Study Material - Sem. 5 - C12T

- Crystal Structure - Dr. T. Kar

Class 4

Derivation of Scattered Wave Amplitude

The Bragg derivation of the diffraction condition gives a neat and clear statement of the condition for the constructive interference of waves scattered by point charges at the lattice points. To determine the intensity of scattering from a spatial distribution of electrons within each cell, we must carry out a deeper analysis.

We know that a crystal is invariant under any translation of the form $\vec{T} = u\bar{a} + v\bar{b} + w\bar{c}$, where u, v, w are integers and $\bar{a}, \bar{b}, \bar{c}$ are crystal axes. Any physical property of the crystal is invariant under $\vec{T}$. The charge concentration, the electron number density, the mass density and the magnetic moment density are invariant under all translation $\vec{T}$.

Thus electron number density $n(\bar{r})$ is a periodic function of $\bar{r}$ with

periods a, b, c in the direction of three crystal axes whence $n(\bar{r}+\bar{T}) = n(\bar{r})$.

With the help of Fourier analysis, we can find a set of vectors $\vec{G}$ such that $n(\bar{r}) = \sum_G n_G e^{i\bar{G}\cdot\bar{r}}$ → (1) is invariant under all lattice translations $\bar{T}$ that leave the crystal invariant. The vectors $\vec{G}$ in the Fourier series (1) are the reciprocal lattice vectors, then the Fourier series for the electron density has the desired invariance under any crystal translation $\vec{T} = u\bar{a} + v\bar{b} + w\bar{c}$:

$$n(\bar{r}+\bar{T}) = \sum_G n_G e^{i\bar{G}\cdot\bar{r}} e^{i\bar{G}\cdot\bar{T}} \rightarrow (2)$$

$$e^{i(\bar{G}\cdot\bar{T})} = \exp\left[i(h\bar{A}+k\bar{B}+l\bar{C}).(u\bar{a}+v\bar{b}+w\bar{c})\right]$$

$$= \exp\left[2\pi i(hu+kv+lw)\right] \rightarrow (3)$$

The argument of the exponential has the form $2\pi i$ times an integer, because $hu+kv+lw$ is the sum of products of integers and is therefore an integer.

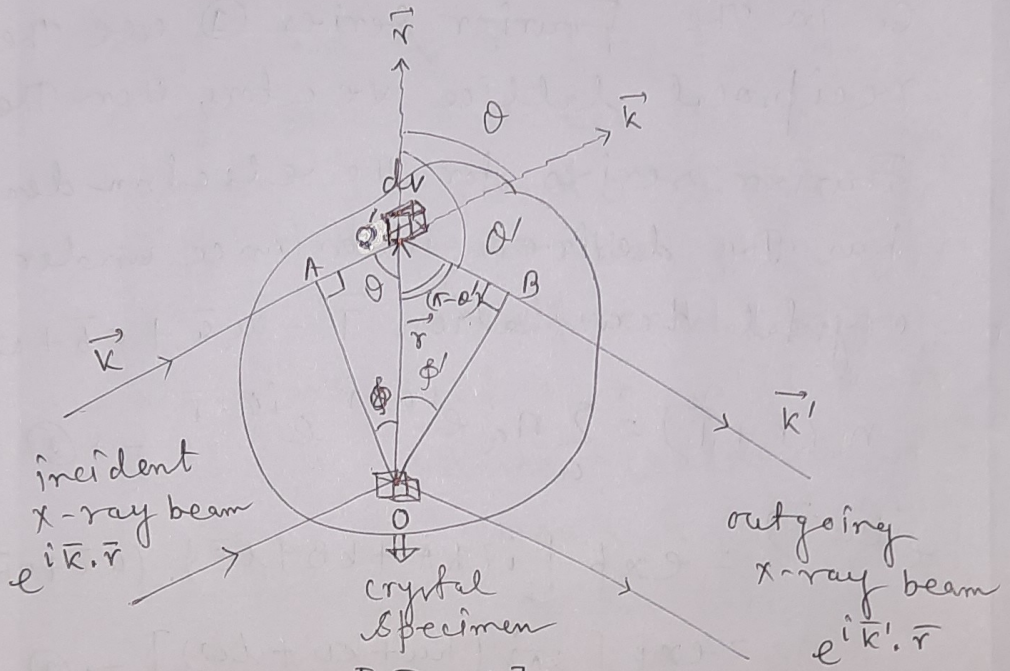
Thus $e^{i\bar{G}\cdot\bar{T}} = 1$, and $n(\bar{r}+\bar{T})$

$$= \sum_G n_G e^{i\bar{G}\cdot\bar{r}} = n(\bar{r})$$

This completes the proof that the Fourier

(3)

analysis of a function periodic in crystal lattice can contain components $n_G \exp[i\vec{G}\cdot\vec{r}]$ only at the reciprocal lattice vectors $\vec{G}$ defined by $\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$.



