Diffraction

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Canadian Neutron Beam Centre

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- Crystal structures (crystal, unit cells, lattice planes, crystallographic notations, Miller indices, $d$-spacing, reciprocal lattice, Ewald sphere)
  - Bragg’s law

- Structure factors, Debye Waller factor, neutrons vs X-rays

- Data analysis – focus on powder diffraction
Applications of Powder Diffraction

chemistry

physics

engineering

life sciences

biochemistry

materials science

geological sciences

archeology
A material **crystalline** if the atoms or ions that compose it are arranged in a regular way (i.e., a crystal has internal order due to the periodic arrangement of atoms in three dimensions*).

Note: this definition is valid for most crystalline materials, but quasicrystals, 1D or 2D–ordered, incommensurate structures are also known.
Content (basis)

- Na atom
- NaCl molecule
- $C_{60}$ molecule
- nucleosome macromolecule

Crystal

- Unit Cell - Basis
Crystal structure is described by a building block called the **unit cell** and atomic coordinates inside the cell.

Three dimensional stacking of the unit cell forms the crystal.

**Unit cell**

a box with 3 sides (a, b and c) and 3 angles (α, β and γ)

Location of atoms inside the unit cell are given by atomic coordinates: \((x_i, y_i, z_i)\), fractions of a, b and c lattice constants.
• There are many possibilities to choose a unit cell

• The choice of the conventional unit cell is a matter of convenience; *it should be the smallest and simplest, but have the highest possible symmetry*
### Wyckoff Positions of Group 225 (Fm-3m)

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Site symmetry</th>
<th>Coordinates</th>
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<tbody>
<tr>
<td>132</td>
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<td>4mm</td>
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<td>c</td>
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<td>(1/4,1/4,1/4) + (1/4,1/4,1/4) + (1/4,1/4,1/4) + (1/4,1/4,1/4)</td>
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</tr>
<tr>
<td>4</td>
<td>b</td>
<td>m-3m</td>
<td>(1/2,1/2,1/2)</td>
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<tr>
<td>4</td>
<td>a</td>
<td>m-3m</td>
<td>(0,0,0)</td>
</tr>
</tbody>
</table>

Some basic crystallography concepts

...so we can read this!

or Bilbao Crystallographic server
http://www.cryst.ehu.es/
### The 7 Crystal Systems

**Shape of the unit cell**

<table>
<thead>
<tr>
<th>System</th>
<th>u.c. symmetry</th>
<th>unit cell parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic</td>
<td>m-3m</td>
<td>( a = b = c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>hexagonal</td>
<td>6/mmmm</td>
<td>( a = b \neq c ) ( \alpha = \beta = 90^\circ \gamma = 120^\circ )</td>
</tr>
<tr>
<td>trigonal*</td>
<td>3/mmm</td>
<td>( a = b \neq c ) ( \alpha = \beta = 90^\circ \gamma = 120^\circ )</td>
</tr>
<tr>
<td>tetragonal</td>
<td>4/mmm</td>
<td>( a = b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>mmm</td>
<td>( a \neq b \neq c ) ( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>monoclinic</td>
<td>2/m</td>
<td>( a \neq b \neq c ) ( \alpha = \gamma = 90^\circ \beta \neq 90^\circ )</td>
</tr>
<tr>
<td>triclinic</td>
<td>-1</td>
<td>( a \neq b \neq c ) ( \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
</tr>
</tbody>
</table>

* also described as rhombohedral: \( a = b = c \) \( \alpha = \beta = \gamma \neq 90^\circ \)
Symmetry Elements in 2D

- **Notation:** $a, b, c, n, \text{ or } d$
  - Rotation by $360^\circ/3$
  - Notation: $3$

- **Notation:** $m$
  - Mirror plane
  - Rotation by $360^\circ/2$
  - Notation: $2$

- **Glide plane**
  - Rotation by $360^\circ/2$
  - Notation: $2$

- **2-fold rotation axis**
  - Rotation by $360^\circ/6$
  - Notation: $6$

- **3-fold rotation axis**
  - Rotation by $360^\circ/4$
  - Notation: $4$
Symmetry elements in 3D

2D symmetry elements

Screw axis = combination of rotation and translation

Notation: \( N_k \) describes a N-fold rotation followed by translation parallel to the axe of rotation by \( k/N \) of the unit cell.

