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Unit-2 X Ray Diffraction and Experimental Methods

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CH2. X-RAY DIFFRACTION AND EXPERIMENTAL METHODS

INTRODUCTION

The wavelength of X rays is of the order of 1 A^0 or 0.1 nm. Hence ordinary devices like diffraction grating do not produce noticeable effects with X ray. In 1812 Laue suggested that a crystal consisting of 3D arrangement of regularly spaced atoms could serve the purpose of grating.

BRAGG'S DIFFRACTION

Bragg diffraction occurs when radiation of wavelength λ comparable to atomic spacings is scattered in a specular fashion (mirror-like reflection) by the atoms.

When a beam of monochromatic X-rays falls on a crystal, it is scattered by individual atoms which are arranged in sets of parallel planes. Each atom becomes a source of scattered radiations.

The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. Because of this, Bragg's scattering is usually referred to as Braggs reflection and these planes are known as Bragg's planes. It is due to the presence of such sets of parallel planes that a crystal acts as reflection grating

For certain incident angles, reflection from these sets of parallel planes are in phase with each other.

BRAGG'S LAW:

In physics Bragg's law is a special case of Laue diffraction. It gives the angles for coherent scattering of waves from a crystal lattice. It includes the superposition of was fronts scattered by lattice planes leading to a strict relation between wavelengths. This law had firstly been devised for X-rays upon crystals but is moreover relevant for all kind of quantum beams such as neutron and electron waves on atomic spacing as well as for visual light on artificial periodic micro-scale lattices.

Bragg's law states the following:

When the X-ray is incident onto a crystal surface its angle of incidence, θ will reflect
with the same angle of scattering θ & When the path difference d is equal to a whole

number n of wavelength constructive interference will occur.

The exact process takes place upon scattering neutron waves via nuclei or a coherent spin interaction with an isolated electron. These wave fields that are re-emitted interfere with each other destructively or constructively creating a diffraction pattern on a film or detector. The diffraction analysis is the resulting wave interference known as Bragg diffraction.

Consider a beam of X-rays of wavelength & is incident at a glancing angle θ on a set of
parallel planes of the crystal as shown in Fig .
The atomic planes allow a part of X-rays to pass through and reflect the other part. The angle of incidence θ is known as Bragg's angle and it is equal to angle of reflection. The first ray is reflected from atom A in the plane 1, whereas the second ray is reflected from atom B lying in the plane 2 immediately below the atom A

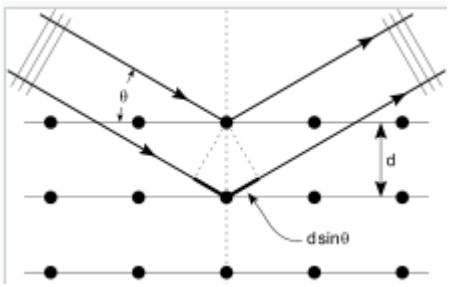


Fig. reflection of X-rays from lattice planes in a crystal

The path difference between the two reflected rays is 2d sin θ. For producing maxima it is equal to nλ.

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

Where, n is order of maxima taking values 1,2,3.....

The above equation is known as Bragg's reflection condition.

As sin θ has maximum value 1 for a typical value of interplanar spacing of 1.5 A^0, above equation gives the upper limit of 1 for obtaining first order reflection.

Therefore, substituting n = 1, sin θ= 1, d=1.5 A^0 in equation , we get

$2 \times 15 (1) = (1) \lambda$

$\lambda = 3$ A°

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

For n = 1 and d = 1.5A, we get

$\sin\theta = \lambda/3$

When λ is greater than 3 A^0, the value of $\sin\theta$ becomes greater than 1 which is not allowed.

Hence there will be no reflection if λ is greater than 3 A^0.

The reflection can be obtained for smaller values of λ for those sets of planes that have spacing less than 1.5 A^0 as well as increasing number of higher order reflection. If wavelength is very small of the order 0.1 A^0 of X-rays, then these rays produce other effects such as knocking off electrons from the atoms of the crystal and getting absorbed in the process.

Applications of Bragg's Law:

There are numerous applications of Bragg's law in the field of science. Some common applications are listed below.

1. In the case of XRF (X-ray fluorescence spectroscopy) or WDS (Wavelength Dispersive Spectrometry crystals of known d-spacings are used as analyzing crystals in the spectrometer.
2. It is used find out wavelength for a known interplaner spacing.
3. In XRD the interplaner spacing is used for characterization and identification.

