Analytical Methods for Materials

Lesson 16
Scattering and Diffraction Analysis of Materials

Suggested Reading
Chapter 3 in Waseda, pp. 67-75

Visible Light: $\lambda \approx 6000 \text{ Å}$
X-rays: $\lambda \approx 0.5 – 2.5 \text{ Å}$
Electrons: $\lambda \approx 0.05 \text{ Å}$

Spectrum of electromagnetic (EM) radiation as a function of frequency (s$^{-1}$) and wavelength (nm).

Self-propagating waves with perpendicular electric and magnetic components
Properties of Electromagnetic Waves

Consist of discrete particles of energy called *photons*.

Photons interact with electrons.

Thus they can be “scattered” by solids.

\[
E = \text{photon of energy} = h\nu = \frac{hc}{\lambda}
\]

\[
h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{J} \cdot \text{s}
\]

\[
\nu = \text{frequency of the wave}
\]

\[
c = \text{speed of light} = 3.00 \times 10^8 \text{m/s}
\]

\[
\lambda = \text{wavelength of radiation}
\]
Scattering of EM Radiation by Crystals

• For a material to yield a diffraction pattern, $\lambda_{\text{EM rad.}} \leq d_{\text{hkl}}$.

• This limits us to using:
  – Neutrons
  – Electrons
  – X-rays → Let’s focus on these for right now

• X-ray scattering (i.e., absorption + re-emission):
  – Elastic (little or no energy loss → diffraction peak)
  – Inelastic (energy loss → no diffraction peak)
X-ray Powder Diffractometer

• Used to assess the crystal structure of a material. How X-rays diffract is sensitive to atom locations in a unit cell.

• Variations on basic equipment are used to assess:
  – Single crystal orientation
  – Polycrystalline orientations (i.e., texture)
  – Residual stresses
  – Thin film epitaxy
  – Etc…
Geometry of the X-ray Diffractometer

- Generically, diffractometers consist of:
  - X-ray source
  - X-ray detector
  - Specimen to be examined
  - Other things
    - Monochromators
    - Filters
    - Slits
    - Etc…


**Fig. 5.5** The geometry of the diffractometer arrangement: DS is the divergence slit, SS is the scatter slit, RS is the receiving slit, So is the soller slit.
Laue’s Equations

• When scattering occurs there is a change in the path of the incident radiation.

\[ \delta_n = \text{path difference between incident and scattered beams} \]
\[ = n\lambda \text{ where } n \text{ is an integer} \]

\[ \delta_x = a(\cos \alpha - \cos \alpha_o) = a(S - S_o) = h\lambda \]
\[ \delta_y = b(\cos \beta - \cos \beta_o) = b(S - S_o) = k\lambda \]
\[ \delta_z = c(\cos \gamma - \cos \gamma_o) = c(S - S_o) = l\lambda \]

[\(h, k, l\) are integers]

• Constructive interference occurs when all three equations are satisfied simultaneously.
Bragg’s Law

\[ \delta = \text{path difference} = AB + BC = 2d \sin \theta \]

\[
\therefore
\]
Bragg's Law

\[ \delta = \text{path difference} = AB + BC = 2d \sin \theta \]

For constructive interference \( \delta = n\lambda \)

\[ \therefore \]

\[ \delta = 2d \sin \theta = n\lambda \]

\[ d_{hkl} = \frac{d}{n} \]

\[ \lambda = 2d_{hkl} \sin \theta \text{ (or } n\lambda = 2d \sin \theta) \]
Bragg’s Law

- Bragg’s law can be expressed in vector form:

\[ S - S_o = 2 \sin \theta = \lambda d_{hkl}^* \]

\[ |d_{hkl}^*| = \frac{1}{d_{hkl}} \]

- Thus:

\[ \frac{S - S_o}{\lambda} = d_{hkl}^* = ha^* + kb^* + lc^* \]

- This tells us that constructive interference occurs when \( S - S_o \) coincides with the reciprocal lattice vector of the reflecting planes.
Laue’s Equations and the Reciprocal Lattice

- Can represent the Laue equation (i.e., diffraction) graphically.

- This is similar to Ewald’s sphere.

- For diffraction to be observed (i.e. Bragg’s law satisfied) \( S \) must end on a reciprocal lattice point.

- Point’s satisfying this criteria represent planes that are oriented for diffraction.