Ex: \( 2_1 \) is a 180° (twofold) rotation followed by a translation of 1/2 of the lattice vector
Bravais Lattices

**CUBIC**
\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**TETRAGONAL**
\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**ORTHORHOMBIC**
\[ a \neq b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**HEXAGONAL**
\[ a = b \neq c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

**MONOCLINIC**
\[ a \neq b \neq c \]
\[ \alpha = \gamma = 90^\circ \]
\[ \beta \neq 120^\circ \]

**TRICLINIC**
\[ a \neq b \neq c \]
\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

---

**4 Types of Unit Cell**

- **P** = Primitive
- **I** = Body-Centred
- **F** = Face-Centred
- **C** = Side-Centred

---

**7 Crystal Classes**

→ **14 Bravais Lattices**
It is often necessary to be able to specify certain directions and planes in the crystal:
- determine the necessary orientation so that the diffraction occurs
- many material may have anisotropic properties

Direction and planes are described using a set of three integers – Miller indices (hkl)
Miller indices \((h \ k \ l)\) = three lattice points used to identify orientation of a set of parallel planes of atoms within a crystal structure.

\((h \ k \ l)\) plane intercepts crystallographic axes \(a\), \(b\) and \(c\) at

\[
\frac{a}{h}, \frac{b}{k}, \frac{c}{l}
\]

where \(h\), \(k\), and \(l\) are relatively prime integers

\[
\frac{1}{h}, \frac{1}{k}, \frac{1}{l}
\]

fractional intercepts

Miller indices

\(h, k, l\)

We will come back to this

what an index=0 means?

reciprocals of fractional intercepts
Cu

Space group: \textit{Fm-3m} (#225)

Lattice parameter: cubic, $a = 3.6147$ Å

Atoms: Cu in $4a (0, 0, 0)$

Wyckoff positions

4 atoms in the unit cell: one at the corners and 3 on the faces

\[ Fm\bar{3}m \]

• Face-centered cubic
• Mirror planes perpendicular to the $x$, $y$ and $z$ axes
• 3 folding along the [111] direction
• Mirror plane perpendicular to (110) plane
Bragg’s law in direct space (sample space)

**Diffraction:** neutrons interact with nuclei → scattered in all directions by every nucleus they encounter. Scattered waves from different nuclei travel different distances → acquire different phase → interfere as they add up!

**Constructive interference** of waves scattered from two lattice points A and D in adjacent planes:

\[ AB + AC = n\lambda \]

\[ 2d \sin \theta = n\lambda \]

Bragg’s Law
Reciprocal Lattice – Inverse and Orthogonal

3 vectors, \( \{a^*, b^*, c^*\} \), the normals to the Miller planes (100), (010), and (001), form the basis of the reciprocal lattice.

Mathematical definitions:

\[
\begin{align*}
  a^* &= 2\pi \frac{b \times c}{V}, \\
  b^* &= 2\pi \frac{c \times a}{V}, \\
  c^* &= 2\pi \frac{a \times b}{V} \\
  a &= 2\pi \frac{b^* \times c^*}{V^*}, \\
  b &= 2\pi \frac{c^* \times a^*}{V^*}, \\
  c &= 2\pi \frac{a^* \times b^*}{V^*}
\end{align*}
\]

Reciprocal space vectors define normals to planes in the direct space, meaning that a set of an infinite number of crystallographic planes in direct space is represented by a vector, or a single point at the end of the vector.
Relationship between direct and reciprocal dimensions

