

Study Material - Sem. 5 - C12T

- crystal structure - Dr. T. Ker

- Class 3

CHAPTER - II

X-RAY DIFFRACTION AND RECIPROCAL LATTICE

2.1 INTRODUCTION

X-rays, being electromagnetic radiations, also undergo the phenomenon of diffraction as observed for visible light. However, unlike visible light, x-rays cannot be diffracted by ordinary optical grating because of their very short wavelengths. In 1912, a German physicist Max Von Laue suggested the use of a single crystal to produce diffraction of x-rays. Since all the atoms in a single crystal are regularly arranged with interatomic spacing of the order of a few angstroms, a crystal can act as a three-dimensional natural grating for x-rays. Friedrich and Knipping later successfully demonstrated the diffraction of x-rays from a thin single crystal of zinc blende (ZnS). The diffraction pattern obtained on a photographic film consisted of a series of dark spots arranged in a definite order. Such a pattern is called the *Laue's pattern* and reflects the symmetry of the crystal. Apart from this, the phenomenon of x-ray diffraction has become an invaluable tool to determine the structures of single crystals and polycrystalline materials. It is also extensively used to determine the wavelength of x-rays.

2.2 X-RAY DIFFRACTION

When an atomic electron is irradiated by a beam of monochromatic x-rays, it starts vibrating with a frequency equal to that of the incident beam. Since an accelerating charge emits radiations, the vibrating electrons present inside a crystal become sources of secondary radiations having the same frequency as the incident x-rays. These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiations is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another. The incident x-rays, however, have the same order of wavelength as that of the atomic dimensions; hence the radiations emitted by electrons are, in general, out of phase with one another. These radiations may, therefore, undergo constructive or destructive interference producing maxima or minima in certain directions.

Consider a one-dimensional row of similar atoms having interatomic spacing equal to a . Let a wave front of x-rays of wavelength λ be incident on the row of atoms such that the wave crests are parallel to the row. The atoms emit secondary wavelets which travel in all possible directions. As shown in Fig. 2.1, the reinforcement of secondary wavelets takes place not only in a direction perpendicular to the row of atoms but also in other directions. These directions correspond to different orders of x-ray diffraction. The zeroth, first and second order diffraction directions are shown in Fig. 2.1. It may be noted that reinforcement takes place in some particular directions only, whereas in other directions the wave fronts interfere destructively and the intensity is minimum. Such reinforcements produce Laue's pattern.

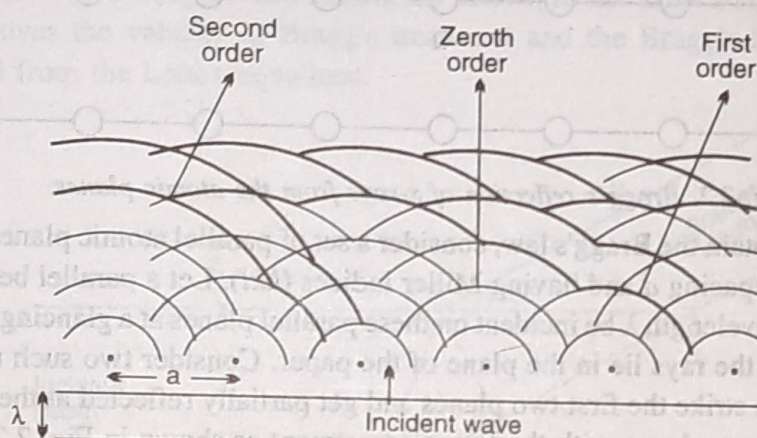


Fig. 2.1. Reinforcement of scattered waves resulting in diffracted beams of different orders.

In actual crystals, the problem is more complicated because of the presence of three-dimensional arrangement of atoms. The conditions for a crystal to diffract x-rays can be determined by using either *Bragg's treatment* or *Von Laue's treatment*.

2.2.1 The Bragg's Treatment : Bragg's Law

In 1912, W.H. Bragg and W.L. Bragg put forward a model which generates the conditions for diffraction in a very simple way. They pointed that a crystal may be divided into various sets of parallel planes. The directions of diffraction lines can then be accounted for if x-rays are considered to be reflected by such a set of parallel atomic planes followed by the constructive interference of the resulting reflected rays. Thus the problem of diffraction of x-rays by the atoms was converted into the problem of reflection of x-rays by the parallel atomic planes. Hence the words 'diffraction' and 'reflection' are mutually interchangeable in Bragg's treatment. Based on these considerations, Braggs derived a simple mathematical

relationship which serves as a condition for the Bragg reflection to occur. This condition is known as the Bragg's law.

