X-ray Diffraction

Interaction of Waves
Reciprocal Lattice and Diffraction
X-ray Scattering by Atoms
The Integrated Intensity
Basic Principles of Interaction of Waves

Periodic waves characteristic:

- Frequency $\nu$: number of waves (cycles) per unit time $- \nu =$ cycles/time. $[\nu] = \text{1/sec} = \text{Hz}.$
- Period $T$: time required for one complete cycle $- T = \text{1}/\nu =$ time/cycle. $[T] = \text{sec}.$
- Amplitude $A$: maximum value of the wave during cycle.
- Wavelength $\lambda$: the length of one complete cycle. $[\lambda] = \text{m, nm, Å}.$

$$ E(t, x) = A \exp( kx - \omega t) $$
$$ = A \exp 2\pi \nu \left( \frac{x}{c} - t \right) = A \exp 2\pi \left( \frac{x}{\lambda} - \nu t \right) $$

$\omega = 2\pi \nu, \quad k = \frac{2\pi}{\lambda}$
Basic Principles of Interaction of Waves

- Consider two waves with the same wavelength and amplitude but displaced a distance $x_0$.
- The phase shift:
  \[ \varphi = 2\pi \left( \frac{x_0}{\lambda} \right) \]

\[ E_1(t) = A \exp(\omega t) \]

\[ E_1(t) = A \exp(\omega t + \varphi) \]

Waves #1 and #2 are 90° out of phase

Waves #1 and #2 are 180° out of phase

When similar waves combine, the outcome can be constructive or destructive interference
Superposition of Waves

- Resulting wave is algebraic sum of the amplitudes at each point

Small difference in phase

Large difference in phase
Superposition of Waves

- Thomas Young's diagram of double slit interference (1803)

The angular spacing of the fringes is given by
\[ \theta_f \approx \frac{\lambda}{d} , \quad \text{where} \quad \theta_f \ll 1 \]
The discovery of X-ray diffraction and its use as a probe of the structure of matter

- The reasoning: x-rays have a wavelength similar to the interatomic distances in crystals, and as a result, the crystal should act as a diffraction grating.

- 1911, von Laue suggested to one of his research assistants, Walter Friedrich, and a doctoral student, Paul Knipping, that they try out x-rays on crystals.

- April 1912, von Laue, Friedrich and Knipping had performed their pioneering experiment on copper sulfate.

Max von Laue

First diffraction pattern from NaCl crystal
The discovery of X-ray diffraction and its use as a probe of the structure of matter

- They found that if the interatomic distances in the crystal are known, then the wavelength of the X-rays can be measured, and alternatively, if the wavelength is known, then X-ray diffraction experiments can be used to determine the interplanar spacings of a crystal.

- The three were awarded Nobel Prizes in Physics for their discoveries.

Friedrich & Knipping's improved set-up

ZnS Laue photographs along four-fold and three-fold axes
The Laue Equations

- If an X-ray beam impinges on a row of atoms, each atom can serve as a source of scattered X-rays.
- The scattered X-rays will reinforce in certain directions to produce zero-, first-, and higher-order diffracted beams.
The Laue Equations

- Consider 1D array of scatterers spaced $a$ apart.
- Let x-ray be incident with wavelength $\lambda$.

\[ a(\cos \alpha - \cos \alpha_0) = h\lambda \]

- In 2D and 3D:
  \[ \begin{align*}
  &a(\cos \alpha - \cos \alpha_0) = h\lambda \\
  &b(\cos \beta - \cos \beta_0) = k\lambda \\
  &c(\cos \gamma - \cos \gamma_0) = l\lambda
  \end{align*} \]

The equations must be satisfied simultaneously, it is in general difficult to produce a diffracted beam with a fixed wavelength and a fixed crystal.
Lattice Planes

\(a\) \hspace{1cm} \(b\)

(11) \hspace{1cm} (21) \hspace{1cm} (41)

(10) \hspace{1cm} (13)
Bragg’s Law

\[ AB + BC = 2d \sin \theta \]
Bragg’s Law

If the path $AB + CD$ is a multiple of the x-ray wavelength $\lambda$, then two waves will give a constructive interference:

$$n\lambda = AB + CD = 2d \sin \theta$$

The diffracted waves will interfere destructively if equation is not satisfied.

