Reciprocal Lattices and Diffraction

Suggested Reading
Appendix A from Cullity & Stock
Many physical properties of crystals as well as the geometry of the three-dimensional patterns resulting from a diffraction event are most easily represented using the concept of the reciprocal lattice!

Diffraction occurs in inverse proportion to the spacing between objects causing diffraction
Reciprocal Lattice

• Vector representation of directions and interplanar spacing of diffracting planes.

• Real Space:
  
  – $a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$

• Reciprocal Space: (just another type of lattice)
  
  – $a^*$, $b^*$, $c^*$, $\alpha^*$, $\beta^*$, $\gamma^*$
Reciprocal Lattice (FCC)
Recall simple vector operations

• Dot product (scalar product):
  \[ x \cdot y = |x||y| \cos \alpha \]

\[ \frac{\sqrt{h^2 + k^2 + l^2}}{\sqrt{h^2 + k^2 + l^2}} \]

• Cross product (vector product):
  \[ x \times y = z = |x||y| \sin \alpha \]

\[ z \text{ is the direction } \perp x-y \text{ plane} \]
Useful Properties of the reciprocal lattice

\[ |c^*| = \frac{(a \times b)}{c \cdot (a \times b)} \]

\[ = \frac{\text{area of base}}{\text{unit cell volume}} \]

\[ = 1 \]

\[ = \frac{1}{\text{height}} \]

\[ = \frac{1}{d_{001}} \]

For orthogonal crystals,

\[ \frac{1}{d_{001}} = c^* = \frac{1}{c} \]
We can define reciprocal lattices

- For an arbitrary lattice \([a \neq b \neq c \text{ and } \alpha \neq \beta \neq \gamma (\neq 90^\circ)]\) in real space.

\[
a^* = \frac{(b \times c)}{a \cdot (b \times c)} = \frac{(b \times c)}{V} \]
\[
b^* = \frac{(c \times a)}{b \cdot (c \times a)} = \frac{(c \times a)}{V} \]
\[
c^* = \frac{(a \times b)}{c \cdot (a \times b)} = \frac{(a \times b)}{V} \]

\[V \equiv \text{unit cell volume} = a \cdot (b \times c) = b \cdot (c \times a) = c \cdot (a \times b)\]

\(a^* \perp bc\) plane in real space; it is the reciprocal lattice vector for \(a\)

\(b^* \perp ac\) plane in real space; it is the reciprocal lattice vector for \(b\)

\(c^* \perp ab\) plane in real space; it is the reciprocal lattice vector for \(c\)
Useful Properties of the reciprocal lattice – cont’d

\[ a^* = \frac{1}{d_{100}} = \frac{1}{a} = a^*; \]
\[ b^* = \frac{1}{d_{010}} = \frac{1}{b} = b^*; \]
\[ c^* = \frac{1}{d_{001}} = \frac{1}{c} = c^*; \]

For orthogonal crystals

\[ \cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \]
\[ \cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \gamma \sin \alpha} \]
\[ \cos \alpha^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \]
Relationship between real and reciprocal

In orthogonal real lattices

\((a = b = c \text{ and } \alpha = \beta = \gamma (= 90^\circ))\)

\[ a^* \perp a; \quad b^* \perp b; \quad c^* \perp c \]

Not necessarily so in non-orthogonal lattices

We can draw an analogy between reciprocal and real lattices:

\[ r_{uvw} = ua + vb + wc \]

We use this to build a real lattice from unit cells

\[ r_{hkl}^* = ha^* + kb^* + lc^* \]

We can use this to build a reciprocal lattice
Construction of a 2D reciprocal lattice

(a) draw the plane lattice and mark the unit cell

Construction of a 2D reciprocal lattice


(b) draw lines perpendicular to the two sides of the unit cell to give the axial directions of the reciprocal lattice basis vectors.
Construction of a 2D reciprocal lattice


What you’re doing first is finding the spacing between the planes making up the unit cell sides.

(c) determine the perpendicular distances from the origin of the direct lattice to the end faces of the unit cell, $d_{10}$ and $d_{01}$, and take the inverse of these distances, $1/d_{10}$ and $1/d_{01}$, as the reciprocal lattice axial lengths, $a^*$ and $b$. 
Construction of a 2D reciprocal lattice


\[
\frac{1}{d_{01}} = a^* \quad \text{and} \quad b^* = 1/d_{01}
\]

Draw reciprocal lattice using axes
\[a^* = 1/d_{10} \quad \text{and} \quad b^* = 1/d_{01}\]

Take reciprocals to get reciprocal lattice parameters.

