Chapter 3 X-ray diffraction

• Bragg’s law
• Laue’s condition
• Equivalence of Bragg’s law and Laue’s condition
• Ewald construction
• geometrical structure factor
Bragg's law

Consider a crystal as made out of parallel planes of ions, spaced a distance $d$ apart. The conditions for a sharp peak in the intensity of the scattered radiation are:

1. That the x-rays should be specularly reflected by the ions in any one plane and
2. That the reflected rays from successive planes should interfere constructively.

Path difference between two rays reflected from adjoining planes:

$$2d \sin \theta$$

For the rays to interfere constructively, this path difference must be an integral number of wavelength $\lambda$:

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

Bragg's condition.
Bragg angle $\theta$ is just the half of the total angle $2\theta$ by which the incident beam is deflected.

There are different ways of sectioning the crystal into planes, each of which will itself produce further reflection.

The same portion of Bravais lattice shown in the previous page, with a different way of sectioning the crystal planes. The incident ray is the same. But both the direction and wavelength (determined by Bragg condition with $d$ replaced by $d'$) of the reflected ray are different from the previous page.
Von Laue formulation of X-ray diffraction by a crystal

- No particular sectioning of crystal planes
- Regard the crystal as composed of identical microscopic objects placed at Bravais lattice site $\vec{R}$
- Each of the object at lattice site reradiate the incident radiation in all directions.
- Diffraction peaks will be observed in directions that the rays scattered from all lattice points interfere constructively.

Incident x-ray: along direction $\hat{n}$
- wavelength $\lambda$
- wave vector $\vec{k} = \frac{2\pi}{\lambda} \hat{n}$

A scattered wave:
- direction $\hat{n'}$
- wavelength $\lambda$
- wave vector $\vec{k'} = \frac{2\pi}{\lambda} \hat{n'}$

$$d \cos \theta + d \cos \theta' = \vec{d} \cdot (\hat{n} - \hat{n'})$$

Condition for constructive interference $\vec{d} \cdot (\hat{n} - \hat{n'}) = m\lambda$ for integer $m$

Multiply $\frac{2\pi}{\lambda}$ $\vec{d} \cdot (\vec{k} - \vec{k'}) = 2\pi n$
The condition \( \vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi n \) holds for all possible \( \vec{d} \)

so

\[ \vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi n \]

Or equivalently

\[ e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}} = 1 \]

therefore \( \vec{k}' - \vec{k} \) is a reciprocal lattice vector

or \( \vec{G} = \vec{k}' - \vec{k} \)

Laue condition:

Constructive interference will occur provided that the change in wave vector \( \vec{G} = \vec{k}' - \vec{k} \) is a vector of reciprocal lattice

Alternative formulation of Laue condition

This formulation involves only incident wave vector \( \vec{k} \), and does not involve \( \vec{k}' \)

Since \( \vec{k}' - \vec{k} \) is a reciprocal lattice vector, so is \( \vec{k} - \vec{k}' \)

\[ \vec{k} - \vec{k}' = \vec{G} \]
\[ \vec{k}' = \vec{k} - \vec{G} \]

\[ |\vec{k}| = |\vec{k}'| = |\vec{k} - \vec{G}| \]

Squaring both sides

\[ k^2 = k^2 + G^2 - 2\vec{k} \cdot \vec{G} \]

\[ G^2 = 2\vec{k} \cdot \vec{G} \]

or \( \frac{G}{2} = \vec{k} \cdot \frac{\vec{G}}{G} \)
$$\frac{G}{2} = \vec{k} \cdot \vec{G}$$
is interpreted as:

The component of the incident wave vector $\vec{k}$ along the reciprocal lattice vector $\vec{G}$ must be half of the length of $\vec{G}$.

An incident wave vector will satisfy the Laue condition if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of the reciprocal space to a reciprocal lattice point. Such k-space planes are called Bragg planes.
Equivalence of the Bragg and von Laue formulations

Suppose the incident and scattered wave vectors $\vec{k}$ and $\vec{k}'$, satisfy the Laue condition that $\vec{G} = \vec{k}' - \vec{k}$ be a reciprocal lattice vector.

Elastic scattering: $|\vec{k}| = |\vec{k}'|$

It follows that $\vec{k}'$ and $\vec{k}$ make the same angle $\theta$ with the plane perpendicular to $\vec{G}$. Therefore the scattering can be viewed as a Bragg reflection with Bragg angle $\theta$, from the family of direct lattice planes perpendicular to the reciprocal lattice vector $\vec{G}$.

The distance between successive planes in this family must satisfy:

$$|\vec{G}_0| = \frac{2\pi}{d}$$

where $\vec{G}_0$ is the shortest wave vector parallel to $\vec{G}$.

