Neutron diffraction of crystalline materials

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Animations made with Blender 2.62
• Diffraction techniques (X-ray, neutron) are used to study thin films, engineering materials, liquids, polymers, crystalline solids.

• Whatever the technique used (Small Angle Scattering, Reflectometry, Strain-Scanning, conventional powder or single crystal Diffraction), all of these refer to the coherent elastic scattering of a beam of neutrons or X-rays.

• The keyword here is “elastic”, which means no energy is transferred between the beam and the sample, which in virtue of the conservation of energy means that the incident and scattered wave have the same wavelength.

• Of course, momentum is also a conserved quantity.
Scope of the lecture

- This lecture will focus on **Crystallography**, i.e. the study of crystalline solids.
- This form of matter is characterized by **infinite translational symmetry** (infinite periodic)
- We will study the periodic arrangement of atoms and magnetic moments *(magnetism :lecture from Prof. A. Wildes)*
Outline

- Direct lattices, symmetry
- Reciprocal system of axes and reciprocal lattice
- Fourier transform of a Dirac comb
- Nuclear scattering from crystalline materials.
- Unit-cell structure factors
- Ewald construction and different type of diffractometers
- Basics of Rietveld refinement
Periodic solids: Crystal systems

7 crystal systems:

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Type of axes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a = b = c$, $\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a = b = c$, $\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
</tbody>
</table>
Periodic solids: Centring translations

It is often inconvenient to work with primitive lattices, and one uses centered lattices:

<table>
<thead>
<tr>
<th>Centring type</th>
<th>Symbol</th>
<th>Translations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td><em>(One face centred)</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-centred</td>
<td>A</td>
<td>$x, y + 1/2, z + 1/2$</td>
</tr>
<tr>
<td>B-centred</td>
<td>B</td>
<td>$x + 1/2, y, z + 1/2$</td>
</tr>
<tr>
<td>C-centred</td>
<td>C</td>
<td>$x + 1/2, y + 1/2, z$</td>
</tr>
<tr>
<td>Body centred</td>
<td>I</td>
<td>$x + 1/2, y + 1/2, z + 1/2$</td>
</tr>
<tr>
<td>Face centred</td>
<td>F</td>
<td>$x + 1/2, y + 1/2, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$x, y + 1/2, z + 1/2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$x + 1/2, y, z + 1/2$</td>
</tr>
<tr>
<td>Rhombohedrally centred</td>
<td>R</td>
<td>$x + 2/3, y + 1/3, z + 1/3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$x + 1/3, y + 2/3, z + 2/3$</td>
</tr>
</tbody>
</table>
Bravais lattice

- Crystal classes + centring translations → 14 Bravais lattices
Symmetry operations

**Rotations (order \( n : 2\pi/n \))**

**Mirror planes (\( m \))**

**Roto-inversion (\( \bar{n} \))**

**Inversion point (\( \bar{1} \))**
Symmetry operations

Screw axis ($n_m$) is a compound operation of:
- rotation of order $n$
- translation of $1/m$

Example: screw axis $2_1$ along $a$

Glide plane is a compound operation of:
- mirror symmetry
- translation

Example: $c$ glide plane $\perp a$
Symmetry operations

\[
\begin{pmatrix}
    x' \\
    y' \\
    z'
\end{pmatrix} =
\begin{pmatrix}
    R_{11} & R_{12} & R_{13} \\
    R_{21} & R_{22} & R_{23} \\
    R_{31} & R_{32} & R_{33}
\end{pmatrix} \cdot
\begin{pmatrix}
    x \\
    y \\
    z
\end{pmatrix} +
\begin{pmatrix}
    t_1 \\
    t_2 \\
    t_3
\end{pmatrix}
\]

- Seitz notation: \((R|t)\)
- Symmetry contained in the coordinate triplet: for example \(2_1\) screw axis along \(b\): \(-x, y+1/2, -z\)

\[\Rightarrow\) Determinant +1 (proper) -1 (improper)\]
Combining the 14 Bravais lattices and all symmetry operations, leads to the 230 space groups.