- Bragg’s law, which describes diffraction in terms of scalars, is generally used for convenience.

\[
d_{hkl}^* = \frac{S - S_o}{\lambda}
\]
Limiting sphere
RADIUS = 2So/λ

Reflecting sphere

To satisfy Bragg’s law

\[
\frac{S_o}{\lambda} + d^*_{hkl} = \frac{S}{\lambda}
\]

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

\[
|d^*_{hkl}| = |g| = \frac{1}{d} = \frac{2\sin \theta}{n\lambda}
\]
Reciprocal Lattice

• The lattice constructed from all diffraction vectors (i.e., \( g \)) for a crystal defines possible Bragg reflections.

• Points that intersect the reflecting sphere will satisfy Bragg's law.

• Changes in wavelength (\( \lambda \)) changes the circle radius, which can lead to diffraction. However, we generally do not change \( \lambda \).
Reciprocal Lattice

- A change in orientation of the incident beam relative to the crystal changes the orientation of the reciprocal lattice, reflecting sphere, and limiting sphere.

- Change will eventually yield a condition where diffraction is possible.

- We mentioned this a few lectures ago.
X-ray Diffractometer

• X-ray source is generally fixed.

• Rotate sample and detector to adjust $\theta/2\theta$.

• On instruments such as our Bruker D8 and Philips MPD, the source and detector move while the sample remains stationary.
Diffraction Directions

- We can determine which reflections are allowed by combining Bragg’s law with the interplanar spacing equations for a crystals.

- **Cubic:**

\[
\lambda = 2d \sin \theta \\
\frac{1}{d^2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right) \\
\sin^2 \theta = \frac{\lambda^2}{4a^2} \left(h^2 + k^2 + l^2\right)
\]

- This equation predicts, for a particular incident \(\lambda\) and a particular cubic crystal of unit cell size \(a\), all of the possible Bragg angles for the diffracting planes \((hkl)\)
Diffraction Directions – cont’d

• Example:
  What are the possible Bragg angles for \{111\} planes in a cubic crystal?

• Solution:

\[
\sin^2 \theta_{111} = \frac{\lambda^2}{4a^2} \left( 1^2 + 1^2 + 1^2 \right) = \frac{3\lambda}{4a^2}
\]
Diffraction Directions

- What about other systems?

- Tetragonal:

\[
\lambda = 2d \sin \theta \\
\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \\
\sin^2 \theta = \frac{\lambda^2}{4a^2} \left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right)
\]

- Solution: must know \(c\) and \(a\). Will be one peak.

- What about \{110\}?

I’ve intentionally given you a family here
• In powder diffraction you generate an infinite number of randomly oriented, but identical, reciprocal lattice vectors.
• They form circles with their ends placed on the surface of Ewald’s sphere.
• They produce powder diffraction cones at different Bragg angles (see the next slide).

\[ |\mathbf{R}^*| = |\mathbf{g}| = d_{\text{hkl}}^* = \frac{1}{d_{\text{hkl}}} \]

Figure 8.2

Diffraction cone

Ewald sphere

X-ray

$\frac{S}{\lambda}$

$\frac{S_o}{\lambda}$

$2\theta$
Diffraction cone and diffraction vector cone illustrated on the Ewald sphere.

Diffraction cone and diffraction vector cone illustrated on the Ewald sphere.

*Adapted from B.B. He, Two-Dimensional X-ray Diffraction, Wiley (2009), p. 20.*
X-ray diffraction patterns: (a) from single crystal, (b) Laue diffraction pattern from single crystal, (c) diffraction cones from polycrystalline solid, and (d) diffraction frame from a polycrystalline solid. (a) and (c) from B.B. He, *Two-Dimensional X-ray Diffraction*, Wiley (2009), p. 22. (d) from Photonic Science (http://photonic-science.co.uk).
Figure 2.11 Formation of a single crystal diffraction pattern in transmission electron microscopy. The short wavelength of electrons makes the Ewald sphere flat. Thus, the array of reciprocal lattice points in a reciprocal plane touches the sphere surface and generates a diffraction pattern on the TEM screen. Adapted from Y. Leng, *Materials Characterization*, Wiley (2008), p. 55.
In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point.

This gives the appearance of a discrete diffraction peak.

Synopsis

• The Ewald sphere construction allows us to represent Bragg diffraction graphically relative to the reciprocal lattice.

• Reciprocal lattice points lying on the Ewald sphere satisfy Bragg’s law yielding strong diffraction spots/peaks.