[Fig. 1]

We want to find out phase difference between x-ray beams scattered from two volume elements which are separated by $\vec{r}$.

Incident wave

$\theta + \phi + \pi/2 = \pi$

$\therefore \phi = (\pi/2 - \theta)$

$\frac{AO'}{OO'} = \sin\phi$

$\therefore AO' = OO' \sin\phi = r\sin\phi$

$\therefore$ Phase difference $= \frac{2\pi}{\lambda} r\sin\phi$

$= k r \sin\phi$

$= k r \sin\left(\frac{\pi}{2} - \theta\right)$

$= k r \cos\theta = \vec{k} \cdot \vec{r}$

Scattered Wave

$\phi' + (\pi - \theta') + \pi/2 = \pi$

$\therefore \phi' = \theta' - \pi/2$

$\frac{BO'}{OO'} = \sin\phi'$

$\therefore BO' = r\sin\phi'$

$\therefore$ Phase difference $= \frac{2\pi}{\lambda} BO' = \frac{2\pi}{\lambda} r\sin\phi'$

$= \frac{2\pi}{\lambda} r\sin(\theta - \pi/2)$

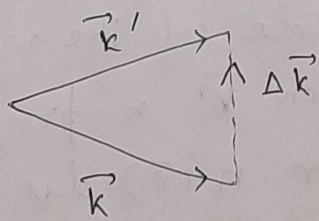
$= -k' r \cos\theta$

$= -\vec{k}' \cdot \vec{r}$

$\therefore$ Total difference in phase angle

$= (\vec{k} - k') \cdot \vec{r}$

$\therefore$ The wave scattered from dv at O' has a the phase factor $\exp[i(\vec{k} - \vec{k}') \cdot \vec{r}]$ relative to the wave scattered from a volume element at O separated by $\vec{r}$.



The definition of scattering vector $\Delta\vec{k}$ such that

$\vec{k} + \Delta\vec{k} = \vec{k}'$

Diffraction Conditions (Reciprocal Lattice Consideration)

The set of reciprocal lattice vectors $\vec{G}$ determines the possible x-ray reflections. Let us take two identical volume elements having volume dv separated by $\vec{r}$ [fig.1]. The phase difference between the incident wave $\vec{k}$ at O and O' is $\vec{k}.\vec{r}$. For the diffracted wave the phase difference is $-\vec{k}'.\vec{r}$. Therefore total difference in phase factors is $e^{i(\vec{k}-\vec{k}').\vec{r}}$ between beams scattered from volume elements $\vec{r}$ apart. The wave vectors of the incoming and outgoing beams are $\vec{k}$ and $\vec{k}'$ respectively. The amplitude of the scattered wave from a volume element is proportional to the local electron concentration, $n(\vec{r})$. Total amplitude of the scattered wave in the direction $\vec{k}'$ is proportional to the integral over $n(\vec{r})\,dv$ times $e^{i(\vec{k}-\vec{k}').\vec{r}}$, i.e,

$$A = \int n(\bar{r})\, e^{i(\bar{k}-\bar{k}')\cdot\bar{r}}\, dV$$

$$= \int n(\bar{r})\, e^{-i\Delta\bar{k}\cdot\bar{r}}\, dV \quad \text{where, } \Delta\bar{k} = \bar{k}' - \bar{k}$$

$\Delta\bar{k}$ measures the change in wavevector on scattering and is called the scattering vector. We can write the Fourier components of $n(\bar{r})$ as

$$n(\bar{r}) = \sum_{G} n_G\, e^{i\bar{G}\cdot\bar{r}}$$

$$\therefore A = \sum_{G} \int n_G\, e^{i(\bar{G}-\Delta\bar{k})\cdot\bar{r}}\, dV$$

A will be maximum if $\vec{G} = \Delta\bar{k}$, i.e, when we get a diffracted beam in the direction of $\bar{k}'$, the scattering vector $\Delta\bar{k}$ is equal to a reciprocal lattice vector, and then $A = n_G V$

$$\therefore \boxed{\Delta\bar{k} = \vec{G}} \Rightarrow \text{Diffraction Condition}$$

$$\therefore \bar{k}' - \bar{k} = \vec{G}$$

$$\text{i.e, } \bar{k}' = \bar{k} + \vec{G}$$

$$\therefore (\bar{k}+\bar{G})^2 = |\bar{k}'|^2 = k^2 \quad \text{as } |\bar{k}| = |\bar{k}'|$$

$$\text{i.e, } 2\bar{k}\cdot\bar{G} + G^2 = 0 \longrightarrow (1)$$

(7)

If $\vec{G}$ is a reciprocal lattice vector then $-\vec{G}$ is also a reciprocal lattice vector.

