Single Crystal Diffraction

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What is a crystal?

- Atoms (molecules) pack together in a regular pattern to form a crystal.
- Periodicity: we superimpose (mentally) on the crystal structure a repeating lattice or unit cell.
- A lattice is a regular array of geometrical points each of which has the same environment.

Unit cells of oxalic acid dihydrate

Quartz crystals
Why don’t the X-rays scatter in all directions?

- X-rays (and neutrons) have wave properties.
- A crystal acts as a diffraction grating producing constructive and destructive interference.
Laue Equations

Scattering from points

\[ a \cdot S_s + a \cdot (-S_i) = a \cdot (S_s - S_i) = h\lambda \]

In three dimensions →

\[ a \cdot (S_s - S_i) = h\lambda \]
\[ b \cdot (S_s - S_i) = k\lambda \]
\[ c \cdot (S_s - S_i) = l\lambda \]
Bragg’s Law

Jointly awarded the 1915 Nobel Prize in Physics

Bragg's law:

$$2d \sin \theta = n \lambda$$
Crystallographic Planes and Miller Indices

The \((hkl)\) plane intercepts \(a/h, b/k, c/l\) on crystallographic axes \(X, Y, Z\), where \(h, k, l\) are relatively prime integers.

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

Fractional intercepts
\[
\frac{1}{h'}, \frac{1}{k'}, \frac{1}{l'}
\]

Reciprocals of the fractional intercepts
\(h, k, l\)

Miller Indices
\((prime\ integers)\)
\(h, k, l\)

\(d\)-spacing = spacing between origin and first plane or between neighboring planes in the family of planes.
Real and reciprocal Space

$$\mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1$$

$$\mathbf{a}^* \cdot \mathbf{b} = \ldots = 0$$

Laue equations:

$$\mathbf{a} \cdot (\mathbf{S}_s - \mathbf{S}_i) = h \lambda, \text{ or } \mathbf{a} \cdot \mathbf{s} = h$$

$$\mathbf{b} \cdot (\mathbf{S}_s - \mathbf{S}_i) = k \lambda, \text{ or } \mathbf{b} \cdot \mathbf{s} = k$$

$$\mathbf{c} \cdot (\mathbf{S}_s - \mathbf{S}_i) = l \lambda, \text{ or } \mathbf{c} \cdot \mathbf{s} = l$$

where

$$\mathbf{s} = (\mathbf{S}_s - \mathbf{S}_i)/\lambda = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$
The Ewald Sphere

\[
\sin(\theta) = \frac{1}{(2d)} \frac{1}{1/\lambda}
\]

\[
2d\sin(\theta) = \lambda
\]
The Ewald sphere: the movie

Courtesy of the CSIC (Spanish National Research Council).
Relative phase shifts related to molecular structure.

\[ F_{hkl} = \sum_i b_i \exp(2\pi is \cdot r) \]

\[ F_{hkl} = \sum_i b_i \exp[2\pi i(hx + ky + lz)] \]

\[ \rho(xyz) = \frac{1}{V} \sum_{hkl} F_{hkl} e^{-2\pi i(hx+ky+lz)} \]

\( b_i \) is the neutron scattering length.
It is replaced by \( f_i \), the x-ray form factor.
The phase problem

\[ I_{hkl} = F_{hkl} \overline{F_{hkl}} = |F_{hkl}| e^{i\phi} |F_{hkl}| e^{-i\phi} = |F_{hkl}|^2 \]

Euler’s formula:

\[ F_{hkl} = |F_{hkl}| e^{i\phi} = |F_{hkl}| (\cos \phi + i \sin \phi) = A + iB \]

\[ F_{hkl} = |F_{hkl}| e^{-i\phi} = |F_{hkl}| (\cos \phi - i \sin \phi) = A - iB \]

\[ \tan \phi = B / A \]

\[ I_{hkl} = (A + iB)(A - iB) = A^2 + B^2 \]

Friedel’s law:

\[ I_{hkl} = F_{hkl} \overline{F_{hkl}} = F_{hkl} F_{-(hkl)} = I_{-(hkl)} \]
θ-2θ Step Scan
1. Detector stationary at $2\theta$ angle.
2. Crystal is rotated about $\theta$ by +/- $\omega$.
3. FWHM is the mosaic spread.
Something completely different - polycrystallography

What is a powder? - polycrystalline mass

All orientations of crystallites possible

Sample: 1µl powder of 1µm crystallites - ~10⁹ particles

Packing efficiency – typically 50%
Spaces – air, solvent, etc.