http://it.iucr.org/
Space groups: Example

$P2_1/m$  $C^{2}_h$  $2/m$

Crystal class

Space group symbol

Monoclinic

Patterson symmetry $P12_1/m$

No. 11

UNIQUE AXIS $b$

Origin at $1_{2}$

Asymmetric unit $0 \leq x \leq 1; \ 0 \leq y \leq \frac{1}{2}; \ 0 \leq z \leq 1$

Symmetry operations

1. $I$
2. $2(0,\frac{1}{2},0)$, $0,0$
3. $I$, $0,0$
4. $m$, $x,\frac{1}{2},z$

Oxford Neutron School – Diffraction - 2013
### Space groups: Example

#### Generators selected

\[(1); \tau(0,0,0); \tau(0,1,0); \tau(0,0,1); (2); (3)\]

#### Positions

<table>
<thead>
<tr>
<th>Multiplicity, Wyckoff letter, Site symmetry</th>
<th>Coordinates</th>
<th>Reflection conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>[f]</td>
<td>[x, y, z]</td>
<td>General:</td>
</tr>
<tr>
<td>[e m]</td>
<td>[x, \frac{1}{2}, z]</td>
<td>(0k0: k = 2n)</td>
</tr>
<tr>
<td>[d]</td>
<td>[\frac{1}{2}, 0, \frac{1}{2}]</td>
<td>Special: as above, plus</td>
</tr>
<tr>
<td>[c]</td>
<td>[0, 0, \frac{1}{2}]</td>
<td>no extra conditions</td>
</tr>
<tr>
<td>[b]</td>
<td>[\frac{1}{2}, 0, 0]</td>
<td>(hkl: k = 2n)</td>
</tr>
<tr>
<td>[a]</td>
<td>[0, 0, 0]</td>
<td>(hkl: k = 2n)</td>
</tr>
</tbody>
</table>

High symmetry points
Reciprocal system

• First introduced by Gibbs:

*Vector analysis: A textbook for the use of students of mathematics and Physics by E. Wilson, New Haven Yale University Press, 1901*

How to express a vector in terms of three non-coplanar vectors?

\[ \vec{r} = \alpha \vec{a} + \beta \vec{b} + \gamma \vec{c} \]
Reciprocal system

\[ \vec{r} \cdot [\vec{b} \times \vec{c}] = \alpha \vec{a} \cdot [\vec{b} \times \vec{c}] + \beta \vec{b} \cdot [\vec{b} \times \vec{c}] + \gamma \vec{c} \cdot [\vec{b} \times \vec{c}] \]

\[ \alpha = \vec{r} \cdot \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \]

Equally, \[ \beta = \vec{r} \cdot \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \] and \[ \gamma = \vec{r} \cdot \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \]

\[ \alpha = \vec{r} \cdot \vec{a}^* \quad \beta = \vec{r} \cdot \vec{b}^* \quad \gamma = \vec{r} \cdot \vec{c}^* \]
Reciprocal system

\[ a^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \]
\[ b^* = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \]
\[ c^* = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \]

\[ \vec{a}_i \cdot a_j^* = \delta_{ij} \]

- For each system of three non-coplanar vectors, one can construct a dual system of vectors, also non-coplanar, called the reciprocal system.

- The reciprocal of a reciprocal system is the direct axis itself.

- Reciprocal and direct systems are equal only for an orthonormal unit lattice.

- Condition (2) is necessary and sufficient for \( \{a_j^*\} \) to be reciprocal system of \( \{a_j\} \).
Reciprocal lattice

Let's construct a periodic lattice from the \( \{a_i\} \) and \( \{a_i^*\} \) systems of vectors called \( \mathbf{R} \) and \( \mathbf{G} \).

