice
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

Triclinic
\[ \alpha, \beta, \gamma \neq 90^\circ \]

Monoclinic
\[ \alpha \neq 90^\circ, \beta, \gamma = 90^\circ \]

Orthorhombic
\[ a \neq b \neq c \]

Tetragonal
\[ a \neq c \]

Rhombohedral
\[ a, \beta, \gamma \neq 90^\circ \]

Hexagonal
\[ a \neq c \]

Cubic
\[ a \]

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

A lattice vector is a vector joining any two lattice points. Written as a 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:

- (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)
Weiss Zone Law

If the lattice vector \([U \, V \, W]\) lies in the plane \((h \, k \, l)\) then:

\[ hU + kV + lW = 0 \]

Electron diffraction:

Electron beam oriented parallel to lattice vector called the “zone axis”

Diffracting planes must be parallel to electron beam
- therefore they obey the Weiss Zone law\(^*\)

\(^*\)at least for zero-order Laue zone

Electron diffraction theory
Optics: scattering from slits

In zone-axis condition our TEM optics and sample are similar to grating in Fraunhofer far-field diffraction geometry.

Incident plane wave (far-field) on diffraction grating =>
Periodic array of spots in diffraction plane

\[ d \sin \theta = m \lambda \]
where \( m = 0, \pm 1, \pm 2, \ldots \)
m is the order of the principal maxima

Optics: scattering from slits – video

Video: From one to many slits
**Diffraction theory – Bragg law**

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

\[
\Rightarrow \text{Bragg law:} \\
n\lambda = 2d_{hkl}\sin\theta
\]

Electron diffraction: \(\lambda \sim 0.001\) nm 
then therefore: \(\lambda \ll d_{hkl}\) 
\[\Rightarrow\] small angle approximation: \(n\lambda \approx 2d_{hkl}\theta\)

Reciprocity: scattering angle \(\theta \propto d_{hkl}^{-1}\)

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**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
Also note Weiss Zone Law obeyed in indexing \((hU + kV + lW = 0)\)

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Scattering from non-orthogonal crystals

With scattering from the cubic crystal we can note that the diffracted beam for plane \((1 \ 0 \ 0)\)
is parallel to the lattice vector \([1 \ 0 \ 0]\): makes life easy

However, not true in non-orthogonal systems - e.g. hexagonal:

\((1 \ 0 \ 0)\) planes

\([1 \ 0 \ 0]\]

**\(g_{100}\)**

\(\Rightarrow\) care must be taken in reciprocal space!
For transmitting object $t(x,y)$ can be proved that diffraction pattern in $X, Y$ plane has amplitude:

$$A(u, v) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} t(x, y) e^{-i2\pi(ux+vy)} dxdy$$

This is the Fourier transform of the object

$\Rightarrow$ TEM diffraction pattern is Fourier transform of the sample

Each diffraction spot contains frequency information on the plane that creates it

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**Basic properties of Fourier transform**

- **Linearity:**
  \[
  FT\{\alpha g(x)\} = \alpha FT\{g(x)\} = \alpha G(u)
  \]
  \[
  FT\{\alpha g(x) + \beta h(x)\} = \alpha FT\{g(x)\} + \beta FT\{h(x)\} = \alpha G(u) + \beta H(u)
  \]

- **Shift:**
  \[
  FT\{g(x - a)\} = e^{-2i\pi ua} FT\{g(x)\}
  \]
  \[
  I(u) = (e^{2i\pi ua} FT\{g(x)\}) \cdot (e^{-2i\pi ua} FT\{g(x)\}) = G^*(u) \cdot G(u)
  \]

- **Reciprocity:**
  \[
  FT\{g(ax)\} = \frac{1}{|a|} G\left(\frac{u}{a}\right)
  \]

- **Convolution:**
  \[
  FT\{g(x)*h(x)\} = FT\{g(x)\} \otimes FT\{h(x)\} = G(u) \otimes H(u)
  \]

- **Conservation of angle**
The reciprocal lattice

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

**Real lattice vector:** \( r_n = n_1a + n_2b + n_3c \)

**Reciprocal lattice vector:** \( r^* = m_1a^* + m_2b^* + m_3c^* \)

where:

\[ a^* . b = a^* . c = b^* . c = b^* . a = c^* . a = c^* . b = 0 \]

\[ a^* . a = b^* . b = c^* . c = 1 \]

i.e. \( a^* = (b^* . c)/V_C \) \( V_C \): volume of unit cell

For scattering from plane \((h k l)\) the diffraction vector:

\[ g_{hkl} = h a^* + k b^* + l c^* \]

**Plane spacing:** \( d_{hkl} = \frac{1}{|g_{hkl}|} \)

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The Ewald sphere

**k_i:** incident beam wave vector

**k_D:** diffracted wave vector

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 => sphere circumference almost flat
**Ewald sphere for Bragg scattering (X-ray)**

Schematic for X-ray: large $\lambda \Rightarrow$ small radius $1/\lambda$

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**Exercise:** prove that Bragg’s law is met when sphere intersects reciprocal lattice node

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**Ewald sphere in 2-beam condition**