Equation is called the Bragg equation and the angle $\theta$ is the Bragg angle.
Bragg’s Law

- The incident beam and diffracted beam are always coplanar.
- The angle between the diffracted beam and the transmitted beam is always $2\theta$.

Since $\sin \theta \leq 1$: \[ \frac{n\lambda}{2d} = \sin \theta \leq 1 \]

For $n = 1$: \[ \lambda \leq 2d \]

For most crystals $d \sim 3 \text{ Å} \quad \rightarrow \quad \lambda \leq 6 \text{ Å}$

UV radiation $\lambda \approx 500 \text{ Å}$

Cu $K\alpha_1$ $\lambda = 1.5406 \text{ Å}$

Rewrite Bragg’s law:

$\lambda = 2d \sin \theta \rightarrow \lambda = 2d' \sin \theta \quad \rightarrow \quad \lambda = 2d \sin \theta$

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

\[
d_{100} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a
\]

\[
d_{200} = \frac{a}{\sqrt{2^2 + 0 + 0}} = \frac{1}{2} a
\]
Reciprocal lattice and Diffraction

It is equivalent to the Bragg law since

\[ |s - s_0| = 2 \sin \theta \]

\[ \frac{|s - s_0|}{\lambda} = \frac{2 \sin \theta}{\lambda} = \frac{|d^*_{hkl}|}{d_{hkl}} = \frac{1}{d_{hkl}} \]

\[ \lambda = 2d_{hkl} \sin \theta \]
Reciprocal lattice and Diffraction

\[ \left| \frac{s - s_0}{\lambda} \right| = \frac{2 \sin \theta}{\lambda} = |d_{hkl}^*| = \frac{1}{d_{hkl}} \]
Sphere of Reflection – Ewald Sphere

\[ |\mathbf{OC}| = \frac{1}{\lambda} \sin \theta = \frac{1}{2} \left| \mathbf{d}_{hkl}^* \right| = \frac{1}{2d_{hkl}} \rightarrow \lambda = 2d_{hkl} \sin \theta \]

\[ |\mathbf{OB}| = d_{hkl}^* \]

Incident beam

1/\lambda

\theta

Crystal at the centre of the sphere

Diffracted beam

Origin of the reciprocal lattice

Reflecting sphere
Sphere of Reflection – Ewald Sphere

- 201 Reflected beam
- Incident beam
- Reflecting sphere

Trace of (201) plane

Non-diametral section of the reflecting sphere
Silicon lattice constant:
\( a_{\text{Si}} = 5.43 \text{ Å} \)

X-ray wavelength:
\( \lambda = 1.5406 \text{ Å} \)

For cubic crystal:
\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

Bragg’s law:
\[ 2d \sin \theta = n\lambda \]
Two perovskites: \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \)

**Differences:**
- Peak position – d-spacing.
- Peak intensity – atom type: Ca vs Sr.

\[ a_{\text{STO}} = 3.905 \text{ Å} \]
\[ a_{\text{CTO}} = 3.795 \text{ Å} \]
Scattering by an Electron

- Elementary scattering unit in an atom is electron
- Classical scattering by a single free electron – Thomson scattering equation:

\[ I = I_0 \frac{e^4}{m^2c^4R^2} \left( \frac{1 + \cos^2 2\theta}{2} \right) \]

The polarization factor of an unpolarized primary beam

\[ \frac{e^4}{m^2c^4} = 7.94 \times 10^{-26} \text{ cm}^2 \]

If \( R = \text{few cm} \):

\[ \frac{I}{I_0} \approx 10^{-26} \]

1 mg of matter has \( \sim 10^{20} \) electrons

Another way for electron to scatter is manifested in Compton effect.

