Diffraction of waves by crystals:

Crystal structures can be studied by using a diffraction method of

(a) Photons *(b)* neutrons *(c)* electrons.

X-ray diffraction and Bragg law:

When the wave length of the beam of incident light is comparable or smaller than the lattice constant (i.e. $\lambda \lesssim a$), then a diffraction pattern may be obtained. The diffracted beams are found when reflections from parallel planes of atoms interfere constructively.

Note: in such elastic scattering of waves from electrons in atoms such that $|\vec{k}|$ of incident wave = $|\vec{k}'|$ of outgoing scattered wave.

The path difference for waves reflected from adjacent planes:

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

Although Bragg law does not refer to the composition of basis of atoms associated with every lattice point, we can show that the composition of the basis determines the relative intensity of the various orders of diffraction (denoted by n) from a given set of parallel planes. (See figure 36).

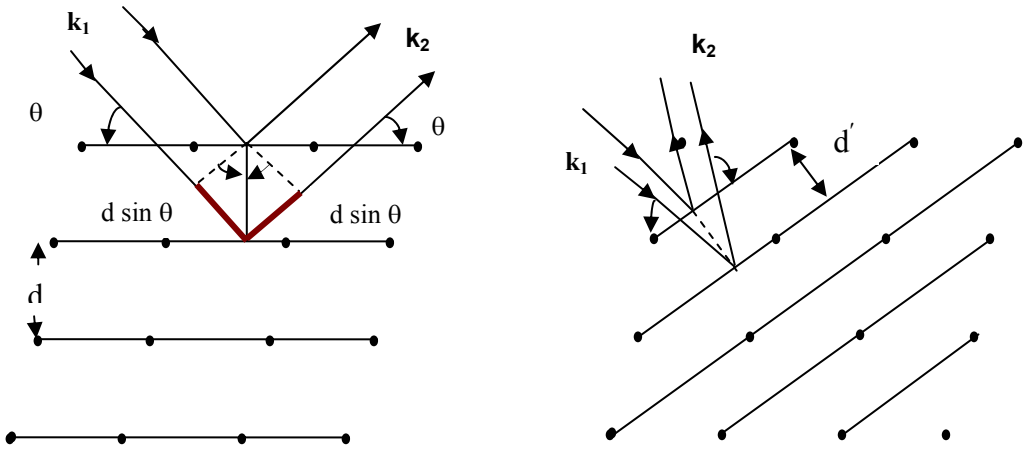

Figure 36: Bragg reflection from two sets of family planes

a) The planes are separated by a distance d and the path difference is $2d \sin\theta$.	b) The planes are separated by d'. Both direction and wave length are different from these in (*a*).

Scattered wave amplitude:

We need to determine the scattering intensity from the basis of atoms or in another meaning from the spatial distribution of electrons within each cell. Physical properties like charge concentration, electron number density, or magnetic moment density are invariant under translation of the form $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$.

Electron number density and Fourier analysis:

The electron number density $n(\vec{r})$ is a periodic function of $\vec{r}$ in the direction of the three crystal axes, namely,

$$n(\vec{r}+\vec{R}) = n(\vec{r}) .$$

This periodicity in crystals is directly related to the Fourier components of the electron density.

One-Dimensional Picture:

For example, in 1-D the electron number density $n(x)$ with a period "a" along the x-axis can be expanded in a Fourier series of sines and cosines, i.e.

$$n(x) = n_\circ + \sum_{m>0}[C_m \cos(\tfrac{2\pi mx}{a}) + C'_m \sin(\tfrac{2\pi mx}{a})] ,$$

where m is a positive integer, C_m and C'_m are real constants (called the Fourier coefficients of the expansion). The factor $\frac{2\pi}{a}$ in the arguments ensures that $n(x)$ has the period a. Thus

$$n(x+a) = n_\circ + \sum_{m>0}[C_m \cos(\tfrac{2\pi mx}{a} + 2\pi m) + C'_m \sin(\tfrac{2\pi mx}{a} + 2\pi m)]$$

$$n(x+a) = n_\circ + \sum_{m>0}[C_m \cos(\tfrac{2\pi mx}{a}) + C'_m \sin(\tfrac{2\pi mx}{a})]$$

Comparing this to the above relation of $n(x)$ we get

$$n(x+a) = n(x) .$$

Here $\frac{2\pi m}{a}$ is a point in the reciprocal lattice or Fourier space of the crystal.

Notes:

1) Reciprocal lattice points correspond to allowed terms in the Fourier series.

2) A term is allowed if it is consistent with the periodicity of the crystal, i.e. $n(x) = \sum n_m e^{i\frac{2\pi m}{a}x}$, n_m are complex numbers and the integer m may be zero, positive and negative.

Exercise: Show that $n(x)$ is a real function if we assume that $n^*_{-m} = n_m$.