(d) mark the lattice points at the appropriate reciprocal distances, and complete the lattice.
Every point on a reciprocal lattice represents a set of planes in the real space crystal!

The vector joining the origin of the reciprocal lattice to a lattice point \( hk \) is perpendicular to the \((hk)\) planes in the real lattice and of length \( 1/d_{hk} \).
Construction of a 3D reciprocal lattice

Figure 2.10 The construction of a reciprocal lattice: (a) the a-c section of the unit cell in a monoclinic (mP) direct lattice; (b) reciprocal lattice aces lie perpendicular to the end faces of the direct cell; (c) reciprocal lattice points are spaced $a^* = 1/d_{100}$ and $c^* = 1/d_{001}$; (d) the lattice plane is completed by extending the lattice; (e) the reciprocal lattice is completed by adding layers above and below the first plane.


Just like 2-D
Cubic Reciprocal Lattice

- Every point on a reciprocal lattice represents a set of planes in the real space crystal!
- Reciprocal lattice vectors are 90° away from real space planes!
Importance of Reciprocal Space

• When a diffraction event occurs, the diffracted waves/pattern will “match” the reciprocal lattice.

► Radiation ‘scatters’ in inverse proportion to the spacings between diffraction centers (i.e., planes in crystals).

• We make the use of this fact in x-ray diffraction and transmission electron microscopy.
Why use reciprocal space

• **Bragg’s Law:** (Defines conditions where a crystal is oriented for coherent scattering)

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

We can combine \( n \) and \( d \) as follows:

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

This allows us to write Bragg's Law as:

\[ \lambda = 2d_{hkl} \sin \theta_{hkl} \]

\[ \sin \theta_{hkl} = \frac{\lambda / 2}{d_{hkl}} = \frac{1}{\frac{2}{\lambda}} = \frac{\text{opposite}}{\text{hypotenuse}} \]

(Simple geometric proof on vg #226)
\[
\sin \theta_{hkl} = \frac{\lambda}{2d_{hkl}} = \frac{1}{2d_{hkl}} = \frac{\text{opposite}}{\text{hypotenuse}} = \frac{BC}{AC}
\]

**Ewald Sphere Construction**

**Reflection or Ewald sphere**

**Limiting sphere**

**CRITICAL**
Only lattice points lying within the limiting sphere can diffract. Points lying on the Ewald sphere will satisfy the Bragg condition.

See this web site for an explanation and example
http://www.msm.cam.ac.uk/doitpoms/tlplib/xray-diffraction/ewald.php
**Ewald’s Sphere Construction**

- Graphical representation of Bragg’s Law in reciprocal space.

\[ \frac{s}{\lambda} = \frac{s - s_o}{\lambda} = g = d_{hkl}^* \]

- Consider incident waves of radiation (i.e., X-rays) moving in a direction \( s_o \), "reflecting" off of crystallographic planes in a direction \( s \).
- Let point O represent the origin of the reciprocal lattice.
- Draw a circle of radius \( 1/\lambda \) w/ center, A, on CO but passing through O.
- Rotation of crystal rotates the reciprocal lattice about O. This will bring different reciprocal lattice points into contact w/ Ewald’s sphere.

\( g \) is the diffraction vector.
To satisfy Bragg’s Law:

\[
\frac{(s - s_o)}{\lambda} = 2 \sin \theta
\]

\[
\frac{s - s_o}{\lambda} = d_{hkl}^* = \frac{1}{d_{hkl}}
\]

\[
\sin \theta = \frac{1}{2} \frac{d_{hkl}}{\lambda} \quad \text{← Bragg's Law}
\]

- Size of sphere corresponds to wavelength of radiation used (see next page).
- Rotation of the crystal will cause points to lie on the sphere.
- When points lie on the sphere, Bragg’s law is satisfied!
\[
\sin \theta = \frac{OB}{CO} = \frac{OB}{2 / \lambda}
\]

Which can be re-written as:

\[
2 \frac{1}{OB} \sin \theta = \lambda
\]

Since \(B\) is a reciprocal lattice point:

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

\[
\therefore \frac{1}{OB} = d_{hkl} \text{ and } 2d_{hkl} \sin \theta = \lambda
\]

[Bragg’s Law]

- Size of sphere corresponds to wavelength of radiation used (see next page).
- Rotation of the crystal will cause points to lie on the sphere.
- When points lie on the sphere, Bragg’s law is satisfied!
If you change $\lambda$, you change the radius of the Ewald’s sphere.