The scalar product between any vector \( \mathbf{R}_i \) in \( \mathbf{R} \) and any vector \( \mathbf{G}_j \) in \( \mathbf{G} \) is an integer!
Fourier transform of a Dirac comb

\[ \text{comb}_a(x) = \sum_{n=-\infty}^{\infty} \delta(x-na) \]

Fourier transform:

\[ \int \sum_{n=-\infty}^{\infty} \delta(x-na) e^{-ikx} \, dx = \sum_{n=-\infty}^{\infty} \int \delta(x-na) e^{-ikx} \, dx = \sum_{n=-\infty}^{\infty} e^{-ikna} \]

\[ \sum_{n=-\infty}^{\infty} e^{-ikna} = \frac{2\pi}{a} \sum_{h=-\infty}^{\infty} \delta\left( k - \frac{2\pi}{a} \right) \]
Fourier transform of Dirac comb in 3D

Let \( L \) be a direct lattice of volume \( V \). Consider a Dirac comb of this lattice (\( \delta \) function at every lattice point)

\[
L(\vec{r}) = \text{comb}_{abc}(\vec{r}) = \sum_{\vec{R}_n \in R} \delta^3(\vec{r} - \vec{R}_n)
\]

**Fourier transform:**

\[
\text{FT}(L(\vec{r})) = \int \sum_{\vec{R}_n \in R} \delta^3(\vec{r} - \vec{R}_n) e^{-i\vec{k} \cdot \vec{r}} \, d\vec{r} = \sum_{-\vec{R}_n \in R} e^{-i\vec{k} \cdot \vec{R}_n}
\]

What is the set of \( k \) vectors that ensure that this sum is non-zero?

\[
\sum_{-\vec{R}_n \in R} e^{-i\vec{k} \cdot \vec{R}_n} = \left(\frac{2\pi}{V}\right)^3 \sum_{\vec{G}_j \in G} \delta^3(\vec{k} - 2\pi \vec{G}_j)
\]

Fourier transform of a Bravais lattice of Dirac functions is a lattice of Dirac functions centred at the reciprocal lattice points!
Reciprocal lattice

From now on, we shall use the alternate definition:

\[
\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \quad \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} \quad \vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot [\vec{b} \times \vec{c}]} 
\]

\[
\vec{a}_i \cdot \vec{a}_j^* = 2\pi \delta_{ij} 
\]

A vector of the reciprocal lattice \( G \) will usually be written as:

\[
\vec{G} = h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^* 
\]

\( h, k, l \) are named the Miller indices.
Scattering by a potential $V(r)$

\[ \frac{dn}{d\Omega} = \Phi d\Omega \sigma(\theta, \phi) \]

- $\sigma$ has the dimension of a surface
- Usually in barns=$10^{-24}$ cm$^2$
**Nuclear scattering**

- Nuclear scattering mediated by the strong force, extremely short range (fm=1.10^{-15} m).

- Neutron wavelength much larger (Å=1.10^{-10} m), can not probe internal nuclear structure: scattering is isotropic.

- The interaction between the neutron and the atomic nucleus is represented by the Fermi pseudo-potential, a **scalar field** that is zero except very close to the nucleus (δ function).

\[
V(r) = \frac{2\pi \hbar^2}{m_r} a \delta^3(r)
\]
Scattering lengths

<table>
<thead>
<tr>
<th>H</th>
<th>Li</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Mn</th>
<th>Zr</th>
<th>Cs</th>
</tr>
</thead>
</table>

![Graph showing scattering lengths vs atomic weight](image)

- **X-rays**
  - H: Small
  - Li: Small
  - C: Small
  - O: Small
  - S: Medium
  - Mn: Large
  - Zr: Medium
  - Cs: Large

- **Neutrons**
  - H: Small
  - Li: Small
  - C: Medium
  - O: Medium
  - S: Large
  - Mn: Large
  - Zr: Medium
  - Cs: Large
Scattering by a potential $V(r)$

The wavefunction at a spatial position $r =$ \textit{sum of transmitted and scattered spherical wavefunction}:

$$\psi = e^{i \vec{k} \cdot \vec{r}} + f_k(\theta, \varphi) \frac{e^{i k \cdot r}}{r}$$
Reminder Born approximation