Cullity p.127
Scattering by an Atom

Atomic Scattering Factor

\[ f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}} \]
Scattering by an Atom

- Scattering by a group of electrons at positions $r_n$:

Scattering factor per electron:

$$ f_e = \int \exp[(2\pi i / \lambda)(s - s_0) \cdot r] \rho dV $$

Assuming spherical symmetry for the charge distribution $\rho = \rho(r)$ and taking origin at the center of the atom:

$$ f_e = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin kr}{kr} dr $$

For an atom containing several electrons:

$$ f = \sum_n f_e n = \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) \frac{\sin kr}{kr} dr $$

$$ k = \frac{4\pi \sin \theta}{\lambda} $$

$f$ – atomic scattering factor

Calling $Z$ the number of electrons per atom we get:

$$ \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) dr = Z $$
Scattering by an Atom

The atomic scattering factor $f = Z$ for any atom in the forward direction ($2\theta = 0$):

$I(2\theta=0) = Z^2$

As $\theta$ increases $f$ decreases → functional dependence of the decrease depends on the details of the distribution of electrons around an atom (sometimes called the form factor)

$f$ is calculated using quantum mechanics
Electron vs nuclear density

Powder diffraction patterns collected using Mo Kα radiation and neutron diffraction
Scattering by an Atom

Atomic Scattering Factors*

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Scattering by a Unit Cell

For atoms A & C

\[ \delta_{21'} = MCN = 2d_{h00} \sin \theta = \lambda \]
\[ d_{h00} = AC = \frac{a}{h} \]

For atoms A & B

\[ \delta_{31'} = RBS = \frac{AB}{AC} \]
\[ MCN = \frac{AB}{AC} \lambda = \frac{x}{a / h} \lambda \]

phase \[ \phi = 2\pi \frac{\delta}{\lambda} \]

\[ \phi_{31'} = 2\pi \frac{\delta_{31'}}{\lambda} = \frac{2\pi hx}{a} \]

If atom B position: \[ u = x / a \]

\[ \phi_{31'} = \frac{2\pi hx}{a} = 2\pi hu \]

For 3D: \[ \phi = 2\pi(hu + kv + lw) \]

\[ F_{hkl} = \frac{\text{amplitude scattered by atoms in unit cell}}{\text{amplitude scattered by single electron}} \]
Scattering by a Unit Cell

We can write:

\[ Ae^{i\phi} = fe^{2\pi i(hu+kv+lw)} \]

\[ F = f_1e^{i\phi_1} + f_2e^{i\phi_2} + f_3e^{i\phi_3} + \ldots \]

\[ F = \sum_{1}^{N} f_n e^{i\phi_n} = \sum_{1}^{N} f_n e^{2\pi i(hu_n+kv_n+lw_n)} \]

\[ I \propto F_{hkl} F_{hkl}^* = |F_{hkl}|^2 \]
Scattering by a Unit Cell

Examples

Unit cell has one atom at the origin

\[ F = fe^{2\pi i 0} = f \]

In this case the structure factor is independent of \( h, k \) and \( l \); it will decrease with \( f \) as \( \sin\theta/\lambda \) increases (higher-order reflections)
Scattering by a Unit Cell

Examples

Unit cell is base-centered

\[ F = f e^{2\pi i 0} + f e^{2\pi i (h/2+k/2)} = f \left(1 + e^{\pi i (h+k)}\right) \]

\[ F = 2f \quad h \text{ and } k \text{ unmixed} \]

\[ F = 0 \quad h \text{ and } k \text{ mixed} \]

(200), (400), (220) \(\cdots\) \(\Rightarrow\) \(|F_{hkl}|^2 = 4f^2\)

(100), (121), (300) \(\cdots\) \(\Rightarrow\) \(|F_{hkl}|^2 = 0\) \(\text{“forbidden” reflections}\)
Body-Centered Unit Cell

Examples

For body-centered cell

\[ F = f e^{2\pi i (h+0+k+0+l+0)} + f e^{2\pi i (h/2+k/2+l/2)} = f \left( 1 + e^{\pi i (h+k+l)} \right) \]

\[ F = 2f \quad \text{when } (h + k + l) \text{ is even} \]

\[ F = 0 \quad \text{when } (h + k + l) \text{ is odd} \]