Single crystal reciprocal lattice
- smeared into spherical shells

Courtesy of R. Von Dreele
Bragg’s Law: \( d^* = \frac{2 \sin \theta}{\lambda} \)

- Usually do not attempt to integrate individual peaks.
- Instead, fit the spectrum using Rietveld profile analysis. Requires functions that describe the peak shape and background.
Why do single crystal diffraction (vs. powder diffraction)?

- Smaller samples
  - neutrons: 1-10 mg vs 500-5000 mg
  - x-rays: μg vs mg
- Larger molecules and unit cells
- Neutrons: hydrogen is ok for single crystals, powders generally need to be deuterated
- Less absorption
- Fourier coefficients are more accurate – based on integrating well-resolved peaks
- Uniquely characterize non-standard scattering – superlattice and satellite peaks (commensurate and incommensurate), diffuse scattering (rods, planes, etc.)

But:

- Need to grow a single crystal
- Data collection can be more time consuming
Some history of single crystal neutron diffraction

• 1951 – Peterson and Levy demonstrate the feasibility of single crystal neutron diffraction using the Graphite Reactor at ORNL.
• 1950s and 1960s – Bill Busing, Henri Levy, Carroll Johnson and others wrote a suite of programs for single crystal diffraction including ORFLS and ORTEP.
• 1979 – Peterson and coworkers demonstrate the single crystal neutron time-of-flight Laue technique at Argonne’s ZING-P’ spallation neutron source.
The Orientation Matrix


**Angle Calculations for 3- and 4- Circle X-ray and Neutron Diffractometers**

**BY WILLIAM R. BUSING AND HENRI A. LEVY**

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

(Received 13 June 1966)

Methods are derived for calculations useful in the operation of 3- and 4-circle X-ray or neutron single-crystal diffractometers. These include: (1) establishing the sample orientation from the cell parameters and the observed angles for two reflections, or from the observed angles for three reflections only, (2) calculating the angles for observing a given reflection either in a special setting or at a specified azimuthal angle, (3) obtaining the vectors needed for calculating absorption corrections, and (4) using observations of several reflections to refine cell and orientation parameters by the method of least squares.

\[
\mathbf{U} = \begin{pmatrix}
1 & b_2 \cos \beta_3 & b_3 \cos \beta_2 \\
0 & b_2 \sin \beta_3 & -b_3 \sin \beta_2 \cos \alpha_1 \\
0 & 0 & 1/\alpha_3
\end{pmatrix}
\]

\( \mathbf{U} \) is a rotation matrix relating the unit cell to the instrument coordinate system.

The matrix product \( \mathbf{U} \mathbf{B} \) is called the *orientation matrix*. 

![Diagram of a four-circle diffractometer](image-url)
Picker 4-Circle Diffractometer
Kappa Diffractometer

- Full 360° rotations about $\omega$ and $\varphi$ axes.
- Rotation about $\kappa$ axis reproduces quarter circle about $\chi$ axis.
Monochromatic diffractometer

- Rotating crystal
- Vary $\sin \theta$ in the Bragg equation:
  \[ 2d \sin \theta = n\lambda \]
Laue diffraction

Polychromatic "white" spectrum

$I(\lambda)$

All $\lambda$'s used

Reflections at one scattering angle ($90^\circ$)
Laue photo from white radiation

X-ray Laue photos taken by Linus Pauling
Time-resolved X-ray Laue diffraction of photoactive yellow protein at BioCARS using pink radiation
Quasi-Laue Neutron Image Plate Diffractometer

Select $\Delta \lambda / \lambda$ of 10-20%

IMAGINE @ HFIR, ORNL

General view of the QLD

QLD schematic (open position)

A typical Laue diffraction pattern from FeTa₂O₆ just above the 3-D ferroelectric ordering temperature (Chung et al. J. Phys.: Condens. Matter, 16 (2004) 1-17). The faint cross of radial streaks about the central hole, which allows passage of the transmitted neutron beam, arises from 2-D magnetic ordering. Results from the Laue diffractometer VIVALDI at the ILL.
Pulsed Neutron Incident Spectrum

\[ \lambda = \frac{h}{mv} = \left( \frac{h}{m} \right) \left( \frac{t}{L} \right) \]

- \( \lambda \) = wavelength
- \( h \) = Planck’s constant
- \( m \) = neutron mass
- \( v \) = velocity
- \( t \) = time-of-flight
- \( L \) = path length