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Direct Dimension</th>
<th>Reciprocal Dimension</th>
<th>General Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic ($a \neq b \neq c$)</td>
<td>$a^* = \frac{1}{a}$</td>
<td>$\alpha^* = \alpha = 90^\circ$</td>
<td>$\frac{1}{\alpha \sin \beta \sin \gamma^*}$</td>
</tr>
<tr>
<td>Tetragonal ($a = b \neq c$)</td>
<td>$b^* = \frac{1}{b}$</td>
<td>$\beta^* = \beta = 90^\circ$</td>
<td>$\frac{1}{b \sin \gamma \sin \alpha^*}$</td>
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<tr>
<td>Cubic ($a = b = c$)</td>
<td>$c^* = \frac{1}{c}$</td>
<td>$\gamma^* = \gamma = 90^\circ$</td>
<td>$\frac{1}{c \sin \alpha \sin \beta^*}$</td>
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<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha^* = \alpha = 90^\circ$</td>
<td>$\frac{1}{a \sin \beta \sin \gamma}$</td>
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<tr>
<td></td>
<td>$\gamma = 120^\circ$</td>
<td>$\beta^* = \beta = 90^\circ$</td>
<td>$\frac{1}{b \sin \gamma \sin \alpha}$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$b^* = \frac{1}{b \sin \gamma}$</td>
<td>$\gamma^* = (180^\circ - \gamma) = 60^\circ$</td>
<td>$\frac{1}{c \sin \alpha \sin \beta}$</td>
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<tr>
<td></td>
<td>$c^* = \frac{1}{c}$</td>
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<td>$\beta^* = \beta = 90^\circ$</td>
<td>$\frac{1}{b \sin \gamma \sin \alpha^*}$</td>
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<td>$\gamma^* = (180^\circ - \gamma) = 60^\circ$</td>
<td>$\frac{1}{c \sin \alpha \sin \beta}$</td>
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<tr>
<td>Monoclinic</td>
<td>$a^* = \frac{1}{a \sin \beta}$</td>
<td>$\alpha^* = \alpha = 90^\circ$</td>
<td>$\frac{1}{b \sin \gamma \sin \alpha^*}$</td>
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<tr>
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<td>$b^* = \frac{1}{b}$</td>
<td>$\beta^* = 180^\circ - \beta$</td>
<td>$\frac{1}{c \sin \alpha \sin \beta^*}$</td>
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<tr>
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<td>$c^* = \frac{1}{c \sin \beta}$</td>
<td>$\gamma^* = \gamma = 90^\circ$</td>
<td>$\frac{1}{c \sin \alpha \sin \beta}$</td>
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Bragg’s law in reciprocal space

- \( k = \frac{2\pi}{\lambda} \)
- \( k = |\mathbf{k}_i| = |\mathbf{k}_f| \)
- \( Q = \frac{2\pi}{d} \)
- \( Q = 2k \sin \theta \)
Ewald Sphere
Geometrical interpretation of diffraction

- For Bragg diffraction $k_i = k_f$, and the $\Delta$ is an isosceles.

- Can construct a sphere (circle in projection) with $r = k = |k_i| = |k_f|$, touching the origin.

- Scattering condition: Constructive interference occurs when a reciprocal lattice point lays on the surface on the Ewald sphere.
The **number of scattered neutrons** as a function of \( Q \) is measured. The result is the scattering function \( S(Q) \) depending only on the properties of the sample.
A single crystal sample gives specific diffracted beams in $(\theta,\phi)$ as intersections (solutions) on the Ewald sphere.

A powder sample has grains in all orientations resulting in conic solutions to scattering for each $hkl$. 

Single Crystal vs. Powder Diffraction
Bragg law gives geometrical condition for diffraction to occur, but no quantitative information on the intensity of the diffracted beam.
Structure factors and Intensity

**Structure factors**

- complex numbers that express both the amplitude and the phase of scattering
- information about how the scattering centers are distributed within the lattice

\[
F_{hkl} = \sum_{j=1}^{N} f_j e^{i\varphi_j}
\]

\[
F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i(hx+ky+lz)}
\]

\(f_j\) (form factor) gives information about individual atoms

We measure **intensities**: \(I_{hkl} \propto |F_{hkl}|^2\)
Structure Factor – Systematic absences

\[ F_{hkl} = \sum_{j=1}^{N} f_j e^{i\varphi_j} \]

**Systematic absences**: complete cancelations due to symmetry

\[ F(110) = f_{\text{grey}} - f_{\text{cyan}} \]

\[ F(220): f_{\text{grey}} + f_{\text{cyan}} \]
**Monoatomic bcc system**

\[
F_{hkl} = be^{2\pi i(h0+k0+z0)} + be^{2\pi i(h/2+k/2+z/2)} = b + be^{\pi i(h+k+l)}
\]

- \(F_{hkl} = 0\) \(h + k + l = 2n + 1\)
- \(F_{hkl} = 2b\) \(h + k + l = 2n\)

**Ex.: Fe, V, Cr, Mo,**

**Fe**

- \(Im \bar{3}m\)
- \(a= 2.8665\text{Å}\)
- Atom position: \(2a (0,0,0)\)

**Systematic absences:** complete cancelations due to symmetry
Form factor, \( f(Q) \), is the Fourier Transform of the scattering density \( \rho(r) \) of an atom:

\[
f(Q) = \int_0^\infty \rho(r) \exp\{iQ \cdot r\} dr
\]

Neutrons are scattered by nucleus and the form factor is not angular dependent. The scattering density is in the form of a \( \delta \)-function.