(200), (400), (220) \( \cdots \) \( \Rightarrow \) \( |F_{hkl}|^2 = 4f^2 \)

(100), (111), (300) \( \cdots \) \( \Rightarrow \) \( |F_{hkl}|^2 = 0 \) \( \text{"forbidden" reflections} \)
Body-Centered Unit Cell

Examples

For body centered cell with different atoms:

\[ F = f_{Cl}e^{2\pi i(h+0+k+0+l)} + f_{Cs}e^{2\pi i(h/2+k/2+l/2)} \]

\[ = f_{Cl} + f_{Cs}e^{\pi i(h+k+l)} \]

\[ F = f_{Cl} + f_{Cs} \quad \text{when} \ (h + k + l) \ \text{is even} \]

\[ F = f_{Cl} - f_{Cs} \quad \text{when} \ (h + k + l) \ \text{is odd} \]

(200), (400), (220) \ \Rightarrow \ \left| F_{hkl} \right|^2 = (f_{Cs} + f_{Cl})^2

(100), (111), (300) \ \Rightarrow \ \left| F_{hkl} \right|^2 = (f_{Cs} - f_{Cl})^2
The fcc crystal structure has atoms at 000, \( \frac{1}{2} \frac{1}{2} 0 \), \( \frac{1}{2} 0 \frac{1}{2} \) and \( 0 \frac{1}{2} \frac{1}{2} \):

\[
F_{hkl} = \sum_{1}^{N} f_{n} e^{2\pi i (h u_{n} + k v_{n} + l w_{n})} = f \left( 1 + e^{\pi i (h+k)} + e^{\pi i (h+l)} + e^{\pi i (k+l)} \right)
\]

- If \( h, k \) and \( l \) are all even or all odd numbers ("unmixed"), then the exponential terms all equal to +1 \( \Rightarrow F = 4f \)
- If \( h, k \) and \( l \) are mixed even and odd, then two of the exponential terms will equal -1 while one will equal +1 \( \Rightarrow F = 0 \)

\[
|F_{hkl}|^2 = \begin{cases} 
16f^2, & h, k \text{ and } l \text{ unmixed even and odd} \\
0, & h, k \text{ and } l \text{ mixed even and odd}
\end{cases}
\]
The Structure Factor

\[ F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (h\alpha_n + k\beta_n + l\gamma_n)} \]

\[ F_{hkl} = \frac{\text{amplitude scattered by all atoms in a unit cell}}{\text{amplitude scattered by a single electron}} \]

- The structure factor contains the information regarding the types \( f \) and locations \( u, v, w \) of atoms within a unit cell.
- A comparison of the observed and calculated structure factors is a common goal of X-ray structural analyses.
- The observed intensities must be corrected for experimental and geometric effects before these analyses can be performed.
Integrated Intensity

Peak intensity depends on
- Structural factors: determined by crystal structure
- Specimen factors: shape, size, grain size and distribution, microstructure
- Instrumental factors: radiation properties, focusing geometry, type of detector

We can say that: \( I(q) \propto |F(q)|^2 \)
Integrated Intensity

\[ I_{hkl}(q) = K \times p_{hkl} \times L \times P \times A \times T \times E_{hkl} \times |F(q)|^2 \]

\( K \) – scale factor, required to normalize calculated and measured intensities.

\( p_{hkl} \) – multiplicity factor. Accounts for the presence of symmetrically equivalent points in reciprocal lattice.

\( L \) – Lorentz multiplier, defined by diffraction geometry.

\( P \) – polarization factor. Account for partial polarization of electromagnetic wave.

\( A \) – absorption multiplier. Accounts for incident and diffracted beam absorption.

\( T_{hkl} \) – preferred orientation factor. Accounts for deviation from complete random grain distribution.

\( E_{hkl} \) – extinction multiplier. Accounts for deviation from kinematical diffraction model.

