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Subject **Material science**

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Paper No. : Crystallography & crystal growth

Module : Experimental methods for x-ray diffraction

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Subject Name	Physics
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Module Name/Title	Experimental methods for x-ray diffraction
Module Id	M8

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LEARNING OBJECTIVES

1. Experimental methods viz., Laue spots method, rotating crystal method and powder crystal method are described.
2. Applications of the Laue diagram to the determination of symmetry and structure of materials, orientating single crystals and investigating distortion or polycrystallinity of materials is explained.
3. The principle of powdered crystal mehod is explained.
4. Measurements of Bragg angle and interplanar spacings in crystal are discussed.
5. The procedure of indexing powder patterns is discussed.
6. Rotating crystal method, its experimental set-up (both simple as well as modified) and procedures, are described.

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8.1 Experimental Methods For X-Ray Diffraction

X─ rays have proved to be of great importance on account of the fact that they have many and varied practical applications which may be summarily classified as follows:

- Purely scientific application, such as in crystallography to analyse and determine the internal structure of crystals and investigate the perfection of crystals
- Industrial application which is also given a general name of radio-metallography.
- Medical application such as radio- diagnosis (radiography) and treatment (X-ray therapy).

Here, we will take up only scientific application relevant to crystallography for analysis of crystal structure.

8.1.1 Experimental Methods

The Bragg's law expressed by an equation $n\lambda = 2d \sin\Theta$ for X-ray diffraction suggests that the diffracted beams can be found only when reflections from parallel planes of atoms interfere constructively and that would happen if the Bragg condition is satisfied. In order to meet this condition for x-ray diffraction it is required to provide for continuous range of values of either Θ or λ In an experiment devoted to analysis of crystal structure. The methods are:

i) Laue spots method
ii) Rotating crystal method
iii) Powdered crystal method.

We shall now consider these methods slightly in more detail as under:

8.1.1.1 Laue Spots Method

In this method, single crystal is kept fixed and a continuous or white spectrum of X-rays is used. Figure 8.1 shows the experimental set up. X-rays from the source are made to fall on a crystal and films are appropriately positioned to detect the transmitted as well as back reflected radiation as shown in the figure. This method is used either in transmission (generally at small angles) or in reflection (popularly known as Laue back-reflection method).

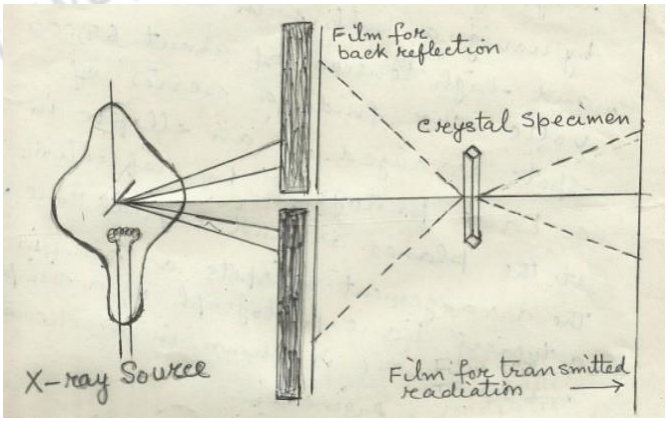

Figure 8.1 : Experimental set-up of laue method

On exposure to radiation, one finds spot on the film in directions and for such wavelengths which correspond to the conditions for diffraction. X-rays of short wavelength and carrying high energy are usually involved for transmission patterns. X-rays of longer wavelengths and lower voltages are used in reflection.

An x-ray beam with continuous range of wavelengths can be obtained by using a bulb with anticathode and high tension of about 65,000 volts. One finds a series of spots arranged on

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an ellipse in a Laue photograph by reflection at the planes around crystal zone. The arrangement of spots as seen in a typical Laue photograph of a simple cubic crystal is shown in a schematic diagram of figure 8.2

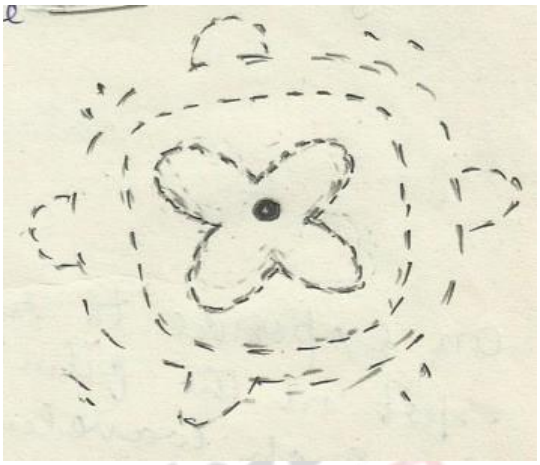


Figure 8.2 : Schematic diagram showing arrangement of spots in a Laue photograph of asimple cubic
crystal

Laue diagrams are used for:

a) Determining the symmetry and structure of materials,
b) Orienting single crystals and
c) Investigating distortion or polycrystallinity of materials.