The Fourier coefficient n_m can be obtained from the inversion of Fourier series as

$$n_m = \frac{1}{a}\int_0^a n(x) e^{-\frac{i2\pi mx}{a}} dx .$$

Here $n(x)$ is expressed as

$$n(x) = \sum n_{m'} e^{i\frac{2\pi m'}{a}x} .$$

Thus the above form of n_m is rewritten as

$$n_m = \frac{1}{a}\sum_{m'}\int_0^a n_{m'} e^{-\frac{i2\pi(m'-m)x}{a}} dx .$$

The final result depends on the integer m'- m.

If $m' \neq m$ then the value of the integral is $\frac{a}{2i\pi(m'-m)}[e^{i2\pi(m'-m)} - 1] = 0$.

This indicates that $e^{i2\pi(m'-m)} = 1$. However when $m' = m$, the integral has the value of a, and then the final result represents the identity because we have $n_m = n'_m$.

Three-dimensional picture:

In 3-D, $n(\vec{r}) = \sum_G n_G e^{i\vec{K}\bullet\vec{r}}$ is invariant under all crystal translations $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$. The coefficient n_G will determine the x-ray scattering amplitude. The Reciprocal vector $\vec{K}$ is an

integral multiple of the shortest reciprocal lattice vector $\vec{G}$, i.e. $\vec{K} = n\vec{G}$

[Hint: the integer n was previously denoted by m].

In a similar manner to above the inversion of Fourier series to $n(\vec{r})$ gives:

$$n_G = \frac{1}{V_{cell}} \int_{cell} n(\vec{r}) e^{-i\vec{G}\bullet\vec{r}} dV .$$

Also we obtain $e^{i\vec{G}\bullet\vec{r}} = 1$, as mentioned above for the case of 1-D, where wave vectors are always drawn in Fourier space, such that every position in Fourier space may have a meaning as a description of a wave.

Thus $e^{i\vec{G}\bullet\vec{r}} = e^{[i(h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3)\bullet(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)]} = e^{i2\pi n}$,

where $n = hn_1 + kn_2 + \ell n_3$ is an integer.

Diffraction conditions:

The set of reciprocal lattice vectors $\vec{G}$ determines the possible x-ray reflections.

The scattering amplitude (F) is defined as follows:

$$F = \int n(\vec{r}) e^{-i\Delta\vec{k}\bullet\vec{r}} dV ,$$

where $\Delta\vec{k} = \vec{k}' - \vec{k}$ is called the scattering vector which measures the change in wave vector. Here $\vec{k} = \frac{2\pi\hat{n}}{\lambda}$ is the wave vector of incident beam and $\vec{k}' = \frac{2\pi\hat{n}'}{\lambda}$ is the wave vector of outgoing scattered beam.

The scattering amplitude F can be rewritten as:

$$F = \sum_G \int n_G e^{-i(\vec{G}-\Delta\vec{k})\bullet\vec{r}} dV ,$$

where $n(\vec{r}) = \sum_G n_G e^{i\vec{G}\bullet\vec{r}}$. When the condition of $\Delta\vec{k} = \vec{G}$ is satisfied then we get the result $F = Vn_G$.

Exercise: Show that F is negligibly small when $\Delta\vec{k}$ differs significantly from any reciprocal lattice vector.

Note:

In the elastic scattering of photon energy $\hbar\omega$, the frequency of outgoing beam $\omega' = ck'$ is equal to that of incident beam $\omega = ck$. This leads to the result of $k = k'$. This latter result also holds for electron and neutron beams.

The result $\Delta\vec{k} = \vec{G}$ or $\vec{k} + \vec{G} = \vec{k}'$ leads to the diffraction condition

$$(\vec{k} + \vec{G})^2 = k^2 \qquad \Rightarrow \qquad 2\vec{k} \bullet \vec{G} + G^2 = 0 .$$

If $\vec{G}$ is a reciprocal lattice vector, so is $-\vec{G}$, then

$$\boxed{2\vec{k}\bullet\vec{G} = G^2}$$

(This is what is called the Bragg condition, see figure 30).

Von Laue formulation of x-ray diffraction by a crystal:

This approach considers the crystal as composed of set of ions (or atoms) located at the sites $\vec{R}$ of a Bravais lattice. Each site that receives the incident beam will reradiate this beam in all directions. The outgoing beams scattered by lattice sites then will interfere constructively and sharp peaks can be observed in directions and at wavelengths of these sites.