X-Ray Diffraction and Experimental Methods

Laue method:

Although the Laue method can also be used to determine the crystal structure, several wavelengths can reflect in different orders from the same set of planes, with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity difficult. Rotating crystal method overcomes this problem.

In Laue method X rays of wavelength 0 .2 A0 to 2 A0 are used on a single crystal to determine its orientation.
After satisfying Bragg's reflection condition, these X rays produce a pattern on the film in terms of spots giving the internal symmetry of the crystal .

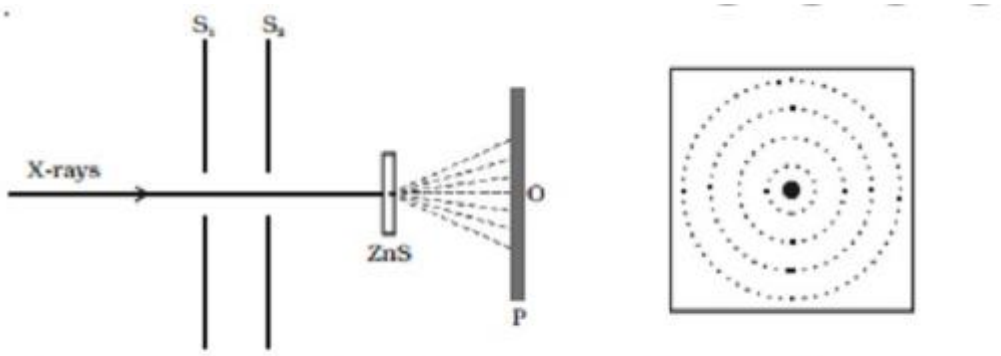


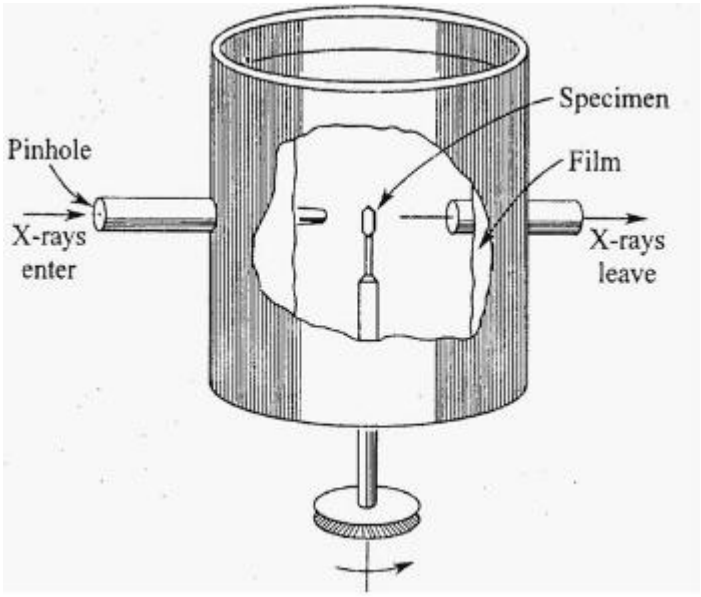
Fig (a) Laue experimental set up *Fig (b) Laue spot*

Rotating crystal method:

In this method, a monochromatic beam of X-rays is incident on a single crystal rotating about a fixed axis. The variation in the angle e brings different atomic planes into the position for reflection satisfying Bragg's condition $2d \sin\theta = n\lambda$, each producing spot on the film. The position on the film when developed indicates orientation of the crystal at which spot is formed. The data obtained from these spots revels information about structures of ordinary and complex molecules.

The film is mounted in a cylindrical holder concentric with a rotating spindle on which the single crystal specimen is mounted. The dimensions of the crystal usually need not be greater than 1 mm. The incident X-ray beam is made nearly monochromatic by a filter or by reflection from an earlier crystal. The beam is diffracted from a given crystal plane whenever in the course of rotation

In the rotating-crystal method a single crystal is rotated about a fixed axis in a beam of monoenergetic X-rays. Due to rotation, there is variation in the angle θ. The variation in the angle θ brings different atomic planes into position for reflection. A modified rotating crystal method is used for structure determination when a single-crystal specimen is available.