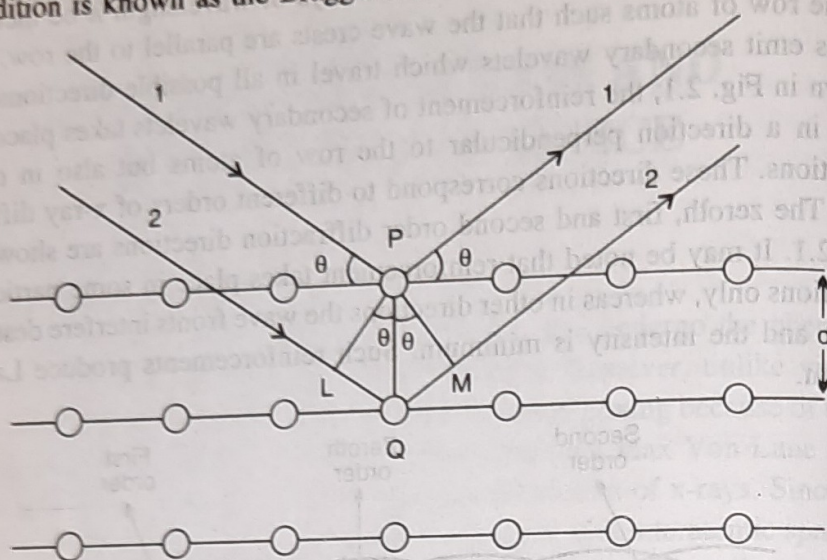


Fig. 2.2. Bragg's reflection of x-rays from the atomic planes.

To obtain the Bragg's law, consider a set of parallel atomic planes with interplanar spacing d and having Miller indices (hkl) . Let a parallel beam of x-rays of wavelength λ be incident on these parallel planes at a glancing angle θ such that the rays lie in the plane of the paper. Consider two such rays 1 and 2 which strike the first two planes and get partially reflected at the same angle θ in accordance with the Bragg's treatment as shown in Fig. 2.2. The diffraction is the consequence of constructive interference of these reflected rays. Let PL and PM be the perpendiculars drawn from the point P on the incident and reflected portions of ray 2 respectively. The path difference between rays 1 and 2 is, therefore, given by $(LQ + QM)$. Since $LQ = QM = d \sin \theta$, we get

$$\text{Path difference} = 2d \sin \theta$$

For constructive interference of rays 1 and 2, the path difference must be an integral multiple of wavelength λ , i.e.,

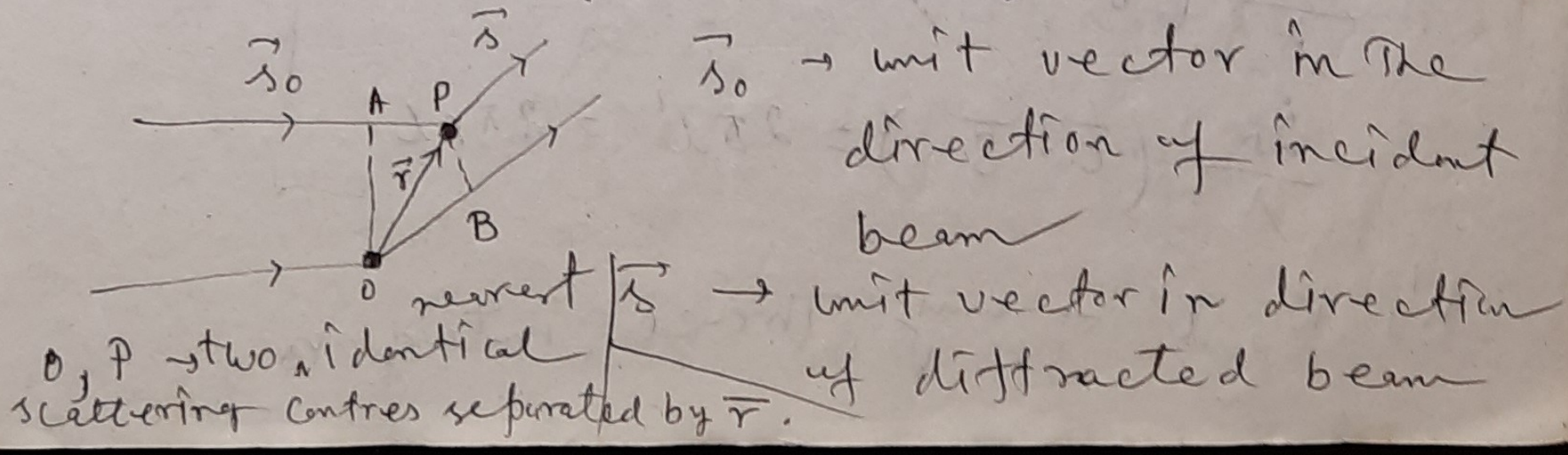
$$2d \sin \theta = n\lambda \quad (2.1)$$

