Introduction to Structure and Single-Crystal X-ray Diffraction

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Structure

Visible Light: 4x10^{-7} - 9x10^{-7} m

Leptons: X-rays 0.1 to 14 Å

Molecular, Extended, Quasi, etc

H

10^{-10} m

Angstrom (Å)

Early microscopes
X-rays scatter is...

- X-ray photon can be described in terms of an electric and magnetic component.
  - Normal to each other and to the direction of the photon
- Collision of the photon with a charged particle causes the component of the particle to oscillate with the same frequency.
- The oscillating particle returns to the resting state by emitting a photon that travels outward.
- The probability that a given incumbent photon will result in a scattered photon is $<10^{-20}$
- For atoms, the X-ray intensity decreases as you scan away from the direct beam because the destructive interference increases between the X-rays scattered by different regions of the electron cloud.
Diffraction is ...

• A phenomenon caused by interference of waves, such as the formation of light and dark regions by the passage of the wave through a gradient.
  – Paul Peter Ewald

• X-ray Diffraction is the observation of X-ray wave interference by crystalline materials.
  – (Roentgenstrahlinterferenzen) (XRD)
  – Max von Laue
The Crystal

A crystal is a solid material whose constituent atoms (molecules and ions) are arranged in an orderly repeating pattern extending in all three spatial dimensions.
The Unit Cell is a parallelepiped that describes the smallest unique volume of the crystal. The unit cell can be described by $a, b, c, \alpha, \beta, \gamma$. The angles between the vectors are:
- Angle between $b$ & $c$ is $\alpha$.
- Angle between $a$ & $c$ is $\beta$.
- Angle between $a$ & $b$ is $\gamma$.
Crystal Systems are ...

1. $a \neq b \neq c \neq \beta \neq \gamma \geq 90^\circ$ \quad \text{Triclinic}^1
2. $a \neq b \neq c \alpha = \beta = 90^\circ \gamma \neq 90^\circ$ \quad \text{Monoclinic}
3. $a \neq b \neq c \alpha = \beta = \gamma = 90^\circ$ \quad \text{Orthorhombic}
4. $a = b \neq c \alpha = \beta = \gamma = 90^\circ$ \quad \text{Tetragonal}
5. $a = b \neq c \alpha = \beta = 90^\circ \gamma = 120^\circ$ \quad \text{Hexagonal}
6. $a = b = c \alpha \neq \beta \neq \gamma \neq 90^\circ$ \quad \text{Rhombohedral}^*$
7. $a = b = c \alpha = \beta = \gamma = 90^\circ$ \quad \text{Cubic}

* In the Trigonal notation $a = b \neq c \alpha = \beta = 90^\circ \gamma = 120^\circ$

Symmetry Describes Order

• Crystal system order
  – Why don’t we use the triclinic system to describe everything?
  – Answer: Because we would miss the symmetry that we can use to describe order.

Symmetry Elements
rotation (1,2,3,4,6), inversion $\overline{1}$, mirror (m), improper rotation $\overline{3}, \overline{4}, \overline{6}$

Triclinic
Inversion center $\overline{1}$
Monoclinic two-fold, mirror and $\overline{1}$

Symmetry of the Monoclinic System is $2/m$ (Hermann-Mauguin) or $C_{2h}$ (Schoenflies)
Objects in Space ...

- Translation
- between unit cells (..., -1, 0, +1...)

-2 -1 0 1 2

in the unit cell

centering, screw axis, glide planes
Objects in Space...

Translation

Lattice Point

Primitive cell 1 (8*1/8) lattice point per cell
Objects in Space

Translation

Centered cell 2 \((8 \times \frac{1}{8} + 2 \times \frac{1}{2})\) lattice points per cell
Objects in Space ...