Bragg's spectrometer method:

It is one of the methods used for studying crystals. The Bragg's law is applied here. An narrow beam of monochromatic X rays is allowed to be incident ion a crystal mounted on a rotating table. The rotating table provided with scale and vernier giving measurements of various angles θ.

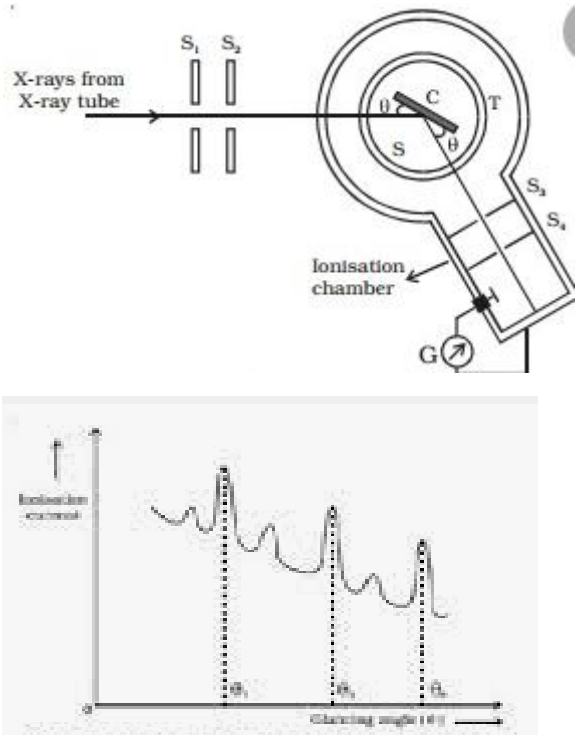


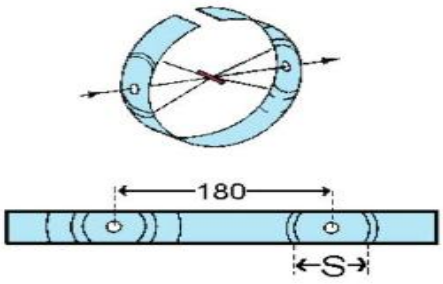
Fig.: Plot of glancing angle θ against ionization current (on Y axis)

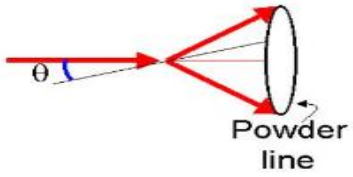
An arm of spectrometer is rotating about the same as as the crystal table carries an ionization chamber. X-rays are made to pass through fine slits 5, and S, which collimate it into a fine pencil. This fine X-ray beam is then made to fall upon the crystal C mounted on spectrometer table. This table is capable of rotation about a vertical axis. Its rotation can be read on a circular graduated scale. The reflected beam after passing through the slits 5, and 5, enters the ionization chamber. The rays reflected from the crystal enter into the ionization chamber and lonize the gas present inside it.

The current produced due to the lonization is measured by the galvanometer G (or ammeter). The current of ionization is a direct measure of the intensity of reflected beam from the crystal For different angles of incidence, the corresponding ionization current is measured from the galvanometer. These values are plotted in the form of the graph. For certain values of glancing angle, the ionization current increases abruptly The first peak corresponds to first order, the second peak to second order and so on. Knowing the angle and wavelength of X-rays, the spacing d for the crystal can be determined.

The Powder Crystal Method (Debye-Scherrer Method):

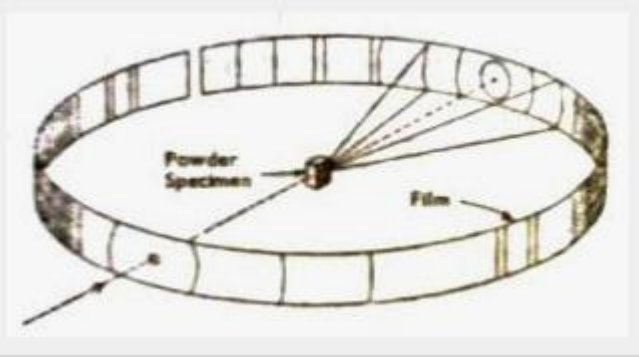
Laue method and rotating crystal method can be applied only for single crystals of reasonable sizes. Most of the crystalline substances naturally available are in the form of polycrystals. The method of preparation of single crystal is quite difficult. If powdered specimen is used instead of a single crystal, then there is no need to rotate the specimen, because there will always be some crystals at an orientation for which diffraction is permitted.