\( L = 10 \text{ m} \)

1.25 msec

0.5 Å

12.5 msec

5.0 Å

SOURCE PULSED AT 60 HZ

16 2/3 millisec
Reflections at one scattering angle (90°) resolved at different TOF's

Sphere of reflection at $t_{\text{max}}$

Incident Beam

$\frac{1}{\lambda_{\text{max}}}$

$\frac{1}{\lambda_{\text{min}}}$
Topaz at the SNS

- The TOPAZ detector array tank with 13 detectors
- Each detector active area is $15 \times 15$ cm$^2$.
- Crystal to detector distance varies from 40 to 450 cm.
- Moderator to crystal distance is 18 m.
- The Crystal Logic goniostat is raised from the tank to mount crystals and lowered into the tank for data collection.
TOPAZ Instrument View with Mantid
Slice View: $l = 5$ reciprocal lattice plane
Analysis of $\text{ZnMn}_2\text{O}_4$ by William Ratcliff II (NIST).

ISAW 3D Reciprocal Space Viewer
Diffuse Magnetic Scattering
Outline of single crystal structure analysis

- Collect some initial data to determine the unit cell and the space group.
  - Auto-index peaks to determine unit cell and orientation
  - Examine symmetry of intensities and systematic absences
- Measure a full data set of observed intensities.
- Reduce the raw integrated intensities, $I_{hkl}$, to structure factor amplitudes, $|F_{obs}|^2$.
- Solve the structure.
- Refine the structure.
**Data reduction - single crystal TOF Laue**

**Data reduction:** convert raw integrated intensities, $I_{hkl}$, into relative structure factor amplitudes, $|F_{hkl}|^2$.

$$I_{hkl} = k \, \phi(\lambda) \, \varepsilon(\lambda) \, A(\lambda) \, y(\lambda) \, (V_s/V_c^2) \, |F_{hkl}|^2 \, \lambda^4 / \sin^2 \theta$$

- $k = \text{scale factor}$
- $\phi(\lambda) = \text{incident flux spectrum}$
- $\varepsilon(\lambda) = \text{detector efficiency as a function of wavelength } \lambda$
- $A(\lambda) = \text{sample absorption}$
- $y(\lambda) = \text{secondary extinction correction}$
- $V_s = \text{sample volume}$
- $V_c = \text{unit cell volume}$
Intensity vs. sample volume and unit cell volume

\[ I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) \left( \frac{V_s}{V_c^2} \right) |F_{hkl}|^2 \frac{\lambda^4}{\sin^2 \theta} \]

\[ I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) \left( \frac{V_s}{V_c} \right) \left( |F_{hkl}|^2 / V_c \right) \frac{\lambda^4}{\sin^2 \theta} \]

\[ I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) N_s \left( |F_{hkl}|^2 / V_c \right) \frac{\lambda^4}{\sin^2 \theta} \]

- **Number of unit cells in the sample**
- **Scattering per unit volume approximately constant**
Wilson plot

\[ \langle |F_{hkl}|^2 \rangle = \sum_{j=1}^{n} b_j^2 = n \langle b_j^2 \rangle \]

\[ \langle |F_{obs}|^2 \rangle = K \sum_{j=1}^{n} b_j^2 e^{-2B (\sin^2 \theta) / \lambda^2} \]

\[ \ln \left( \frac{\langle |F_{obs}|^2 \rangle}{\sum_{j=1}^{n} b_j^2} \right) = \ln K - 2B (\sin^2 \theta) / \lambda^2 \]

\[ V_c = \sum_{j=1}^{n} v_j = n \langle v_j \rangle \]

\[ \frac{\langle |F_{hkl}|^2 \rangle}{V_c} = \frac{\langle b_j^2 \rangle}{\langle v_j \rangle} \]

\[ n = \text{number of atoms in the unit cell} \]

\[ b_j = \text{neutron scattering length, or} \]

\[ f_j = x\text{-ray form factor} \]

\[ K = \text{scale factor} \]

\[ B = \text{temperature or thermal parameter} \]

\[ \ln \left( \frac{\langle |F_{obs}|^2 \rangle}{\sum_{j=1}^{n} b_j^2} \right) \]

\[ \text{slope} = -2B \]

\[ \text{intercept} = \ln K \]

\[ V_c = \text{unit cell volume} \]

\[ v_j = \text{volume of atom } j \]

For crystals containing similar types of atoms in similar ratios, this is a constant.