- In the quantum mechanical treatment of scattering by a central potential, the stationary states $\varphi(r)$ verify:

$$[\Delta + k^2] \varphi(r) = \frac{2\mu}{\hbar^2} V(r) \varphi(r)$$

- In the integral equation of scattering, the stationary wave-function is written:

$$\varphi_{scat}^k(r) = e^{ik_r \cdot r} + \frac{2\mu}{\hbar^2} \int G_+(r-r') V(r') \varphi_{scat}^k(r') d^3r'$$

- One can expend iteratively this expression (Born expansion). If the potential is weak, one can limit the expansion to the first term, this is the first Born approximation.

In this case the scattering amplitude is related to the Fourier transform of the potential function:

$$I = |f_k(\theta, \phi)|^2 = |V(\vec{Q})|^2$$

Quantum Mechanics,
Claude Cohen-Tannoudji et al., Vol 2, Chapt 8
Conventions for this lecture

\[ f_k(\theta, \phi) \propto -\int V(r) e^{-iQr} d^3r \]

\( V(r) \) is positive for a repulsive potential

\[ \vec{Q} = \vec{k}_f - \vec{k}_i \] = momentum transferred from the crystal to the neutron

\[ \| \vec{k}_f \| = \| \vec{k}_i \| \] (elastic scattering)
Nuclear scattering

Imagine a crystal with only one atom per unit-cell. For which $Q$, is the intensity non zero?

$V(r)$ is a 3D Dirac comb!

During a diffraction experiment, a crystalline material can only provide discrete momentum kicks!
Diffraction condition in real and reciprocal space

\[ 2d \sin(\theta) = n \lambda \]
Diffraction condition in real and reciprocal space

- Lattice planes (Miller planes) are indexed by the indices h,k,l.
- A (h,k,l) plane intercept the real crystal axes at a/h, b/k, l/c.
- $d_{hkl}$ is the distance to the origin.
- Diffraction can be considered as the coherent superposition of scattered waves from these the set of planes parallel to the (h,k,l) plane and equidistant.

- The reciprocal lattice vector $G = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is:
  - Perpendicular to the lattice plane (h,k,l)
  - Of length: $2\pi/d_{hkl}$
More than one atom/unit cell (1D example)

\[ V(x) = V_{UC}(x) \otimes \text{comb}_a(x) \]
Unit cell structure factor (approximation: no atomic displacement)

From the convolution theorem, the Fourier transform of a convolution is the product of the individual Fourier transforms:

$$V(Q) = FT(V(r)) = FT(V_{UC}(\vec{r}) \otimes comb_{abc}(\vec{r}))$$

$$= FT(V_{UC}(\vec{r})) \times FT(comb_{abc}(\vec{r}))$$

=0 unless Q is a reciprocal lattice vector

$$\sum_{atom \ j \in \ UC} b_j e^{-i \vec{Q} \cdot \vec{r}_j}$$
Nuclear from factor (X-ray comparison)

Neutrons

10-10 m

10-15 m

X-ray

f(Q)

1.0

Q

f(Q)

1.0

Q
Unit cell structure factor (including Atomic Displacement)

- There is one approximation in the previous slide: We haven't taken into account the effect of thermal motion, i.e. the fact that the atoms are not a fixed position but undergo very large displacements with respect to the Fermi length.
- Needs to consider a Quantum Harmonic Oscillator

\[ E_n = \hbar \omega \left( n + \frac{1}{2} \right) \]
Unit cell structure factor (including Atomic Displacement)

- Probability to find the atom displaces by \( u \) is related to the Boltzmann distribution:

\[
P(u) = \frac{\sum_n \psi_n^2(u) e^{-\frac{E_n}{kT}}}{\sum e^{-\frac{E_n}{kT}}} = \frac{1}{\sqrt{2\pi\langle u^2 \rangle}} e^{-\frac{u^2}{2\langle u^2 \rangle}} \quad \text{….a Gaussian distribution}
\]
Unit cell structure factor (Isotropic ADP)