Symmetry followed by translation
screw axis
  – rotation followed by translation
    • $N_m$ (N sub m) N-fold rotation followed by m/N translation
      $2_1 \ 3_1 \ 3_2 \ 4_1 \ 4_3 \ 6_1 \ 6_6$

glide planes
  – $m$ reflection followed by translation
    • a, b, c (along face)
    • n (diagonal face)
    • d (diagonal cell)
Symmetry

- **Object Order**
  - **Crystalline Lattices**
    - P (primitive), C (centered, A,B,C), F (face centered), I (body centered), R (rhombohedral)
  - **Space Groups**
    - The 230 ways to describe how identical objects can be arranged in orderly arrays in an infinite three dimensional lattice
    - \( L_{ijk} \) : \( L = \) lattice, ijk = symmetry elements
    - **Examples**
      - \( P 2/m.2/n.2_1/a \) or shorten \( P \) mna
      - \( C 1.2/c.1 \) or shorten \( C 2/c \)

Auguste Bravais  
Arthur Schoenflies  
Yevgraf Fyodorov  
William Barlow
Miller Indices

• Unit cell can be dissected by sets of rational (parallel) planes

• Miller Indices is the reciprocal of the intercepts of the plane with the crystallographic axes.
  – a/2 or 2, b/3 or 3, c/1 or 1
  • Indices (231) \((hkl)\)
  – Indices can have negative intercepts.
    • e.g. \((-231)\) \((-hkl)\)
  – \(d\) is the distance between planes
    • Each indices has \(d_{hkl}\)
The scattering for an atom is simply the value for a free electron multiplied by the atomic number. The INTENSITY of the scattered X-ray will fall off as a function of theta.
Bragg’s Law is 

\[ \frac{l}{d} = \sin \theta \]

\[ l = dsin \theta \]

(since \( \lambda = l + l \) then)

\[ \lambda = 2dsin \theta \]

\[ \lambda = \lambda \sin \theta + d \sin \theta \]

3. Since the two waves can be in phase for \( \lambda \) to \( n \lambda \)

Then

2. When \( l + l = \lambda \) then the two waves are in phase

Bragg Angle = \( 2\theta \)

Angle relative to the X-ray beam

\[ n\lambda = 2dsin \theta \]
The angle $\theta$ to indices...

\[ \lambda = 2d_{hkl} \sin \theta_{hkl} \]
\[ \frac{1}{d_{hkl}} = \frac{2 \sin \theta_{hkl}}{\lambda} \]
\[ d_{hkl}^* = \frac{2 \sin \theta_{hkl}}{\lambda} \]

Reciprocal Space

\[ d_{100}^* = a^* = \frac{bc \sin \alpha}{V} \]
\[ d_{010}^* = b^* = \frac{ac \sin \beta}{V} \]
\[ d_{001}^* = c^* = \frac{ab \sin \gamma}{V} \]

Bragg angle can be expressed as

\[ 2\theta_{hkl} \rightarrow d_{hkl} \rightarrow (hkl) \]

\[ d_{hkl}^2 = h^2 a^2 + k^2 b^2 + l^2 c^2 + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2hla^*c^* \cos \beta^* \]

\[ 2\theta_{hkl} = 2 \times \sin^{-1} \left( \frac{\lambda \times (h^2 a^2 + k^2 b^2 + l^2 c^2 + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2hla^*c^* \cos \beta^*)^{1/2}}{2} \right) \]
Bragg angle

\[ d_{hkl}^{*2} = \begin{pmatrix}
  a^* & a^* \cdot b^* & a^* \cdot c^* \\
  b^* \cdot a^* & b^* & b^* \cdot c^* \\
  c^* \cdot a^* & c^* \cdot b^* & c^* \\
\end{pmatrix} \begin{pmatrix}
  h \\
  k \\
  l \\
\end{pmatrix} \]

\[ d_{hkl}^{*2} = h^2 a^* + k^2 b^* + l^2 c^* + 2hka^* b^* \cos \gamma^* + 2kbc^* \cos \alpha^* + 2hla^* c^* \cos \beta^* \]

\[ 2\theta_{hkl} = 2 \times \sin^{-1} \left( \frac{\lambda \times (h^2 a^* + k^2 b^* + l^2 c^* + 2hka^* b^* \cos \gamma^* + 2kbc^* \cos \alpha^* + 2hla^* c^* \cos \beta^*)^{1/2}}{2} \right) \]

