Single Crystal Diffraction

Arthur J. Schultz
Argonne National Laboratory

National School on Neutron and X-Ray Scattering
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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.

X-ray precession photograph (Georgia Tech, 1978).
The Bragg Equation

Reflection from a series of equally spaced planes:

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

Scattering from points

\[ \mathbf{a} \cdot \mathbf{S} + \mathbf{a} \cdot (-\mathbf{S}_i) = \mathbf{a} \cdot (\mathbf{S} - \mathbf{S}_i) = h\lambda \]

In three dimensions →

\[ \mathbf{a} \cdot (\mathbf{S} - \mathbf{S}_i) = h\lambda \]
\[ \mathbf{b} \cdot (\mathbf{S} - \mathbf{S}_i) = k\lambda \]
\[ \mathbf{c} \cdot (\mathbf{S} - \mathbf{S}_i) = l\lambda \]
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:

\[ \mathbf{a} \cdot (\mathbf{S}_o - \mathbf{S}_i) = h\lambda, \text{ or } \mathbf{a} \cdot \mathbf{s} = h \]

\[ \mathbf{b} \cdot (\mathbf{S}_o - \mathbf{S}_i) = k\lambda, \text{ or } \mathbf{b} \cdot \mathbf{s} = k \]

\[ \mathbf{c} \cdot (\mathbf{S}_o - \mathbf{S}_i) = l\lambda, \text{ or } \mathbf{c} \cdot \mathbf{s} = l \]

where

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

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

\[
2d \sin(\theta) = \lambda
\]
Bragg Peak Intensity

Relative phase shifts related to molecular structure.

\[ F_{hkl} = \sum_{i} b_i \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_i) \]

\[ F_{hkl} = \sum_{i} b_i \exp[2\pi i (hx_i + k y_i + lz_i)] \]

\[ F_{hkl}^2 \approx I_{hkl} \]
$\theta$-$2\theta$ Step Scan (1)
$\theta-2\theta$ Step Scan (2)
$\theta$-2$\theta$ Step Scan (3)
Omega Step Scan

1. Detector stationary at 2\(\theta\) angle.
2. Crystal is rotated about \(\theta\) by +/- \(\omega\).
3. FWHM is the mosaic spread.
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.

\[
B = \begin{pmatrix}
  b_1 & b_2 \cos \beta_3 & b_3 \cos \beta_2 \\
  0 & b_2 \sin \beta_3 & -b_3 \sin \beta_2 \cos \alpha_1 \\
  0 & 0 & 1/\alpha_3
\end{pmatrix}
\]

U is a rotation matrix relating the unit cell to the instrument coordinate system.

The matrix product UB is called the orientation matrix.
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 – Busing, 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.
Picker 4-Circle Diffractometer
4-Circle Diffractometer: Euler Angle Rotations

1. Rotate $\omega$ by $\theta$ so that the normal to the $\chi$ plane bisects $2\theta$.

2. Rotate $\varphi$ so that the diffraction vector $S_{hkl}$ is in the plane of the $\chi$ circle.

3. Rotate $\chi$ so that $S_{hkl}$ is in the horizontal plane of the incident and diffracted beam.

View normal to $\chi$ circle from source for steps 2 and 3.
Kappa Diffractometer

- Full 360° rotations about ω and φ axes.
- Rotation about κ axis reproduces quarter circle about χ axis.

Figure 6-13. Kappa geometry. Adapted from operating manual for ENRAF-NOMIUS CAD 4 diffractometer (angles ω, φ, and χ are opposite in sign to those of Enraf-Nomius). (By permission of ENRAF-NOMIUS Service Corp., Bohemia, New York.)
Monochromatic diffractometer

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

$$2d \sin \theta = n\lambda$$
Laue diffraction

Polychromatic “white” spectrum

$\lambda$ for $I(\lambda)$

All $\lambda$'s used

Reflections at one scattering angle ($90^\circ$)

Portion of reciprocal space sampled for $2\theta_{\text{min}} < 2\theta < 2\theta_{\text{max}}$ and $\lambda_{\text{min}} < \lambda < \lambda_{\text{max}}$
Laue photo from white radiation

X-ray Laue photos taken by Linus Pauling
Quasi-Laue Neutron Image Plate Diffractometer

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

General view of the QLD

QLD schematic (open position)

A typical Laue diffraction pattern from FeTa$_2$O$_6$ 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

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

- \( t_0 \) to 1.25 msec: 0.5 Å
- 1.25 msec to 12.5 msec: 5.0 Å
- L = 10 m

SOURCE PULSED AT 30 HZ

COUNTS

33 1/3 msec
**NEUTRON DIFFRACTION**

**MEASURE F(d)**

\[ d = \frac{\lambda}{2\sin\theta} \]

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**STEADY STATE TECHNIQUE**

- Reactor → Monochromator Crystal
- Sample
- \( \lambda_0 \) → \( 2\theta \)

**TIME OF FLIGHT TECHNIQUE**

- Pulsed Source → Sample
- \( 2\theta \) → \( \lambda = (h/m) \cdot (t/L) \)

**Graphs:**

- **I(\lambda):** Small \( \Delta\lambda \) used
- **I(t) on Sample:** Source on all the time
- **I(t) at Detector:** Time →