- Fourier transform of a Gaussian is also a Gaussian

\[ P(u) = \frac{1}{\sqrt{2\pi\langle u^2 \rangle}} e^{\frac{-u^2}{2\langle u^2 \rangle}} \xrightarrow{FT} e^{\frac{-1}{2} u^2 Q^2} = e^{-8\pi^2 \langle u^2 \rangle \sin^2(\theta) / \lambda^2} \]

- If the motion is isotropic, the Atomic Displacement Parameter for atom j is:

\[ B_j = 8\pi^2 \langle u_j^2 \rangle \]

Unit-cell structure factor:

\[ F(\vec{Q}) = \sum_{\text{atom } j \in UC} b_j e^{-i\vec{Q} \cdot \vec{r}_j} e^{-B_j \frac{\sin(\theta)^2}{\lambda^2}} \]

\[ F(h, k, l) = \sum_{\text{atom } j \in UC} b_j e^{-i 2\pi (h x_j + k y_j + l z_j)} e^{-B_j \frac{\sin(\theta)^2}{\lambda^2}} \]

Unit cell structure factor (Anisotropic ADP)

- The Atomic Displacement parameter can be anisotropic, in which case a trivariate Gaussian is assumed.
- In the most general case (no constraint from point symmetry of the site), there are 6 independent $u_{ij}$ displacement parameter (second rank tensor).

$$
\begin{pmatrix}
  u_{11} & u_{12} & u_{13} \\
  u_{21} & u_{22} & u_{23} \\
  u_{31} & u_{32} & u_{33}
\end{pmatrix}
$$

$$
F(\vec{h}) = F(\vec{h}, k, l) = \sum_{\text{atom } j \in \text{UC}} b_j e^{-i2\pi(h \cdot x_j + k \cdot y_j + l \cdot z_j)} \cdot e^{-2\pi^2(\vec{u} \cdot \vec{h})^2}
$$
Effect of ADP on intensities

- Scattering function is damped at high momentum transfer

\[
\sin \left( \frac{\theta}{\lambda} \right)
\]

Reduction of \( F(h,k,l) \)
for \( B=1\text{Å}^2 \)

Reduction of \( |F(h,k,l)|^2 \)
for \( B=1\text{Å}^2 \)
Reminder: the phase problem

Now that you know how to write structure factors:

- Reminder: We measure $F^2$!

$$F(u,v) = M(u,v) e^{i\Phi}$$

$$F(u,v) = \frac{1}{N_x N_y} \sum_x \sum_y f(x,y) e^{-2\pi i \left( \frac{xu}{N_x} + \frac{yv}{N_y} \right)}$$

$$f'(x,y) = \frac{1}{N_u N_v} \sum_u \sum_v M(u,v) e^{2\pi i \left( \frac{xu}{N} + \frac{yv}{N} \right)}$$

Loss of information in a physical measurement:

The phase information is crucial to reconstruct the image.
One can not determine $V(r)$ without model.
Symmetry in reciprocal space (Friedel's law)

Friedel's law, relates the scattering intensity of inverse $Q$ points and stems from the property of Fourier transforms of real functions:

$$F(\vec{Q}) = \sum_j f_j e^{i\vec{Q} \cdot \vec{R}_j}$$

If $f_j$ is real then:

$$F(-\vec{Q}) = \sum_j f_j e^{-i\vec{Q} \cdot \vec{R}_j} = F^*(\vec{Q})$$

Since the scattered intensity is proportional to $FF^*$:

$$I(\vec{Q}) = F(\vec{Q}) F^*(\vec{Q}) = F^*(-\vec{Q}) F(-\vec{Q}) = I(-\vec{Q})$$

Even if the lattice lacks inversion symmetry, in the case when $f_j$ are reals, the scattered intensity of Friedel pairs are equal.
Symmetry in reciprocal space (Friedel's law)

- Friedel's law is violated if we are close to a resonance, in which case one needs to consider the anomalous part of the scattering length: \( b = b' - ib'' \).