where n is an integer. This equation is called the *Bragg's law*. The diffraction takes place for those values of d , θ , λ and n which satisfy the Bragg's condition. In Eq. (2.1), n represents the order of reflection. For $n = 0$, we get the zeroth order reflection which occurs for θ equal to zero, i.e., in the direction of the incident beam and hence it cannot be observed experimentally. For the given values of d and λ , the higher order reflections appear for larger values of θ . The diffraction lines appearing for $n = 1, 2$ and 3 are called first, second and third order diffraction lines respectively and so

on. The intensity of the reflected lines decreases with increase in the value of n or θ . The highest possible order is determined by the condition that $\sin \theta$ cannot exceed unity. Also, since $\sin \theta \leq 1$, λ must be $\leq d$ for Bragg reflection to occur. Taking $d \approx 10^{-10}$ m, we obtain $\lambda \leq 10^{-10}$ m or 1\AA . X-rays having wavelength in this range are, therefore, preferred for analysis of crystal structures.

Laue Treatment

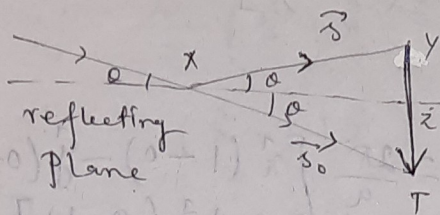
Laue treatment illustrates effectively the way in which x-ray scattered from different atoms can combine for the formation of diffracted beam. It also provides the validity of Bragg's picture. Bragg's eq. can be derived as a direct consequence of Laue equation.



Path diff. = PA - QB = $\vec{r} \cdot \vec{s}_0 - \vec{r} \cdot \vec{s}$

= $\vec{r} \cdot (\vec{s}_0 - \vec{s}) = \vec{r} \cdot \vec{S}$, $\vec{S} \rightarrow$ Scattering normal
The vector \vec{S} represents

The direction of normal to the reflecting plane.



$$\frac{YZ}{YX} = \sin \theta$$

$$\therefore YZ = \vec{S} \sin \theta$$

$$\text{or } YZ = \vec{s}_0 \sin \theta$$

$$TY = (\vec{s}_0 + \vec{s}) \sin \theta = 2\vec{S} \sin \theta$$

$$\text{or } \vec{S} = 2\vec{S} \sin \theta$$

$$|\vec{S}| = 2 \sin \theta$$

Phase diff = $\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{S})$

If \vec{S} is a direction of diffraction maxima, then ϕ must be equal to

some integral multiple of 2π . In a

3D crystal \vec{r} may coincide any of the crystallographic axes, \vec{a} , \vec{b} and \vec{c} .

So to get a diffraction maxima,

following three conditions have to be satisfied simultaneously —

$$\frac{2\pi}{\lambda} (\vec{a} \cdot \vec{S}) = 2\pi h' = 2\pi n h$$

$$\frac{2\pi}{\lambda} (\vec{b} \cdot \vec{S}) = 2\pi k' = 2\pi n k$$

$$\frac{2\pi}{\lambda} (\vec{c} \cdot \vec{S}) = 2\pi l' = 2\pi n l$$

h' , k' , l' \rightarrow any three integers

∴ h, k, l and h', k', l' are nearest neighbours, h', k', l' and h, k, l differ only by a common factor n , which may be equal to or greater than 1. h, k, l resemble the Miller indices of a plane which happens to be a reflecting plane. Let α, β, γ be the angle between S and $\bar{a}, \bar{b}, \bar{c}$ respectively.