\( F_{hkl} \) – the structure factor. Defined by crystal structure of the material.
The Multiplicity Factor

- The multiplicity factor arises from the fact that in general there will be several sets of \( hkl \)-planes having different orientations in a crystal but with the same \( d \) and \( F^2 \) values.
- Evaluated by finding the number of variations in position and sign in \( \pm h, \pm k \) and \( \pm l \) and have planes with the same \( d \) and \( F^2 \).
- The value depends on \( hkl \) and crystal symmetry.
- For the highest cubic symmetry we have:

\[
\begin{align*}
100, & \quad \bar{1}00, 010, 0\bar{1}0, 001, 00\bar{1} \\
110, & \quad \bar{1}10, 1\bar{1}0, \bar{1}\bar{1}0, 101, 10\bar{1}, \bar{1}0\bar{1}, \bar{1}01, 011, 0\bar{1}1, 01\bar{1}, 0\bar{1}\bar{1} \\
111, & \quad 11\bar{1}, 1\bar{1}1, \bar{1}11, 1\bar{1}1, \bar{1}\bar{1}1, \bar{1}1\bar{1}, 1\bar{1}\bar{1}, \bar{1}\bar{1}\bar{1}
\end{align*}
\]

\( p_{100} = 6 \) 
\( p_{110} = 12 \) 
\( p_{111} = 8 \)
The Polarization Factor

- The polarization factor $p$ arises from the fact that an electron does not scatter along its direction of vibration.
- In other directions electrons radiate with an intensity proportional to $(\sin \alpha)^2$:

\[ p = \frac{1 + \cos^2 2\theta}{2} \]

The polarization factor (assuming that the incident beam is unpolarized):
The Lorentz-Polarization Factor

- The Lorenz factor $L$ depends on the measurement technique used and, for the diffractometer data obtained by the usual $\theta$-2$\theta$ or $\omega$-2$\theta$ scans, it can be written as

$$L = \frac{1}{\sin \theta \sin 2\theta} = \frac{1}{\cos \theta \sin^2 \theta}$$

- The combination of geometric corrections are lumped together into a single Lorentz-polarization ($LP$) factor:

$$LP = \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta}$$

The effect of the $LP$ factor is to decrease the intensity at intermediate angles and increase the intensity in the forward and backwards directions.
The Absorption Factor

- Angle-dependent absorption within the sample itself will modify the observed intensity.

- Absorption factor for infinite thickness specimen is:
  \[ A = \frac{\mu}{2} \]

- Absorption factor for thin specimens is given by:
  \[ A = 1 - \exp\left( -\frac{2\mu t}{\sin \theta} \right) \]

where \( \mu \) is the absorption coefficient, \( t \) is the total thickness of the film.
The Extinction Factor

- Extinction lowers the observed intensity of very strong reflections from perfect crystals

In powder diffraction usually this factor is smaller than experimental errors and therefore neglected.
The Temperature Factor

As atoms vibrate about their equilibrium positions in a crystal, the electron density is spread out over a larger volume. This causes the atomic scattering factor to decrease with $\sin \theta / \lambda$ (or $|S| = 4\pi \sin \theta / \lambda$) more rapidly than it would normally:

The temperature factor is given by:

$$-B \frac{\sin^2 \theta}{\lambda^2}$$

where the thermal factor $B$ is related to the mean square displacement of the atomic vibration:

$$B = 8\pi^2 \times \overline{u^2}$$

This is incorporated into the atomic scattering factor:

$$f \rightarrow f_0 e^{-M} \Rightarrow f^2 \sim e^{-2M}$$
Diffracted Beam Intensity

\[ I \propto F_{hkl} F_{hkl}^* = |F_{hkl}|^2 \]

\[ I_C(q) = K A p(LP)|F(q)|^2 + I_b \]

where \( K \) is the scaling factor, \( I_b \) is the background intensity, \( q = 4\sin \theta / \lambda \) is the scattering vector for x-rays of wavelength \( \lambda \).

For thin films:

\[ I_C(q) = K \left[ 1 - \exp \left( -\frac{2\mu t}{\sin \theta} \right) \right] \frac{1 + \cos^2 \theta}{\cos \theta \sin^2 \theta} |F(q)|^2 + I_b \]