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

Fourier transforms and reciprocal lattice

Real lattice is not infinite, but is bound disc of material with diameter of selected area aperture and thickness of specimen - i.e. thin disc of material.

$$\text{Real lattice} \times \text{Specimen} = \text{Reciprocal lattice}$$

2 lengths scales in reciprocal space!
Ewald sphere intersects Relrods

Relrod shape

Shape (e.g. thickness) of sample is like a “top-hat” function

Therefore shape of Relrod is: \((\sin(x)/x)^2\)

Can compare to single-slit diffraction pattern with intensity:

\[ I \propto \left(\frac{\sin x}{x}\right)^2 \]
Relrod shape

Intensity in the electron diffraction pattern
Tilted slightly off Bragg condition, intensity of diffraction spot much lower
Introduce new vector \( s \) - “the excitation error” that measures deviation from exact Bragg condition
Tilting effect on SADP

- Zone axis diffraction pattern: Ewald sphere is tangential to zero-order Laue zone of reciprocal lattice

Quiz: what changes occur in SADP when tilt the crystal a little (e.g. 1–3°)?

- Loci of intersections of Ewald sphere with relrods hardly changes, therefore the projected positions of reflections in the SADP do not move.

- However, the excitation errors for the relrods change a lot, so reflection intensities also change significantly.
Quiz: graphite $\rightarrow$ graphene

Diffraction pattern of graphite on [0 0 1] zone axis:

What happens to relrod shape as graphite thinned $\rightarrow$ graphene?
How will this affect diffraction spot intensity for tilted sample?


Zone axis diffraction and symmetry

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
Symmetry quiz

• Defining symmetry of cubic material are four 3-fold rotation axes (triads) on the \( <1\ 1\ 1> \) body diagonals.

• Inversion symmetry element is combination of rotation axis with centre of symmetry (e.g. \( \bar{2}, \bar{3}, \bar{6} \)).

• FCC Al has space group \( \text{Fm}\bar{3}m \). If we take SADP on \([1\ 1\ 1]\) zone axis what symmetry does ZOLZ pattern have?

• In ZOLZ lose 3rd dimension of information (i.e. have 2D projection). Therefore \( \bar{3} \) symmetry “flattened” to give 6-fold symmetry in \([1\ 1\ 1]\) SADP ⇒ loss of higher symmetry

\[ \rightarrow \text{Friedel’s Law: } I_{hkl} = I_{\bar{h}\bar{k}\bar{l}} \]

Elastic scattering theory
Electron diffraction: Elastic scattering

Assumptions $\implies$ elastic scattering

$\vec{k}_i$: incident wavevector

$\vec{k}_g$: scattered wavevector

$\vec{g}$: reciprocal lattice vector

$\vec{s}_g$: deviation from exact Bragg condition

1. Energy conservation: $|\vec{k}_g| = |\vec{k}_i|$.
2. Momentum transfer: $\vec{k}_i + \vec{g} + \vec{s}_g = \vec{k}_g$.

Scattering theory - Atomic scattering factor

Consider coherent elastic scattering of electrons from isolated atom

Differential elastic scattering cross section:

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

Atomic scattering factor

$$f(\theta) = \left(1 + \frac{E_\theta}{m_0 c^2}\right) \left(\frac{\lambda}{\sin \frac{\theta}{2}}\right) (Z - f_x)$$
Structure factor

Amplitude of a diffracted beam from a unit cell:

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

\( r_i \): position of each atom \( r_i = xi a + yi b + zi c \)

\( K = g \):

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

Define structure factor:

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

Intensity of reflection:

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

Note \( f_i \) is a function of \( s \) and \((h k l)\)

Forbidden reflections

Consider FCC lattice with lattice point coordinates:

\( 0,0,0; \ 1/2,1/2,0; \ 1/2,0,1/2; \ 0,1/2,1/2 \)

Calculate structure factor for plane \((h k l)\) (assume single atom motif):

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

where:

\[ e^{i\theta} = \cos \theta + i \sin \theta \]

For atomic structure factor \( f \) find:

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

Since:

\[ e^{n\pi i} = (-1)^n \]

For \( h k l \) all even or all odd:

\[ F_{hkl} = 4f \]

For \( h k l \) mixed even and odd:

\[ F_{hkl} = 0 \]
Extinction rules

Face-centred cubic: reflections with mixed odd, even \( h, k, l \) absent:

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

Body-centred cubic: reflections with \( h + k + l = \text{odd} \) absent:

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

Reciprocal lattice of FCC is BCC and vice-versa

Theory of electron diffraction in TEM – Resources

- “Transmission Electron Microscopy” by Williams and Carter Chapters 3, 11, 12: Derivation of Bragg and Laue equations, introduction of diffraction vector \( g \), excitation error \( s \)

- “Large Angle Convergent Beam Electron Diffraction”, Morniroli (electronic on-line from EPFL library), Chapters 2 and 3: Elegant pictorial way to understand electron diffraction with parallel incident beam

- JEMS – Pierre Stadelmann’s electron microscopy simulation software: contact Prof. Stadelmann (CIME) to use