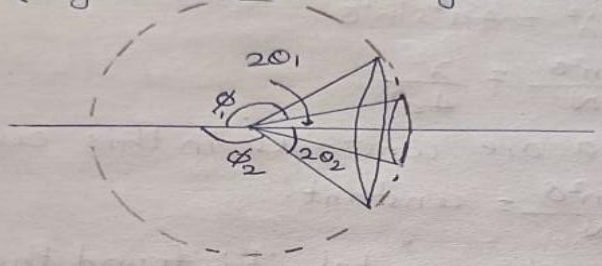
Camera radius = R

$$\frac{S}{2\pi R} = \frac{4\theta}{360}$$



* Analysis of cubic structure by powder method:-

. The circular symmetrical lines on the film can be identified by an experimental parameter ϕ related to θ (angle of diffraction) by the relation $2\theta + \phi = \pi$.



. We know that interplanar distance between two parallel planes having Miller indices (hkl) for cubic crystal is given by the relation

$$d_{(hkl)} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

where a is the lattice spacing.

The Bragg's diffraction condition is,

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

or $$d = \frac{n\lambda}{2\sin\theta}$$

$$\therefore \frac{n\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Squaring both sides of above equation and rearranging the terms, we get

$$n^2\lambda^2(h^2+k^2+l^2) = 4a^2\sin^2\theta.$$

Since n, h, k and l are integers, $n^2(h^2+k^2+l^2)$ must be a positive integer, say N.

$$N\lambda^2 = 4a^2\sin^2\theta.$$

or $$\frac{\sin^2\theta}{N} = \frac{\lambda^2}{4a^2}.$$

But, λ and a are constants in this case.

$$\therefore \frac{\sin^2\theta}{N} = \text{constant}.$$

For a single cubic crystal, it is found that,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

- The above relation can be verified for planes 100, 110, 111 by taking specific experimental data of cubic crystal. Suppose for $\lambda = 1.3A^\circ$, the maxima of reflected X-rays are obtained at glancing angles $\theta_1 = 19.2^\circ$, $\theta_2 = 27.72^\circ$ and $\theta_3 = 34.73^\circ$ for parallel planes having interplanar spacings d_1, d_2 and d_3 respectively.
- To find lattice constant 'a' and interplanar spacing of for a set of parallel planes, let us prepare a table for $\left(\frac{\sin^2\theta}{N}\right)$ values for glancing angles θ_1, θ_2 and θ_3.

N	$\frac{\sin^2\theta}{N}$	$\theta_1 = 19.2^\circ$, $\sin^2\theta_1 = 0.1082$	$\theta_2 = 27.72^\circ$, $\sin^2\theta_2 = 0.2163$	$\theta_3 = 34.73^\circ$, $\sin^2\theta_3 = 0.3246$
2	→	0.0541	0.1081	0.1623
3		0.0361	0.0721	0.1082
4		0.0271	0.0541	0.0812
5		0.0216	0.0433	0.0649
6		0.0180	0.0361	0.0541

From table, constant value of $\frac{\sin^2\theta}{N} = 0.0541$.

But $$\frac{\sin^2\theta}{N} = \frac{\lambda^2}{4a^2}$$

$$\therefore \quad a^2 = \frac{\lambda^2}{4 \times \frac{\sin^2\theta}{N}} = \frac{(1.3)^2}{4 \times 0.0541} = 7.81.$$

$$\therefore \quad a = 2.794\text{A}^\circ \approx 2.79\text{A}^\circ$$

From this value of lattice constant, the interplanar distance d for a particular set of parallel planes having Miller indices (hkl) can be obtained using the equation,

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

The interplanar spacing between (1,0,0) planes is $d_{100} = \frac{2.79^\circ}{\sqrt{1}}$ i.e. $d_{100} = 2.79\text{A}^\circ$

The interplanar spacing between (1,1,0) planes is $d_{110} = \frac{2.79^\circ}{\sqrt{2}}$, i.e., $d_{110} = 1.973\text{A}^\circ$.

The interplanar spacing between (1,1,1) planes is $d_{111} = \frac{2.79^\circ}{\sqrt{3}}$, i.e., $d_{111} = 1.61\text{A}^\circ$.

$$\therefore d_1 : d_2 : d_3 = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

The ratio can be confirmed by Bragg's condition.