$\vec{G}$ must be an integral multiple of $\vec{G}_0$, since reciprocal lattice is a Bravais lattice

$$\vec{G} = n\vec{G}_0$$

$$|\vec{G}| = n|\vec{G}_0| = \frac{2\pi n}{d}$$

From the figure, $|\vec{G}| = 2k \sin \theta$
\[
\therefore \quad k \sin \theta = \frac{\pi n}{d}
\]
\[n \lambda = 2d \sin \theta \quad \text{Bragg condition}
\]

Note that \(k = \frac{2\pi}{\lambda}
\]

A Laue diffraction peak corresponding to a change in the wave vector given by the reciprocal lattice vector corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to \(\vec{G}\). The order, \(n\), of the Bragg reflection is just the length of \(\vec{G}\) divided by the length of the shortest reciprocal lattice vector parallel to \(\vec{G}\) is the measurement direction. Only structural information along \(\vec{G}\) i.e. the set of planes perpendicular to \(\vec{G}\), is being measured.

Rewrite Bragg condition: 
\[
\lambda = 2d \frac{d(h,k,l)}{n} \sin \theta
\]

Define \(d\) spacing: \(d(h,k,l) = \frac{d}{n} = \frac{2\pi}{|\vec{G}|} = \frac{2\pi}{n|\vec{G}_0|}
\]

So \(\lambda = 2d(h,k,l) \sin \theta
\]

\(h, k, l\) are the coordinates of the reciprocal lattice vector associated with the diffraction \(\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3
\]

\(\vec{G} = n\vec{G}_0\) So \(h, k, l\) have a common factor \(n\).

For example (222) direction peak is actually the 2\(^{nd}\) order (\(n=2\)) diffraction peak of the (111) plane.
Experimental geometries suggested by the Laue condition

General observations

An incident wave vector \( \vec{k} \) will lead to a diffraction peak (or “Bragg reflection”) if and only if the tip of the wave vector lies on a reciprocal space Bragg plane.

Since Bragg planes are a discrete family of planes, a fixed incident wave vector – i.e., for a fixed x-ray wavelength and fixed incident direction relative to the crystal axes – there will be in general no diffraction peaks at all.

If one wishes to search experimentally for Bragg peaks, one must therefore relax the constraint for fixed \( \vec{k} \), either varying the magnitude of \( \vec{k} \) (i.e. varying wavelength) or varying its direction (in practice, varying the orientation of the crystal with respect to incident direction).
The Ewald construction

Draw a sphere in reciprocal space centered on the tip of the incident wave vector $k$ of radius $k$ (so that it passed through the origin)

There will be some wave vector satisfying the Laue condition if and only if some reciprocal lattice point (in addition to the origin lies on the surface of the sphere)

In general, a sphere in reciprocal space with the origin on its surface will have no other reciprocal lattice points on its surface
So in general, there are no diffraction peaks.

The following methods are used to relax the constrains in order to achieve diffraction peaks

1. Laue method

   Fix the orientation of the single crystal. Search for Bragg peaks by using not a monochromatic x-ray beam, but one containing wavelength for $\lambda_i$ up to $\lambda_{ij}$.
The Ewald sphere will expand into the region, contained between the two spheres determined by \( \mathbf{k}_0 = \frac{2\pi}{\lambda_0} \hat{n} \) and \( \mathbf{k}_1 = \frac{2\pi}{\lambda_1} \hat{n} \), and Bragg peaks will be observed corresponding to any reciprocal lattice vectors laying within the region.

Laue method is best suited for determining the orientation of a single crystal specimen whose structure is known.

2. The rotating crystal method

Fix the wavelength, allow the angle of incidence to vary in practice, the incident direction is fixed, and the orientation of the crystal varies.

The crystal is rotated about the same fixed axis. As the crystal rotates, the reciprocal lattice it determines will rotate by the same amount about the same axis.
The Ewald sphere is fixed in space, while the entire reciprocal lattice rotates about the axis of rotation of the crystal.

During this rotation, each reciprocal lattice point traverses a circle about the rotation axis, and a Bragg reflection occurs whenever this circle intersects the Ewald sphere.
3. The powder or Debye-Scherrer method

Equivalent to a rotating crystal experiment in which, in addition, the axis of rotation is varied over all possible orientations. In practice this is achieved by using a polycrystalline sample or powder, grains of which are still enormous on the atomic scale.

Bragg reflections are determined by fixing the incident \( \vec{k} \) vector, and with it the Ewald sphere, and allowing the reciprocal lattice to rotate through all possible angles about the origin, so that each reciprocal lattice vector generates a sphere of radius \( | \vec{G} | \) about the origin.
Diffraction by a lattice with a basis: the geometrical structure factor

The diffraction conditions (either Bragg or Laue) tells only the location of the diffraction peaks, but not the magnitude.

The magnitude of the diffraction peaks are determined by the electron density distribution of the basis. It is related to the Fourier transformation of the basis.