Bragg angle = \( 2\theta_{hkl} \)
X-ray Camera

Rosalind Franklin
Maurice Wilkins
Raymond Gosling

James Watson
Francis Crick
The X-ray Diffractometer

1. X-ray Tube: the source of X Rays
2. Incident-beam optics: condition the X-ray beam before it hits the sample
3. The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
4. The sample & sample holder
5. (Receiving-side optics: condition the X-ray beam after it has encountered the sample) powder
6. Detector: count the number of X Rays scattered by the sample

Bragg Spectrometer Labels: L, lead box; A, B, D, slits; C, crystal; I, ionization chamber; V', vernier of ionization chamber; K, earthing key; E, electroscope; M, microscope.

W. H. Bragg
SCD X-ray Diffractometer

Modern Single-Crystal Diffractometer
The Results

- Two items of information are produced by the X-ray instrument.
  1. The reflections (Bragg) angle \((2\theta) \rightarrow d^* \rightarrow hkl\)
  2. The intensity of the reflection.

\[ I(hkl) = \text{Reflections} \]

- \(hkl\) => where the atoms are
  - \(hkl \sim d^* = \text{Position in reciprocal space}\)
- \(I(hkl) = \text{Reflections}\)
  - \(I\) => what the atoms are
    - Intensity \(\sim\) number of scattering electrons

\[ |F(hkl)|_{observed} = \sqrt{kI(hkl)} \]

Observed Structure Factor
Electron Density

\[ F_{hkl} = \iiint_{hkl} \rho(xyz) e^{2\pi i (hx + ky + lz)} dV \quad (1) \]

\[ F_{hkl} = |F_{hkl}|_{\text{observed}} e^{i\alpha_{hkl}} \quad \alpha_{hkl} \text{ is the phase angle which is NOT measured!} \]

Amplitude: \[ |F_{hkl}|_{\text{observed}} = \sqrt{k I_{hkl}} \]

Problem: \( \rho(xyz) \) wrong side of the equation
Solution: Fourier Transform of Eq. 1

\[ \rho(xyz) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l} |F_{hkl}|_{\text{observed}} \cos 2\pi \left( hx + ky + lz - \alpha'_{hkl} \right) \]
The Math ...

\[ F_{hkl} = \iiint_{V} \rho(xyz) e^{-2\pi i (hx + ky + lz)} \, dV \]

Fourier series:
\[ h = (h_x + k_y + l_z) \text{ and } F_{hkl} = |F_{hkl}| e^{i\alpha_{hkl}} \]

From the periodic function
\[ \rho(xyz) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} e^{-2\pi ihx} \]

Substituting for \( F_{hkl} \)
\[ \rho(xyz) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos(2\pi(h\alpha_{hkl})) \]

Rearranging
\[ \rho(xyz) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| e^{-i(2\pi \alpha_{hkl})} \]

Thus \( 2\cos \alpha_{\text{hkl}} = \alpha_{\text{hkl}} \) then
\[ \rho(xyz) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos(2\pi(h - \alpha_{\text{hkl}})) - i \sin 2\pi(h - \alpha_{\text{hkl}}) \]

Pitot's law states \( F_{hkl} = F_{hkl}^* \) (for \( h \) and \( -h \)) and summing \( h = 0 \) to \( h = \infty \)
\[ \rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos(2\pi(h \cos \alpha_{\text{hkl}})) - i \sin 2\pi(h \cos \alpha_{\text{hkl}}) \]

Given that \( \cos(h) = \cos(\alpha_{\text{hkl}}) \) and \( \sin(h) = -i \sin(\alpha_{\text{hkl}}) \) and \( F_{hkl} = F_{hkl}^* \) then
\[ \rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos(2\pi(h \cos \alpha_{\text{hkl}})) - i \sin 2\pi(h \cos \alpha_{\text{hkl}}) \]

Substituting
\[ \rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| [\cos(2\pi(h \cos \alpha_{\text{hkl}})) - i \sin 2\pi(h \cos \alpha_{\text{hkl}})] \]

Summing from \( h = 0 \) to \( h = \infty \) leaves
\[ \rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos(2\pi(xh + ky + l \alpha_{\text{hkl}})) \]

Because \( \alpha_{\text{hkl}} = \frac{\alpha_{\text{hkl}}}{2\pi} \)
The Model ...