We can write from eqn. (1) as —

$$\boxed{2\vec{k}\cdot\vec{G} = G^2} \Rightarrow \text{Diffraction condition}$$

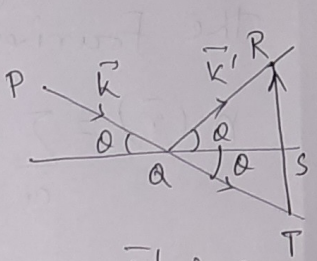
Now, the spacing between parallel planes d_{hkl} is $\frac{2\pi}{|\vec{G}|}$.

If the indices of the peak have a common divisor 'n', then

$$|\Delta\vec{k}| = n|\vec{G}|$$

$$\therefore \frac{4\pi}{\lambda}\sin\theta = n\left[\frac{2\pi}{d_{hkl}}\right]$$

$$\therefore \boxed{2d_{hkl}\sin\theta = n\lambda}$$ Bragg Law.



$RS = \vec{k}'\sin\theta = \frac{2\pi}{\lambda}\sin\theta$

$ST = \vec{k}\sin\theta = \frac{2\pi}{\lambda}\sin\theta$

$TR = |\Delta\vec{k}| = \frac{4\pi}{\lambda}\sin\theta$

$\Delta\vec{K} = \vec{G}$ can be expressed in another way to give Laue equations.

$$\Delta\vec{K} = \vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

$$\left.\begin{aligned} \vec{a}\cdot\Delta\vec{k} &= \vec{a}\cdot\vec{G} = 2\pi h \\ \vec{b}\cdot\Delta\vec{k} &= \vec{b}\cdot\vec{G} = 2\pi k \\ \vec{c}\cdot\Delta\vec{k} &= \vec{c}\cdot\vec{G} = 2\pi l \end{aligned}\right\}$$ Laue equation on the scattering vector

Ewald Constructions

To obtain an elastic diffraction peak, Δk must satisfy the Laue conditions and $\bar{k}'$ must have the same magnitude as $\bar{k}$. These conditions severely limit the number of elastic scattering peaks obtained for a fixed wavelength, incident direction and crystal orientation. The vector $\bar{k}$ is drawn in the direction of incident x-ray beam and it terminates at any reciprocal lattice point. We draw a sphere of radius $k = \frac{2\pi}{\lambda}$ about the origin of $\bar{k}$. A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The sphere as drawn intercepts a point connected with the end of $\bar{k}$ by a reciprocal lattice vector $\vec{G_R}$. The diffracted x-ray beam is in the direction $\bar{k}' = \bar{k} + \bar{G}_R$. This construction is due to P. P. Ewald.

Brillouin Zones

For solid state physics the most important statement of the diffraction condition was given by Brillouin. This is the only construction used in electron energy band theory, and in the expression of the elementary excitations of crystals. A Brillouin zone is defined as a Wigner-Seitz

cell in the reciprocal lattice. The Brillouin zone gives a vivid geometrical interpretation of the diffraction condition-

$$2\bar{k}\cdot\bar{G} = G^2 \quad \text{or,} \quad \boxed{\bar{k}\cdot(\bar{G}/2) = \left(\frac{G}{2}\right)^2} \rightarrow (20)$$

We construct a plane normal to the vector $\vec{G}$ at the midpoint. any vector $\bar{k}$ from origin to the plane will satisfy the diffraction condition. The plane thus described forms a part of zone boundary. An X-ray beam incident on the crystal will be diffracted if its wavevector has the magnitude and direction required by (20) and the diffracted beam will be in the direction of the vector $(\bar{k}-\bar{G})$.

The set of planes that are the perpendicular bisectors of the reciprocal lattice vectors are of particular importance in the theory of wave propagation in crystals, because a wave whose wave-vectors drawn from origin terminates on any of these planes will satisfy the conditions for diffraction. These planes divide the Fourier space of the crystal into odd bits and pieces. The central square is a primitive cell of the reciprocal lattice. The central cell in the reciprocal lattice is of special importance in the theory of solids and is known as the first Brillouin zone.

The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from origin.

The zone boundaries of a linear lattice are at $k = \pm \pi/a$, where a is the primitive axis of the crystal lattice. The Brillouin construction exhibits all the incident wavevectors $\vec{k}$ which can be Bragg-reflected by the crystal.