- In such case, and in the absence of inversion symmetry in the crystal:

\[
F(-\vec{Q}) = \sum_j f_j e^{-i \vec{Q} \cdot \vec{R}_j} \neq F^*(\vec{Q})
\]

- This property can be used to determine the absolute handedness of chiral crystals for example. (most commonly X-ray anomalous scattering is used)
Symmetry in reciprocal space

- Friedel's law holds most of the time (especially in neutron scattering unless very high incident energies are employed)
- The symmetries that we have listed in real space, are also valid symmetries in reciprocal space once their translational part has been taken away.
- Combining the two → 11 Laue groups

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Laue Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>-1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2/m</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>mmm</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4/m ; 4/mmm</td>
</tr>
<tr>
<td>Trigonal</td>
<td>-3 ; -3/m</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6/m; 6/mmm</td>
</tr>
<tr>
<td>Cubic</td>
<td>m3 ; m3m;</td>
</tr>
</tbody>
</table>
Systematic absences

Systematic absences referred to the systematic lack of intensity (for some crystal symmetries) for certain lines or planes in reciprocal space and are due to:

- Lattice centering
- Symmetry operations with translations (screw axes and glide planes)

This is a direct consequence of exact cancellation of structure factors. Example: C-centering

\[ F(h, k, l) = b \left( e^{2\pi i (hx + ky + lz)} + e^{2\pi i (h(x+1/2) + k(y+1/2) + lz)} \right) \]

\[ F(h, k, l) = b e^{2\pi i (hx + ky + lz)} \left( 1 + e^{\pi i (h+k)} \right) \]

\[ h + k = 2n \]
Ewald construction (monochromatic source)

- The idea of P. P. Ewald is to decouple real and reciprocal spaces.
- The crystal is drawn at the center of the figure.
- Use incident wavenumber $s_i = k_i / 2\pi$
- Draw a sphere of radius $s = 1/\lambda$
- Origin of reciprocal space is at the extreme point of $s_i$
Ewald construction ($\omega$-scan)
Ewald construction ($\omega$-$2\theta$ scan)

Rotate the crystal and the detector simultaneously.
4-circle diffractometer

- Detector in place in the horizontal scattering plane.
- Crystal is rotated through a 3-axis goniometer (Like Euler rotations ZYZ)
- Access a large number of Bragg peaks by rotating the crystal
Ewald construction (Laue method)
“During my first stay in Gottingen I had made a half-hearted attempt to attend a mineralogy course but had given up very soon. From books I then learned the rudiments of crystallography, that is to say, crystal classes, that was all.”
Laue method

Neutron Laue Cyclops @ILL
T.O.F Single Crystal

For each pixel on the Detector:

This volume is available in a single shot

TOF Laue SXD @ ISIS
Debye-Scherrer cones (powder method)

Intersection of Ewald sphere with spheres in reciprocal space.
Debye-Scherrer cones (powder method)

Intersection of scattering cones with cylindrical detector
CW powder instruments

D2B, ILL

- Graphite filter
- Collimator
- Neutron flight tube
- Monochromator
- Adjustable slits
- Monitor
- Adjustable slits
- Collimator
- Detector He³
- Multidetector
- Sample
- Beam stop

D20, ILL

- Collimator
- Monochromators
- Slits
- Shutter
- Monitor
- Diaphragms
- Evacuated tube
- Sample
- Beam stop
- PSD (Position Sensitive Detector)
$\frac{\Delta d}{d} = \frac{1}{2} \sqrt{U \cdot \cot^2(\theta) + V \cdot \cot(\theta) + W}$

**CW powder instrument: Resolution function**

**3T2 Resolution Curve ($\alpha_1 = 10'$)**

**LLB, Saclay, 3T2**
The D20 instrument at the ILL: a versatile high-intensity two-axis neutron diffractometer

Thomas C Hansen, Paul F Henry, Henry E Fischer, Jacques Torregrossa and Pierre Convert