$$\bar{a} \cdot \bar{S} = a S \cos \alpha = 2a \sin \theta \cos \alpha$$

$$\bar{b} \cdot \bar{S} = b S \cos \beta = 2b \sin \theta \cos \beta$$

$$\bar{c} \cdot \bar{S} = c S \cos \gamma = 2c \sin \theta \cos \gamma$$

$$\frac{2\pi}{\lambda} (2a \sin \theta \cos \alpha) = 2\pi h' = 2\pi n h$$

$$\therefore 2a \sin \theta \cos \alpha = h' \lambda = n h \lambda$$

$$2b \sin \theta \cos \beta = k' \lambda = n k \lambda$$

$$2c \sin \theta \cos \gamma = l' \lambda = n l \lambda$$

These conditions are called Laue equations

We have,

$$d = \frac{a}{h} \cos \alpha$$

Interplanar spacing of (hkl) plane

$$= \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

$$2a \sin \theta \cos \alpha = n h \lambda$$

$$\therefore 2a \sin \theta \frac{dh}{a} = n h \lambda$$

$$\boxed{2d \sin \theta = n \lambda}$$

Bragg's Law

Reciprocal Lattice

X-ray diffraction is equivalent to reflection of X-ray by sets of parallel lattice planes in the crystal. But in a crystal, there are many sets of interpenetrating planes with a variety of orientations and spacings, that can diffract X-ray. The visualization of all these is very difficult. P. P. Ewald simplified the problem and developed a new method of representing these interpenetrating planes. To know this method, we first note that the orientation of a plane is determined by its normal. Further, if the length of the normal is made proportional to the reciprocal of interplanar spacing i.e. $\frac{1}{d_{hkl}}$, its length and direction uniquely describes the set of parallel planes. The terminal points of all such possible normals corresponding to all sets of parallel planes form a lattice array. This array is called the reciprocal lattice. Each point preserves all the important characteristics of a particular

set of planes it represents. If $\vec{a}, \vec{b}, \vec{c}$ are primitive vectors of the crystal lattice and $\vec{A}, \vec{B}, \vec{C}$ are primitive vectors ~~in a~~ ^{of the} reciprocal lattice then we can construct the ~~axes~~ $\vec{A}, \vec{B}, \vec{C}$ as

$$\vec{A} = 2\pi \left(\frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}} \right); \quad \vec{B} = 2\pi \left(\frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}} \right)$$

$$\vec{C} = 2\pi \left(\frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}} \right)$$

$\vec{A}, \vec{B}, \vec{C}$ have the property -

$$\begin{array}{l|l|l} \vec{A} \cdot \vec{a} = 2\pi & \vec{B} \cdot \vec{a} = 0 & \vec{C} \cdot \vec{a} = 0 \\ \vec{A} \cdot \vec{b} = 0 & \vec{B} \cdot \vec{b} = 2\pi & \vec{C} \cdot \vec{b} = 0 \\ \vec{A} \cdot \vec{c} = 0 & \vec{B} \cdot \vec{c} = 0 & \vec{C} \cdot \vec{c} = 2\pi \end{array}$$

Any reciprocal lattice vector can be written as $\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$ where h, k, l are integers.

Every crystal structure has two lattices associated with it — i) crystal lattice and ii) reciprocal lattice.

The diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal whereas the microscopic image is a map of the real crystal structure. When

we rotate a crystal, we rotate both the direct and reciprocal lattice. Vectors in the crystal lattice have the dimension [length] but vectors in reciprocal lattice have the dimension [length]⁻¹. The crystal lattice is a lattice in real or ordinary space whereas the reciprocal lattice is a lattice in the associated Fourier space.

Reciprocal lattice of SC lattice

The primitive translation vectors of a SC lattice are —

$$\vec{a} = a\hat{x}, \vec{b} = a\hat{y}, \vec{c} = a\hat{z}$$

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

$$\text{Volume of the cell} = \vec{a} \cdot (\vec{b} \times \vec{c}) = a^3$$

$$\vec{A} = 2\pi \left(\frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}} \right) = \frac{2\pi}{a} \hat{x}, \vec{B} = \frac{2\pi}{a} \hat{y}, \vec{C} = \frac{2\pi}{a} \hat{z}$$

Thus the reciprocal lattice is itself is a simple cubic lattice having lattice constant $\left(\frac{2\pi}{a}\right)$.

Reciprocal lattice of bcc lattice

The primitive translation vectors of bcc lattice are —

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

$$\vec{c}' = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z})$$

The volume of The primitive cell is

$$= |\vec{a}' \cdot \vec{b}' \times \vec{c}'| = \frac{a^3}{2}$$

$$\vec{A} = \frac{2\pi}{(a^{3/2})} \left(\frac{a^2}{4} \right) \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{vmatrix}$$

$$= \frac{2\pi}{2a} \left[\hat{x} (1+1) - \hat{y} (-1-1) + \hat{z} (1-1) \right]$$

$$= \frac{2\pi}{2a} [2\hat{x} + 2\hat{y}] = \frac{2\pi}{a} (\hat{x} + \hat{y})$$

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

These ^{are} The primitive translation vectors of fcc lattice. Thus reciprocal lattice of ~~fcc~~ bcc lattice is fcc lattice.