Consider two scattering centers (two ionic or atomic sites) separated by a displacement vector $\Delta\vec{r} = \Delta r\hat{r}$, as shown in figure 37. The incident beam with a wave vector $|\vec{k}| = \frac{2\pi}{\lambda}$ is along the direction of $\hat{n}$ while the scattered beam of a wave vector $|\vec{k}'| = \frac{2\pi}{\lambda}$ is

in the direction of $\hat{n}'$, as shown in figure 37. The two beams will interfere constructively if the path difference between them is an integral number of wavelengths, i.e.

$$\Delta\vec{r} \bullet (\hat{n} - \hat{n}') = d\cos\theta + d\cos\theta' \text{, where } d=\Delta r$$

It can be shown from figure 37 that:

$$\Delta\vec{r} \bullet (\hat{n} - \hat{n}') = n\lambda .$$

The latter equation, (when it is multiplied by $2\pi/\lambda$ can be rewritten as:

$$\Delta\vec{r} \bullet (\vec{k} - \vec{k}') = 2\pi n .$$

Any two scattering centers (or an array of centers) in the Bravais lattice can be chosen provided that they are displaced by the Bravais lattice vector $\vec{R}$ and satisfy the condition of constructive interference, namely,

$$\vec{R} \bullet (\vec{k} - \vec{k}') = 2\pi n .$$

This is equivalent to the case of $e^{i\vec{R}\bullet\Delta\vec{k}} = 1$ when $\Delta\vec{k}$ are characterized as set of wave vectors in reciprocal lattice and this case is applicable for all $\vec{R}$ in the Bravais lattice.

Conclusion:

Laue condition implies that constructive interference will occur provided that the change in wave vector $\Delta\vec{k} = n\vec{G}$ is a vector of the reciprocal lattice.

Note:

Again the integer n could be set equal one when the distance between successive planes is considered. This integer also represents the common factor used to obtain the Miller indices. It will also be shown that such integer represents the order of the corresponding reflection in Bragg reflection. Here we must realize

that a beam of x-rays may contain different wave lengths, which in turn, correspond to different observed reflections. Also we must realize that there are several different ways of sectioning the crystal into planes which will result into further reflections. (See figure 36).

Thus an incident wave vector $\vec{k}$ will satisfy the Laue condition if and only if the head of the vector lies in a plane that is perpendicular bisector of a line joining the origin of k-space to a reciprocal lattice point $\vec{G}$. Such k-space planes are called Bragg planes. [*i.e.* $\boxed{2\vec{k}\bullet\vec{G}=G^2}$, as shown in figure 37.b].

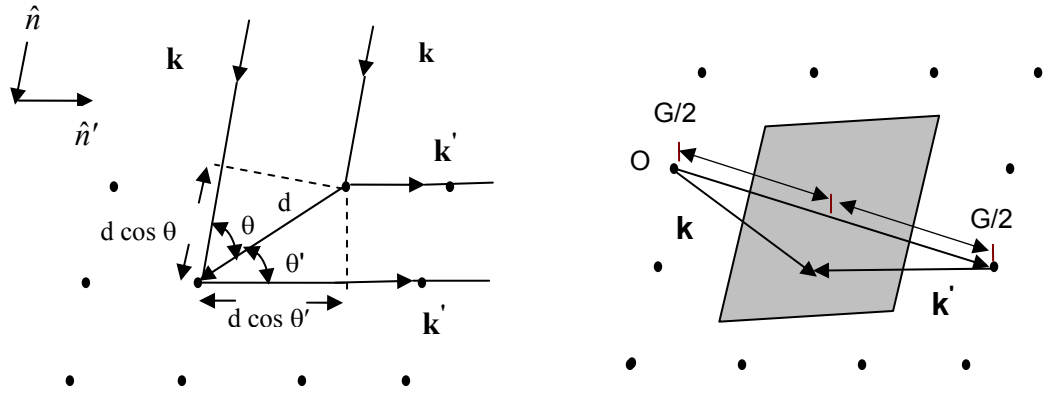

Figure 37: Bragg reflection from two lattice sites separated by d.

a) The path difference $2d\ sin\ \theta$ for rays scattered from two lattice points separated by a distance *d*.

b) The Laue condition is satisfied when $\vec{G} = \vec{k} - k'$ and $\vec{k}$ and $\vec{k}'$ have the same length.

Equivalence of the Bragg and Von Laue formulations:

The relation between vectors of reciprocal lattice and families of direct lattice planes implies that constructive interference of x-rays by a crystal can be established due to two equivalent criteria i.e. Bragg law and Laue approach.

Question: How can we tell whether these two approaches are equivalent or not?

Example: Show that the expression $d(hk\ell) = \frac{2\pi}{n\left|\vec{G}\right|}$ can be rewritten as $2\,d\,\sin\theta = n\lambda$, where θ is the angle between the incident beam of x-radiation and the crystal plane. [Note that the integer n is the same as the integer m mentioned above].

Solution:

Since Laue condition implies that the change in wave vectors $\Delta\vec{k} = n\vec{G}$ where $\left|\vec{G}\right| = \frac{2\pi}{d}$, and d is the distance between two successive planes.

From figure 37.b it can be shown that $\left|\Delta\vec{k}\right| = 2k\sin\theta$, and thus we get

$$k\sin\theta = \frac{n\pi}{d},$$

But we know that $k = 2\pi/\lambda$, then we obtain a gain the Bragg relation $2d\sin\theta = n\lambda$.