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TOF- powder diffraction

\[ p = \frac{h}{\lambda} = \frac{h}{2d \sin(\theta)} \]

\[ p = m \frac{L}{t} \]

\[ d = \frac{ht}{2mL \sin(\theta)} \]

The x-axis is simply the time-of-flight usually given in microseconds.
TOF powder data from WISH@ISIS
TOF powder data from WISH@ISIS
Geometric focussing

\[ t = \frac{2dml \sin \theta}{h} \]

- \( L \cdot \sin(\theta) = \text{const.} \)
- \( L = \text{total flight path} \)
Electronic focussing


**Electronically Focused Time-of-Flight Powder Diffractometers at the Intense Pulsed Neutron Source**


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\[
t^* = \frac{t_i(l_0 \sin \theta_0)}{(l_i \sin \theta_i)}
\]

Reference detector
TOF resolution function

\[
\frac{\Delta d}{d} = \frac{1}{2} \sqrt{W \cot^2 \theta + V \cot \theta + U}
\]

\[
U = \frac{\alpha_1^2 + \alpha_2^2}{\tan^2 \theta_M}
\]

\[
V = -\frac{2\alpha_2^2}{\tan \theta_M}
\]

\[
W = \alpha_2^2 + \alpha_3^2
\]

\[
\frac{\delta d}{d} = \sqrt{\left(\frac{\delta t}{t}\right)^2 + \left(\frac{\delta L}{L}\right)^2 + \left(\delta \theta \cot \theta\right)^2}
\]
Powder data: peak overlap

In powder data there is a substantial amount of overlap from the compression of data to 1D.
Powder diffraction: The Rietveld method

The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram." H. M. Rietveld
In the powder case, the data is compressed to 1 Dimension. Several equivalent Bragg peaks contribute to the intensity at the same scattering angle. To calculate the intensity, one needs to include this "multiplicity" ($j$)

$$F(h, k, l) = \sum_{\text{atom } j \in UC} b_j e^{-i 2\pi (h \cdot x_j + k \cdot y_j + l \cdot z_j)} \cdot e^{-B_j \frac{\sin(\theta)^2}{\lambda^2}}$$

$$I(h, k, l) \propto j \left| F(h, k, l) \right|^2$$
TOF profile function(1): Back to back exponential

Profile functions for CW, usually Pseudo-Voigt including asymmetry

In the case of TOF, requires convolution with “pulse” function

\[ \Omega(x) = pV(x) \otimes E(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt \]

\[ E(t) = 2Ne^{\alpha t} \quad t \leq 0 \]
\[ E(t) = 2Ne^{-\beta t} \quad t > 0 \]

\[ N = \frac{\alpha \beta}{2(\alpha + \beta)} \]
TOF profile function(2): Ikeda-Carpenter

\[ S_k(t) = \frac{\alpha^3}{2} t^2 e^{-\alpha t} \]

\[ R_k(t) = (1 - R) \delta(t) + R \beta e^{-\beta t} \]

Slow-down spectrum

Mixing:
- Delta function
- Exponential decay

More complex analytic expression but often used
Microstructure (strain/size)

The profile function results from:

1) the specific instrumental resolution
2) broadening from microstructural effects
   - Microsize: small coherent diffracting domain (not quite crystallite size but often related)
   - Microstrain: crystal lattice distortion with a coherent domain due to dislocations

The two later effects have different Q dependences and usually can be separated.

Size effects: $\Delta Q = \text{cste}$

Strain effects: $\Delta Q/Q = \text{cste}$
Microstructure (example)

Example of anisotropic strain (given in FullProf Manual)

Instrumental resolution function

Refinement with anisotropic strain to model the peak-shape function

Nd$_2$NiO$_4$, LT

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S_400  S_040  S_004  S_220
22.04(78) 17.74(57) 0.016(2) -38.8(1.2)
Lorentzian Parameter: 0.093(2)