Reciprocal lattice of fcc lattice

The primitive translation vectors of

fcc lattice is, $\vec{a}' = \frac{a}{2} (\hat{x} + \hat{y}), \vec{b}' = \frac{a}{2} (\hat{y} + \hat{z})$

$$\vec{c}' = \frac{a}{2} (\hat{z} + \hat{x})$$

Volume of the primitive cell is

$$V = |\vec{a}' \cdot (\vec{b}' \times \vec{c}')| = \frac{a^3}{4}$$

$$\vec{A} = \frac{2\pi}{(a^3/4)} \frac{a^2}{4} [\vec{x}(\vec{y} + \vec{z}) \times (\vec{z} + \vec{x})]$$

$$= \frac{2\pi}{a} \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{vmatrix} = \frac{2\pi}{a} [\hat{x}(1-0) - \hat{y}(0-1) + \hat{z}(0-1)]$$

$$= \frac{2\pi}{a} (\hat{x} + \hat{y} - \hat{z})$$

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

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

▣ Reciprocal lattice vector \vec{G} is perpendicular to (hkl) plane

The orientation of a plane is described by a vector normal to it. The vector product of any two non-parallel vectors is normal to the plane containing the vectors. The three vectors $(\vec{b} \times \vec{c})$, $(\vec{c} \times \vec{a})$ and $(\vec{a} \times \vec{b})$ form

a fundamental set such that normals to all lattice planes can be written as linear combinations of them with integer coefficients.

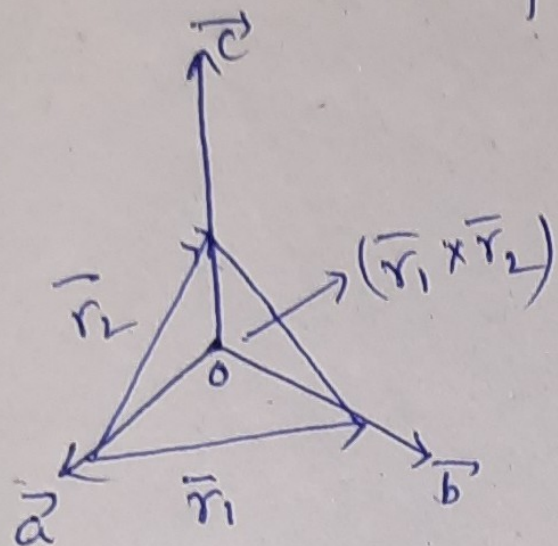


Fig. 1.

Fig. 1 shows the fundamental vectors of a lattice drawn from origin 'o' at a lattice point. A lattice plane is drawn and it intersects the \bar{a} axis at $x\bar{a}$, the \bar{b} axis at $y\bar{b}$ and the \bar{c} axis at $z\bar{c}$. The two vectors

$\bar{r}_1 = y\bar{b} - x\bar{a}$ and $\bar{r}_2 = z\bar{c} - x\bar{a}$ lie in the plane,

so, $\bar{r}_1 \times \bar{r}_2 = xyz \left[\frac{\bar{b} \times \bar{c}}{x} + \frac{\bar{c} \times \bar{a}}{y} + \frac{\bar{a} \times \bar{b}}{z} \right]$ is a vector normal to the plane. As the plane is a lattice plane, then the ratios $\frac{y}{x}$, $\frac{z}{x}$ and $\frac{y}{z}$ are rational numbers.

Therefore, $\vec{r}_1 \times \vec{r}_2 = A [h(\vec{b} \times \vec{c}) + k(\vec{c} \times \vec{a}) + l(\vec{a} \times \vec{b})]$

where h, k, l are the Miller indices of the plane and A is a number whose magnitude is immaterial.

Let $\vec{g} = h(\vec{b} \times \vec{c}) + k(\vec{c} \times \vec{a}) + l(\vec{a} \times \vec{b})$ is a vector perpendicular to (hkl) plane.

The reciprocal lattice vector,

$$\vec{G} = \frac{2\pi}{\vec{a} \cdot (\vec{b} \times \vec{c})} [h(\vec{b} \times \vec{c}) + k(\vec{c} \times \vec{a}) + l(\vec{a} \times \vec{b})] \text{ has}$$

The same form like \vec{g} . Therefore, the reciprocal lattice vector \vec{G} is perpendicular to the lattice plane with Miller indices (hkl) .