This is how the Laue technique works.

Diffractometers generally use fixed $\lambda$ and variable $\theta$.

Diffractometers generally use fixed $\lambda$ and variable $\theta$. 

Increasing diffraction angle
Synopsis

1. The reciprocal lattice allows us to compute the spacing between successive lattice planes in a crystal lattice.

2. The reciprocal lattice vector $d_{hkl}^*$ with components $(hkl)$ is perpendicular to the plane with Miller indices $(hkl)$.

3. The length of the reciprocal lattice vector is equal to the inverse of the spacing between the corresponding planes.

4. Diffraction of X-rays (and electrons) is described by the Bragg equation, which relates the radiation wavelength ($\lambda$) to the diffraction angle ($\theta$) and the spacing between crystal planes ($d_{hkl}$).
Diffraction and the Reciprocal Lattice

Suggested Reading


Electromagnetic (EM) Radiation

Self-propagating waves with perpendicular electric and magnetic components

Properties of Electromagnetic Waves – cont’d

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

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

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

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

\[ \lambda = \text{wavelength of radiation} \]
- **Visible Light**: $\lambda \sim 6000$ Å
- **X-rays**: $\lambda \sim 0.5 - 2.5$ Å
- **Electrons**: $\lambda \sim 0.05$ Å

Penetrates Earth's Atmosphere?

<table>
<thead>
<tr>
<th>Radiation Type</th>
<th>Wavelength (m)</th>
<th>Approximate Scale of Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio</td>
<td>$10^2$</td>
<td>Buildings</td>
</tr>
<tr>
<td>Microwave</td>
<td>$10^{-2}$</td>
<td>Humans</td>
</tr>
<tr>
<td>Infrared</td>
<td>$10^{-5}$</td>
<td>Butterflies</td>
</tr>
<tr>
<td>Visible</td>
<td>$0.5 \times 10^{-6}$</td>
<td>Needle Point</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>$10^{-8}$</td>
<td>Protozoans</td>
</tr>
<tr>
<td>X-ray</td>
<td>$10^{-10}$</td>
<td>Molecules</td>
</tr>
<tr>
<td>Gamma ray</td>
<td>$10^{-12}$</td>
<td>Atoms</td>
</tr>
</tbody>
</table>

Frequency (Hz)

- $10^4$
- $10^6$
- $10^{12}$
- $10^{15}$
- $10^{16}$
- $10^{18}$
- $10^{20}$

Temperature of objects at which this radiation is the most intense wavelength emitted

- 1 K, -272 °C
- 100 K, -173 °C
- 10,000 K, 9,727 °C
- 10,000,000 K, ~10,000,000 °C

Scattering of EM Radiation by Crystals

• For a material to yield a diffraction pattern, the EMR wavelength ≤ lattice spacing.
  – Neutrons
  – Electrons
  – X-rays

• X-radiation is scattered (i.e., absorbed + re-emitted):
  – Elastic (little or no energy loss → diffraction peak)
  – Inelastic (energy loss → no diffraction peak)
Laue’s Equations

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

\[ \delta_n = \text{path difference between incident and scattered beams.} \]

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

\([h,k,l \text{ are integers}]\)

• Constructive interference occurs when all 3 equations are satisfied simultaneously.
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 as:

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

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

- 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.

Ref p. 61 in text
Laue’s Equations and the Reciprocal Lattice

• We can represent the Laue equations graphically.

• Similar to Ewald’s sphere.

• **For diffraction** to be observed (i.e. Bragg’s law satisfied) $\mathbf{S}$ 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.
\[ d_{hkl}^* = \frac{S - S_o}{\lambda} \]

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 \( \lambda \).
• 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, the source and detector move while the sample remains stationary.
Bragg’s Law

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

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

\[ \therefore \]

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

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

\[ \lambda = 2d_{hkl} \sin \theta \]
Diffraction Directions

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

• **Cubic:**

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

• 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:

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

• What about other systems?

• Tetragonal:

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

For \{111\}, \sin^2 \theta = \frac{\lambda^2}{4a^2} \left(\frac{2}{a^2} + \frac{1}{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 a circle with their ends placed on the surface of Ewald’s sphere.

• They produce powder diffraction cones at different Bragg angles (see the next slide).

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

Ewald’s sphere

Incident Beam

Figure 8.2
In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.

Figure 8.4
Exercises

1. Develop equations for the angles of diffraction for a tetragonal (a = 3 Å, c = 9 Å) crystal.