Intensities drop off at high angles in an X-ray diffraction pattern because the form factor decreases. The scattering density is the electron cloud distribution.
Neutrons vs. X-ray:

- light elements scatter as strongly as the heavy elements
- contrast between neighboring atoms
Why different diffraction peak intensities?

\[ I_{hkl} = |F_{hkl}|^2 \times t(\theta)^2 \times M_{hkl} \times LP(\theta) \]

- Debye Waller factor
- Multiplicity factor (equivalent d-spacings)
- Lorentz & Polarization factor

Multiplicity factor – cubic system

- \{100\} family: (100), (010), (001), (-100), (0-10), (00-1) \[ M=6 \]
- \{110\} family: (110), (-110), (1-10), (-1-10), (101), (-101)
  (10-1), (-10-1), (011), (0-11), (01-1), (0-1-1) \[ M=12 \]
- in general: \( M(n_100)=6 \), \( M(n_1n_10)=12 \), \( M(n_1n_1n_2)=24 \), \( M(n_1n_1n_1)=8 \)
  \( M(n_1n_20)=24 \), \( M(n_1n_2n_3)=48 \)

Multiplicities are lower in lower symmetry systems.
Debye-Waller Factor
(Temperature Factor, Atomic Displacement Parameter)

- measure of atoms vibrations or displacement (static disorder) from the crystallographic site
- the more an atom vibrates, the more the diffracted intensity is decreased because the scattering power of the atom is smeared out

\[ t_j = \exp\left( -B_j \frac{\sin^2 \theta}{\lambda^2} \right) \]

Isotropic displacement parameter (Å²)

Note: The displacement parameter is not necessary isotropic. In the single crystal diffraction it is treated as anisotropic.

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scattering density

\[ \rho_{\text{xyz}} = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F_{hkl} \exp[-2\pi i (hx + ky + lz)] \]

structure factor

\[ F_{hkl} = \int_{\text{cell}} \rho_{\text{xyz}} \exp[2\pi i (xh + yk + zl)] \]
Information in the Diffraction Pattern

- **Peak Positions**
  - information about the translational symmetry, namely the size and shape of the unit cell

- **Peak Intensities**
  - tell you about the distribution of the scattering density inside the unit cell, namely where the atoms are located and sites occupancies

- **Peak Shapes and Widths**
  - information about deviations from a perfect crystal, i.e. small crystallite size, defects, microstrain

- **Background**
  - incoherent scattering; broad features signal the presence of amorphous components in the sample
Rietveld – a structural refinement method

**Whole pattern refinement method**, overcoming the problem of moderate overlapping of peaks

- **requires** a fairy good knowledge of the crystal structure (lattice parameters, space group, atom positions...) – a model
- **requires** good quality data up to large enough $d$-spacings
- **provides** a validation of the model
- **provides** accurate information about the atom positions, occupancies and thermal parameters (i.e. distances and angles between the atoms, bond lengths...) and quantitative phase analysis
Rietveld – a structural refinement method

\[ y_{i}^{\text{calc}} = s \sum_{hkl} LP_{hkl} |F_{hkl}|^2 \Gamma_{hkl}(2\theta_i) A_{i} + \text{bkgrd}_i \]

- compare the calculated and measured pattern
- minimize the difference between experimental and calculated diffraction pattern in a least squares refinement by varying a number of parameters; minimize:

\[ S_y = \sum_{j} w_j (y_j - y_{ij})^2 \]

\[ w_j = \frac{1}{y_j} \quad y_j = \text{observed intensity} \quad y_{ij} = \text{calculated intensity} \]
Evaluation of fitting quality (R-factors):

- **R-pattern, $R_p$:**
  \[ R_p = \frac{\sum |y_i - y_{ci}|}{\sum y_i} \]

- **R-weighted pattern, $R_{wp}$:**
  \[ R_{wp} = \left( \frac{\sum w_i (y_i - y_{ci})^2}{\sum w_i (y_i)^2} \right)^{1/2} \]

- **R-Bragg factor, $R_B$:**
  \[ R_B = \frac{\sum |I_{(hkl)}('obs') - I_{(hkl)}(calc)|}{\sum I_i('obs')} \]

- **R-expected, $R_e$:**
  \[ R_e = \left( \frac{(N - P)}{\sum w_i y_i^2} \right)^{1/2} \]

**Goodness of fit, $S$:**
\[ S = \frac{R_{wp}}{R_e} \]

*Visual inspection of the difference curve during the iteration process is critical in evaluating the model, the R-factors do not point to the origins of a possible problem!*