Thick samples can be used for back – reflection method which offers the advantage of higher resolution as compared to transmission method.

Very fast diffusion -transfer films and luminescent screens have been used which to a very great extent shorten the exposure time required for Laue photographs. Films are being replaced by Geiger – or scintillation – counter techniques coupled with data processing equipment.

8.1.2 The Powdered Crystal Method

All the methods, be it Laue method or rotating crystal method, require a single crystal specimen whose size is greater than microscopic dimensions. However, in a very large number of crystalline solids, individual crystals of the desired size as required for the rotation photograph either do not occur or are not available. Such materials are readily examined by this method. This method was devised independently by Debye and Scherrer in Germany and by Hull in America about the same time in 1916 and called powdered crystal method or powder photograph method.

The principle of this method is as follows:

Let a monochromatic x-ray beam be allowed to fall on a small specimen of the material which is ground to a fine powder. The sample is obviously in a polycrystalline form which is an aggregate of extremely tiny crystallites randomly oriented with respect to a given direction and as such all possible orientations of all lattice planes are present in the powdered sample . There is bound to be a certain number of crystal grains which will be positioned with a given set of lattice planes making the correct angle with the incident beam for reflection to occur, while another fraction of the grains will have another set of planes in the correct position for reflection and so on. Further, reflections are possible not only from the different set of planes but also in the orders for each set.

The powdered crystal method is the only technique which is readily applicable to all crystalline solids. The diffraction data which depend on the lattice parameters are unique for a given material and, therefore, can be used for its identification. To identify a human being we make use of his

fingerprints. In the same way, diffraction data of powdered crystalline samples are unique which becomes a means of their identification.

Let us consider a monochromatic beam of x- rays which is incident at Bragg angle Θ on a set of lattice planes with interplanar spacing d in some particular crystallite so that the Bragg condition $2d\sin\Theta = \lambda$ for the above said lattice planes is satisfied. Considering the diffracted beam from a large number of randomly oriented crystallites , and take into account the diffraction from the planes with the same interplanar spacing as the first one , the locus of the diffracted beams would lie on a cone with half – apex angle 2Θ because the angle between the incident beam and the diffracted beam is 2Θ. The situation is shown in figure 8.3

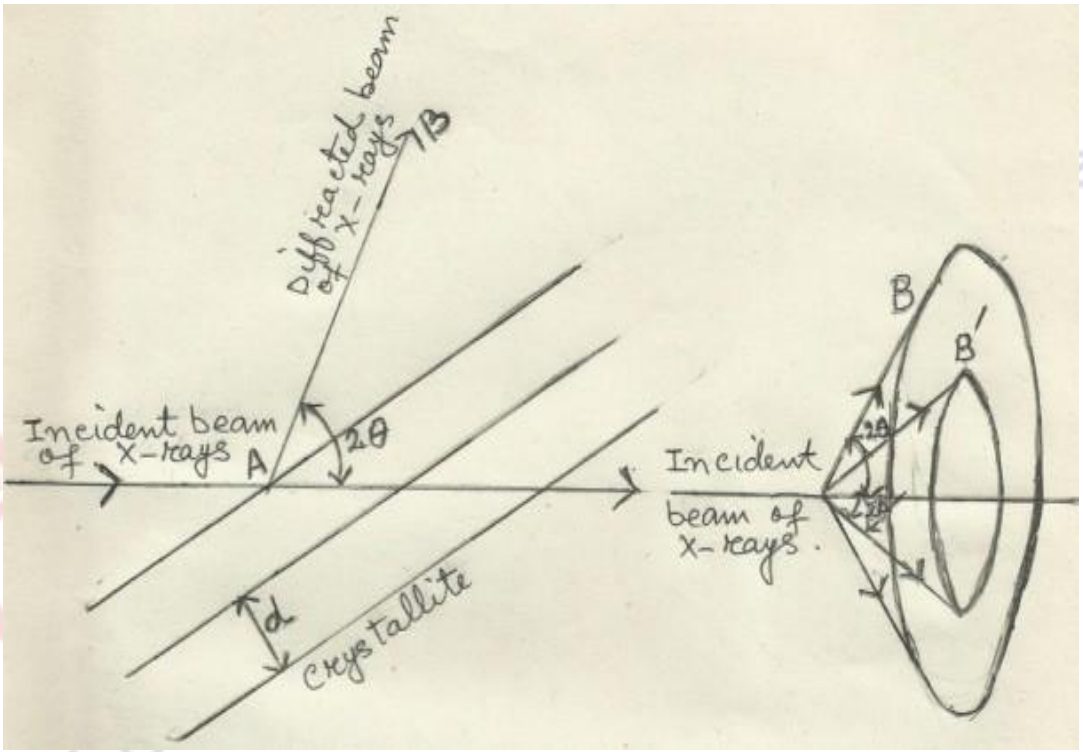


Figure 8.3 : locus of the diffracted X-ray beams due to same Bragg angle is a cone with half-apex Schematic diagram showing arrangement of spots in a Laue photograph of a simple cubic crystal

The diffracted beams from other sets of lattice planes with different interplanar spacings , say d_1 , d_2 , d_3 , d_4 and so on , would lie along different cones with different half-apex angles , $2\Theta_1$, $2\Theta_2$, $2\Theta_3$, $2\Theta_4$ and so on. Since the incident beam direction is the same for all these lattice planes, the cones would be coaxial.