- **All \( \lambda \)'s used**
- **Source on for short time**

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Reflections at one scattering angle (90°) resolved at different TOF’s
## SCD Instrument Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderator</td>
<td>liq. methane at 105ºC</td>
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<tr>
<td>Source frequency</td>
<td>30 Hz</td>
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<tr>
<td>Sample-to-moderator dist.</td>
<td>940 cm</td>
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<tr>
<td>Number of detectors</td>
<td>2</td>
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<tr>
<td>Detector active area</td>
<td>155 x 155 mm²</td>
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<tr>
<td>Scintillator</td>
<td>GS20 ⁶Li glass</td>
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<tr>
<td>Scintillator thickness</td>
<td>2 mm</td>
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<tr>
<td>Efficiency @ 1 Å</td>
<td>0.86</td>
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<tr>
<td>Typical detector channels</td>
<td>100 x 100</td>
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<tr>
<td>Resolution</td>
<td>1.75 mm</td>
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<td>Detector 1: angle</td>
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<tr>
<td>sample-to-detector dist.</td>
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<tr>
<td>Detector 2: angle</td>
<td>120º</td>
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<tr>
<td>sample-to-detector dist.</td>
<td>18 cm</td>
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<tr>
<td>Typical TOF range</td>
<td>1–25 ms</td>
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<tr>
<td>wavelength range</td>
<td>0.4–10 Å</td>
</tr>
<tr>
<td>d-spacing range</td>
<td>~0.3–8 Å</td>
</tr>
<tr>
<td>TOF resolution, Δt/t</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### Sample Environments

- **Hot-Stage Displex**: 4-900 K
- **Displex Closed Cycle Helium Refrigerator**: 12–473 K
- **Furnaces**: 300–1000 K
- **Helium Pressure Cell Mounted on Displex**: 0–5 kbar @ 4–300 K

Now operating in Los Alamos.
ISAW hkl plot
Analysis of $\text{ZnMn}_2\text{O}_4$ by William Ratcliff II (NIST).

ISAW 3D Reciprocal Space Viewer
Diffuse Magnetic Scattering
ORTEP of oxalic acid dihydrate from data measured on SNAP in December, 2008.
Topaz Detector Coverage

- Project Execution Plan requires a minimum of 2 steradian (approx. 23 detectors) coverage.
- Each detector active area is 150 mm x 150 mm.
- Secondary flight path varies from 400 mm to 450 mm radius and thus cover from 0.148 to 0.111 steradian each.
Data Reduction

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

$$I_{hkl} = k \, \tau(\lambda) \, \phi(\lambda) \, \varepsilon(\lambda,r) \, A(\lambda) \, y(\lambda) \, |F_{hkl}|^2 \, \lambda^4 / \sin^2 \Theta$$

- $k =$ scale factor
- $\tau(\lambda) =$ deadtime loss
- $\phi(\lambda) =$ incident flux spectrum, obtained by measuring the incoherent scattering from a vanadium sample
- $\varepsilon(\lambda,r) =$ detector efficiency calculated as a function of wavelength $\lambda$ and position $r$ on the detector for each Bragg peak since the slant path through the flat $^6$Li glass varies with $r$
- $A(\lambda)$ = sample absorption; includes the wavelength dependence of the linear absorption coefficients
- $y(\lambda) =$ extinction correction is evaluated during the least-squares refinement of the structure
Structure solution and Fourier syntheses

- **Measured intensity**
  \[ I_{hkl} \propto |F_{hkl}|^2 \]

- **Electron (X-ray) or nuclear (neutron) density at point \( x,y,z \) in the unit cell**
  \[ \rho(xyz) = \frac{1}{V} \sum_{hkl} F_{hkl} e^{-2\pi i (hx+ky+lz)} \]

- **Phase angle**
  \[ F_{hkl} = |F_{hkl}|e^{-i \phi} = |F_{hkl}| \cos \phi + i|F_{hkl}| \sin \phi = A + iB \]
  \[ \phi = \tan^{-1} \frac{B}{A} \]

- **Sum over \( j \) atoms in the unit cell**
  \[ F_{hkl} = \int_{\text{cell}} \rho_{xyz} e^{2\pi i (s \cdot r)} \, dv = \sum_{j} b_{j} e^{2\pi i (hx_{j}+ky_{j}+lz_{j})} \]

- Neutron scattering length or X-ray form factor for \( j^{\text{th}} \) atom

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Diagram:
- Crystal
- X-rays lead to diffraction pattern
- Phases lead to electron density map
- Refinement
- Fitting
- Atomic model
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Structure Refinement

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

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

GSAS, SHELX, CRYSTALS…

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.
On-line Tutorials

• Th. Proffen, R. Neder, S. Billinge: http://www.totalscattering.org/teaching/
• Dissemination of IT for the Promotion of Materials Science (DoITPoMS): http://www.doitpoms.ac.uk/tlplib/xray-diffraction/index.php
• Bragg’s Law (Stony Brook): http://www.eserc.stonybrook.edu/ProjectJava/Bragg/index.html
• X-ray 101 by Bernard Rupp: http://www.ruppweb.org/Xray/101index.html
• IPNS SCD tutorial by Paula Piccoli: http://www.pns.anl.gov/instruments/scd/subscd/scd.shtml