**Lorentz factor**

The Lorentz factor is geometric integration factor related to the time or angular range during which a peak is reflecting.

Laue integration:

\[
I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) N_s \left( |F_{hkl}|^2 / V_c \right) \frac{\lambda^4}{\sin^2 \theta}
\]

\[
I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) N_s \left( |F_{hkl}|^2 / V_c \right) \lambda^2 \frac{d^2}{4}
\]

Constant wavelength integration:

\[
I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) N_s \left( |F_{hkl}|^2 / V_c \right) \frac{\lambda^3}{\sin 2\theta}
\]

\[
I_{hkl} = k \phi(\lambda) \varepsilon(\lambda) A(\lambda) y(\lambda) N_s \left( |F_{hkl}|^2 / V_c \right) \lambda^2 \frac{d}{\cos \theta}
\]
Fourier transforms

\[ \rho(xyz) = \frac{1}{V} \sum_{hkl} F_{hkl} e^{-2\pi i (hx + ky + lz)} \]

\[ I_{hkl} \propto |F_{hkl}|^2 \]
\[ F_{hkl} = |F_{hkl}| e^{i\phi} \]

\[ F_{hkl} = \int_{cell} \rho_{xyz} e^{2\pi i (s \cdot r)} dv = \sum_{j} b_{j} e^{2\pi i (hx_{j} + ky_{j} + lz_{j})} \]

Sum over \( j \) atoms in the unit cell.

Neutron scattering length of the \( j \)th atom,

Solutions to the phase problem

- Patterson synthesis using the $|F_{\text{obs}}|^2$ values as Fourier coefficients
  - Map of inter-atom vectors
  - Also called the heavy atom method

- Direct methods
  - Based on probability that the phase of a third peak is equal to the sum of the phases of two other related peaks.
  - J. Karle and H. Hauptman received the 1985 Nobel Prize in Chemistry

- Shake-and-bake
  - Alternate between modifying a starting model and phase refinement

- Charge flipping
  - Start out with random phases.
  - Peaks below a threshold in a Fourier map are flipped up.
  - Repeat until a solution is obtained

- MAD
  - Multiple-wavelength anomalous dispersion phasing

- Molecular replacement
  - Based on the existence of a previously solved structure with of a similar protein
  - Rotate the molecular to fit the two Patterson maps
  - Translate the molecule
Structure Refinement

GSAS, SHELX, CRYSTALS, OLEX2, WinGX… Nonlinear least squares programs. Vary atomic fractional coordinates $x, y, z$ and temperature factors $U$ (isotropic) or $u_{ij}$ (anisotropic) to obtain best fit between observed and calculated structure factors.

$$\chi^2 = \sum_{hkl} w(|F_0| - |F_c|)^2$$

$$F_{hkl} = \sum_i b_i \exp[2\pi i (hx_i + ky_i + lz_i)] \exp[-8\pi^2 U_i \sin^2 \theta / \lambda^2]$$

Neutron single crystal instruments in the US

- **SNAP** @ SNS: high pressure sample environment (http://neutrons.ornl.gov/instruments/SNS/SNAP/)
- **TOPAZ** @ SNS: small molecule to small protein, magnetism, future polarized neutron capabilities (http://neutrons.ornl.gov/instruments/SNS/TOPAZ/)
- **Four-Circle Diffractometer (HB-3A)** @ HFIR: small molecule, high precision, magnetism (http://neutrons.ornl.gov/instruments/HFIR/HB3A/)
- **MaNDi** (Macromolecular Neutron Diffractometer) @ SNS: neutron protein crystallography, commissioning in 2012 (http://neutrons.ornl.gov/instruments/SNS/MaNDi/)
- **IMAGINE** (Image-Plate Single-Crystal Diffractometer) @ HFIR: small molecule to macromolecule crystallography, commissioning in 2012 (http://neutrons.ornl.gov/instruments/HFIR/imagine/)
- **SCD** @ Lujan Center, Los Alamos: general purpose instrument, currently not available due to budget constraints (http://lansce.lanl.gov/lujan/instruments/SCD/index.html)
- **PCS** (Protein Crystallography Station) @ Lujan Center, Los Alamos: neutron protein crystallography (http://lansce.lanl.gov/lujan/instruments/PCS/index.html)
Books and on-line tutorials

- Interactive Tutorial about Diffraction: www.totalscattering.org/teaching/
- An Introductory Course by Bernhard Rupp: http://www.ruppweb.org/Xray/101index.html