Phase difference between beams scattered from volume elements \( \vec{r} \) apart: \( e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} \)

The amplitude of the wave scattered from a volume element is proportional to local electron concentration \( n(\vec{r}) \)

The total scattering amplitude:

\[
F = \int dV \ n(\vec{r}) \ e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \int dV \ n(\vec{r}) \ e^{-i\Delta\vec{k} \cdot \vec{r}}
\]

Under diffraction condition \( \Delta\vec{k} = \vec{G} \)
\[ F_\vec{G} = \int dV \ n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = \sum_{\vec{R}} \int dV \ n(\vec{r} + \vec{R}) e^{-i\vec{G} \cdot (\vec{r} + \vec{R})} = \sum_{\vec{R}} \int dV \ n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = N \int dV \ n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} \]

\[ F_\vec{G} = N \int dV \ n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} = NS_\vec{G} \]

Fourier transform of wave vector \( \vec{G} \) or magnitude of Fourier term \( e^{i\vec{G} \cdot \vec{r}} \)

Note that

\[ n(\vec{r}) = \sum_\vec{G} n_\vec{G} e^{i\vec{G} \cdot \vec{r}} = \sum_\vec{G} \frac{F_\vec{G}}{V} e^{i\vec{G} \cdot \vec{r}} \]

\[ n(\vec{r}) = \sum_{j=1}^{s} n_j (\vec{r} - \vec{r}_j) \]

Contribution of the \( j \)th atom in the basis to the electron density at \( \vec{r} \)

\[ \vec{r}_j \]

position vector of the \( j \)th atom

\[ n_j(\vec{r}) \]

The electron density of the \( j \)th atom in its own coordinates.

\[ S_\vec{G} = \sum_j \int dV \ n_j (\vec{r} - \vec{r}_j) e^{-i\vec{G} \cdot \vec{r}} \]

\[ = \sum_j e^{-i\vec{G} \cdot \vec{r}_j} \int dV \ n_j (\vec{r}) e^{-i\vec{G} \cdot \vec{r}} \]

\[ \vec{\rho} = \vec{r} - \vec{r}_j \]

AtOMIC form factor

\[ f_j = \int dV \ n_j(\vec{\rho}) e^{-i\vec{G} \cdot \vec{\rho}} \]

\[ S_\vec{G} = \sum_j f_j e^{-i\vec{G} \cdot \vec{r}_j} \]
Diffraction by a monatomic lattice with a basis

\[ S_{\tilde{G}} = f \sum_{j} e^{-i\tilde{G} \cdot \tilde{r}_j} \]

Bcc structure

Regard as simple cubic with a basis:

Basis: \( \tilde{d}_1 = 0 \quad \tilde{d}_2 = \frac{a}{2} (\hat{x} + \hat{y} + \hat{z}) \)

\[ \tilde{G} = \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \]

\[ S_{\tilde{G}} = f \left( 1 + e^{-i\pi(n_1 + n_2 + n_3)} \right) \]

\( S_{\tilde{G}} = 0 \) \quad \text{When } n_1 + n_2 + n_3 = \text{odd integer} \n
\( S_{\tilde{G}} = 2f \) \quad \text{When } n_1 + n_2 + n_3 = \text{even integer} \n
\( (n_1, n_2, n_3) \) are actually the coordinates of reciprocal lattice vector (h,k,l)

To have an diffraction peak, \( h + k + l = \text{even} \)

Diffraction pattern does not contain lines such as (100), (300), (111), or (221), but lines such as (200), (110) and (222) will be present.

The corresponding d spacing can be calculated using

\[ d(h,k,l) = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]
Physical interpretation of the fact that (100) reflection vanishes:

Decipher the reciprocal lattice from the structural factor analysis

\[ S_{\vec{G}} = 0 \quad \text{When } n_1 + n_2 + n_3 = \text{odd integer, no diffraction.} \]

\[ S_{\vec{G}} = 2f \quad \text{When } n_1 + n_2 + n_3 = \text{even integer, diffraction peak exists} \]

Reciprocal lattice is fcc
Fcc structure:

Regard as simple cubic cell with a basis

\[ \begin{align*}
\vec{d}_1 &= 0 \\
\vec{d}_2 &= \frac{a}{2} (\hat{y} + \hat{z}) \\
\vec{d}_3 &= \frac{a}{2} (\hat{x} + \hat{z}) \\
\vec{d}_4 &= \frac{a}{2} (\hat{x} + \hat{y})
\end{align*} \]

\[ \vec{G} = \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \]

\[ S_{\vec{G}} = f \left( 1 + e^{-i\pi(n_2+n_3)} + e^{-i\pi(n_1+n_3)} + e^{-i\pi(n_1+n_2)} \right) \]

\[ S_{\vec{G}} = 4f \quad \text{if } n_1, n_2, \text{ and } n_3 \text{ are all even or all odd} \]

\[ S_{\vec{G}} = 0 \quad \text{otherwise} \]

To have diffraction peaks, \( h, k, l = \text{all even or all odd} \)

(111), (200), (220), (311), (222), (400), etc. peaks will be observed.

d spacings can be calculated by

\[ d(h,k,l) = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]