For atom (i) which has position \(x_i, y_i, z_i\) and the idealized scattering of \(f_i\) then

\[
F(hkl)_{\text{cal}} = \sum_i f_i \exp[2\pi(hx_i + ky_i + lz_i)]
\]

Calculated Structure Factor

\[
\alpha_{hkl} = \tan^{-1}\left(\frac{\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)}{\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)}\right)
\]

Calculated phase angle
Structure refinement is the process of building a model to fit the data. The data is fixed and the model is adjusted to “fit” by the method of Non-Linear Least Squares.
Model building

\[
I(hkl) = K |F(hkl)_{obs}|^2
\]

**Structure Solution**

\[
F(hkl)_{cal} = \sum_i f_i \exp[2\pi (hx_i + ky_i + lz_i)]
\]

**Phase Refinement**

Non-linear Least Squares

\[
D = \sum_{hkl} w_{hkl}\left(|F_{obs}|^2 - |kF_{calc}|^2\right)^2
\]

\[
wR2 = \left(\frac{\sum_{hkl} (w|F_{obs}|^2 - |kF_{calc}|^2)^2}{\sum_{hkl} (w|F_{obs}|^2)^2}\right)^{1/2}
\]

Minimize \(D\) (modify \(x,y,z\) + Thermal p’s)

\[
\frac{\partial D}{\partial p} \sim \frac{\Delta D}{\Delta p}
\]

**Fourier**

\[
\rho(xyz) = \frac{1}{V} \sum_{h=\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| \cos 2\pi (hx + ky + lz - \alpha_{hkl})
\]

\[
\alpha_{hkl} = \tan^{-1}\left(\frac{\sum_j f_j \sin 2\pi (hx_j + ky_j + lz_j)}{\sum_j f_j \cos 2\pi (hx_j + ky_j + lz_j)}\right)
\]

Modify phase angle

atom (i)

Guess?
The Model

- Unit Cell/Symmetry/Coordinates

  _symmetry_cell_setting: Monoclinic
  _symmetry_space_group_name_H-M: P2(1)/c
  _cell_length_a: 11.379(11)
  _cell_length_b: 39.43(3)
  _cell_length_c: 9.824(8)
  _cell_angle_alpha: 90.00
  _cell_angle_beta: 109.87(3)
  _cell_angle_gamma: 90.00

  ATOM Element  X         Y         Z     Thermal P.
  F1A  F  -0.4863(6)  0.09196(14)  1.2353(7)  0.084(2)
  F2A  F   0.4873(6)  0.07626(13)  0.6898(7)  0.072(2)
  O1A  O   0.3271(8)  0.03134(15)  1.1028(9)  0.067(3)
  O2A  O  -0.0537(7)  0.03345(15)  1.2981(8)  0.057(2)
  ....
Summary

- Crystal – periodicity
  - Reduce $N \times 10^{20}$ $\rightarrow$ $N$ problem
- Lattice/Symmetry describes the periodicity
  - Visual and Mathematical
- Scattered X-rays describe the atomicity
  - $\text{Intensity} \sim e^{- \text{density}} [\rho(xyz)] \quad |F(hkl)| \sim \sqrt{I(hkl)}$
- A Model is fit (L.S.) to the $\rho(xyz)$ map.
  - Minimize the difference between the observed $F(hkl)$ and the calculated $F(hkl)$.
- Report the Model
How do you learn more?

• Books ..
  – “Crystal Structure Determination”
    • Werner Massa : ISBN-10: 3540206442
  – “Crystal Structure Analysis: Principles and Practice ”
  – “Crystal Structure Refinement: a crystalloigrapher’s guide to SHELXL”

• On – line ..
  – xray.tamu.edu/courses ...
    • Eight full lectures for Single-Crystal
    • Eight full lectures for Powder Diffraction