For first order, Bragg's condition is $2d \sin\theta = \lambda$.

$$\lambda = 2d_1 \sin\theta_1, \quad \lambda_2 = 2d_2 \sin\theta_2, \quad \lambda_3 = 2d_3 \sin\theta_3.$$

$$d_1 : d_2 : d_3 = \frac{1}{\sin\theta_1} : \frac{1}{\sin\theta_2} : \frac{1}{\sin\theta_3}$$

$$= \frac{1}{0.3289} : \frac{1}{0.4651} : \frac{1}{0.5697}$$

$$= 3 : 2.15 : 1.75$$

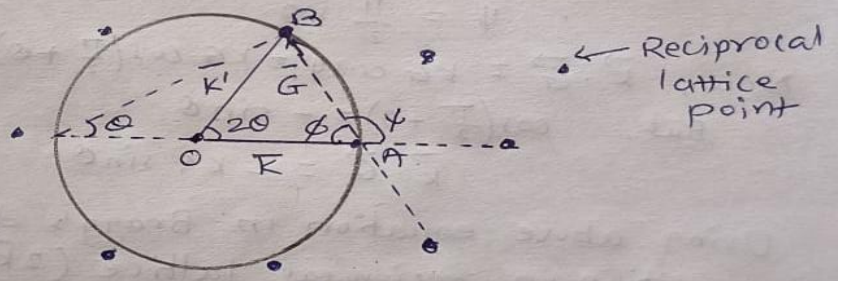
$$= 1 : 0.716 : 0.58$$

$$= 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

The $d_1 : d_2 : d_3$ shows that the given structure is simple cubic crystal.

* Ewald's Construction :-

- The Ewald's sphere is a geometric construction used in X-ray crystallography which demonstrates the relationship between the wave vector of the incident and diffracted x-ray beams, the diffraction angle for a given reflection and the reciprocal lattice of the crystal.
- We have seen that the incident and reflected X-ray beams are seperated by an angular seperation of angle 2θ. Consider reciprocal lattice points as shown in fig.



- Let us select direction of propagation of wave such that incident wave vector $\vec{K}$ terminates on one of the lattice points, say A. Let 'O' be the origin of $\vec{K}$. Now, construct a sphere in a reciprocal lattice space with radius OA and having centre O.

If the tip of $\vec{k}$ and $\vec{k'}$ are joined, we get,

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

where $\vec{G}$ is a reciprocal lattice vector.

since $\text{seg}(OA) \cong \text{seg}(OB)$, the ΔOAB is isosceles triangle.

$\therefore \angle OAB \cong \angle OBA$ (say ϕ).

In ΔOAB, $\quad 2\theta + 2\phi = \pi$

or $\quad \phi = \left(\frac{\pi}{2} - \theta\right)$

The angle between positive directions of $\vec{k}$ and $\vec{G}$ is

$$\psi = \pi - \phi = \pi - \left(\frac{\pi}{2} - \theta\right).$$

$$\therefore \psi = \frac{\pi}{2} + \theta.$$

Now, $\vec{k} \cdot \vec{G} = kG \cos\psi = kG \cos\left(\frac{\pi}{2} + \theta\right)$.

But, $\cos\left(\frac{\pi}{2} + \theta\right) = -\sin\theta$

$$\therefore \vec{k} \cdot \vec{G} = -kG \sin\theta.$$

Using above equation in Bragg's diffraction condition in reciprocal lattice ($2\vec{k} \cdot \vec{G} + G^2 = 0$), we get

$$-2kG \sin\theta + G^2 = 0.$$

or $\quad G = 2k \sin\theta \quad (\text{since } G \neq 0).$

where G is a reciprocal lattice vector.

The reciprocal lattice vector $\vec{G}$ is always expressed as,

$$G = n\frac{2\pi}{d}$$

where n is integer and d is the interplanar distance is the direct lattice.

$$n\frac{2\pi}{d} = 2k\sin\theta.$$

But, $k = \frac{2\pi}{\lambda}$

$$\therefore \quad n\frac{2\pi}{d} = 2\frac{2\pi}{\lambda}\sin\theta.$$

or $\quad d\sin\theta = n\lambda$

which is Bragg's condition in direct lattice.

Thus, Bragg's diffraction condition in the reciprocal lattice is exactly equivalent to Bragg's condition in direct lattice.