Reciprocal Lattice to sc Lattice

The primitive translation vectors of a simple cubic lattice may be taken as the set —

$$\bar{a} = a\hat{x}\,; \quad \bar{b} = a\hat{y}\,; \quad \bar{c} = a\hat{z} \longrightarrow (21)$$

The volume of the cell is $\bar{a}.\ \bar{b}\times\bar{c} = a^3$. The primitive translation vectors of the reciprocal lattice are found to be —

$$\vec{A} = 2\pi\frac{\bar{b}\times\bar{c}}{\bar{a}.\ \bar{b}\times\bar{c}} = \frac{2\pi}{a}\hat{x}\,; \quad \vec{B} = \frac{2\pi}{a}\hat{y} \text{ and } \vec{C} = \frac{2\pi}{a}\hat{z} \longrightarrow (22)$$

Thus the reciprocal lattice is itself a simple cubic lattice, now of lattice constant $2\pi/a$.

The boundaries of the first Brillouin zones are the planes normal to the six reciprocal lattice vectors $\pm\vec{A}, \pm\vec{B}, \pm\vec{C}$ at their midpoints :

$$\pm\frac{\vec{A}}{2} = \pm\frac{\pi}{a}\hat{x}\,; \quad \pm\frac{\vec{B}}{2} = \pm\frac{\pi}{a}\hat{y}\,; \quad \pm\frac{\vec{C}}{2} = \pm\frac{\pi}{a}\hat{z} \longrightarrow (23)$$

The six planes bound a cube of edge $\frac{2\pi}{a}$ and volume $\left(\frac{2\pi}{a}\right)^3$; This cube is the first Brillouin zone of the sc crystal lattice.

Reciprocal Lattice to bcc Lattice

The primitive translation vectors of the bcc lattice are —

$$\vec{a}' = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})\,; \quad \vec{b}' = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z})\,; \quad \vec{c}' = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z}) \longrightarrow (24)$$

where a is the side of the conventional cube and $\hat{x}, \hat{y}, \hat{z}$ are orthogonal unit vectors parallel to the cube edges. The volume of the primitive cell is

$$V = |\bar{a}'.\ \bar{b}'\times\bar{c}'| = \frac{1}{2}a^3 \longrightarrow (25)$$

Therefore, the primitive translation vectors of the reciprocal lattice are given by [using (14)],

$$\vec{A} = \frac{2\pi}{a}(\hat{x}+\hat{y})\,; \quad \vec{B} = \frac{2\pi}{a}(\hat{y}+\hat{z})\,; \quad \vec{C} = \frac{2\pi}{a}(\hat{z}+\hat{x}) \longrightarrow (26)$$

which are just the primitive vectors of an fcc lattice; thus fcc lattice is the reciprocal lattice of bcc lattice.

If h, k, l are integers, the general reciprocal lattice vector is —

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

$$= \frac{2\pi}{a}\left[(h+l)\hat{x} + (h+k)\hat{y} + (k+l)\hat{z}\right] \longrightarrow (27)$$

The primitive cell of the reciprocal lattice is the parallelepiped described by $\vec{A}$, $\vec{B}$ and $\vec{C}$ defined by (26). The volume of the primitive cell of the reciprocal lattice is $|\vec{A}.\vec{B}\times\vec{C}| = 2\left(\frac{2\pi}{a}\right)^3$. The first Brillouin zone of the bcc lattice is a regular rhombic dodecahedron.

Reciprocal Lattice to fcc Lattice

The primitive translation vectors of the fcc lattice are—

$$\vec{a}' = \frac{a}{2}(\hat{x}+\hat{y}); \quad \vec{b}' = \frac{a}{2}(\hat{y}+\hat{z}); \quad \vec{c}' = \frac{a}{2}(\hat{z}+\hat{x}) \longrightarrow (28)$$

The volume of the primitive cell is

$$V = |\vec{a}'.\vec{b}'\times\vec{c}'| = \frac{1}{4}a^3 \longrightarrow (29)$$

The primitive translation vectors $\vec{A}$, $\vec{B}$, $\vec{C}$ of the reciprocal lattice to the fcc lattice are—

$$\vec{A} = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z}); \quad \vec{B} = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z}); \quad \vec{C} = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z}) \rightarrow (30)$$

which are the primitive translation vectors of a bcc lattice. Therefore, the bcc lattice is the reciprocal lattice of the fcc lattice.

The volume of the primitive cell in the reciprocal lattice is $|\vec{A}.\vec{B}\times\vec{C}| = 4\left(\frac{2\pi}{a}\right)^3$.

The general reciprocal lattice vector is

$$\vec{G} = \frac{2\pi}{a}\left[(h-k+l)\hat{x} + (h+k-l)\hat{y} + (-h+k+l)\hat{z}\right] \longrightarrow (31)$$

The first Brillouin zone of the fcc lattice is a truncated octahedron.