So, the different beams from different set of planes (hkl) would all lie on a circular cone. If the same is recorded on a flat plate perpendicular to the incident beam, each diffraction from hkl planes would appear to be like a ring or halo around the central spot as shown in figure 8.4.

Different film placements are possible. If the film is placed normal to the incident x-ray beam beyond the powder in figure 8.3, the powder diffraction pattern gets recorded in the form of concentric circles or circular rings (as shown in figure 8.4) and the Θ values can be easily evaluated. However, this type

of film placement has a disadvantage and it is that several powder lines with $2\Theta > 90^0$(known as high angle lines) do not get recorded. On account of this limitation this type of film placement (flat film) is not used. To overcome this limitation of a flat film, a cylindrical film strip is used so that all the lines corresponding to 2Θ from 0^0 to 180^0 get recorded on the film as shown in figure 8.5 (a). This technique is due to Debye -Scherrer and the camera is named after them as "Debye -Scherrer Camera" On unrolling the film one finds that the pattern on it is of the type as shown in figure 8.5(b).The

diffracted rays which are at small angles make arcs around the central spot on the film. Those which get diffracted through 90^0 and the corresponding trace on the film is a straight line.

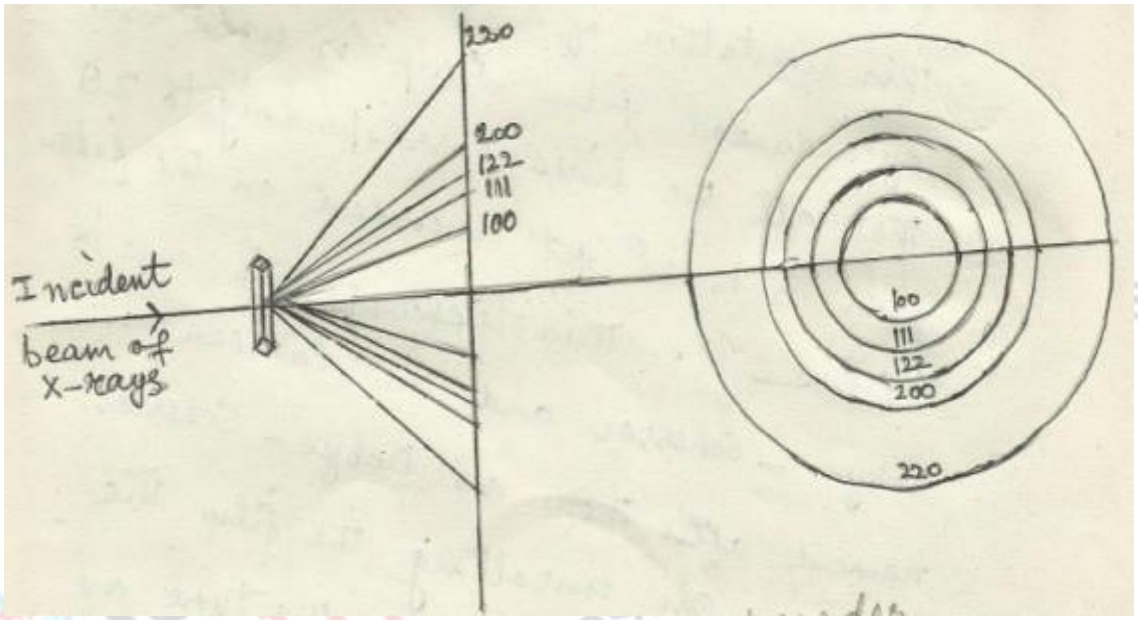
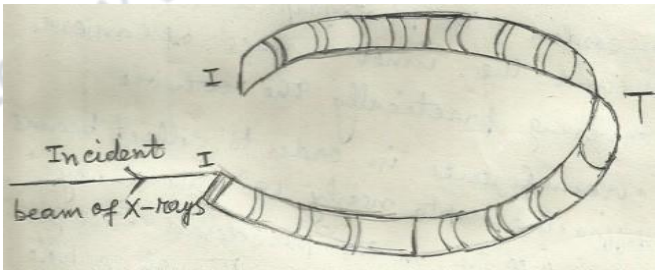
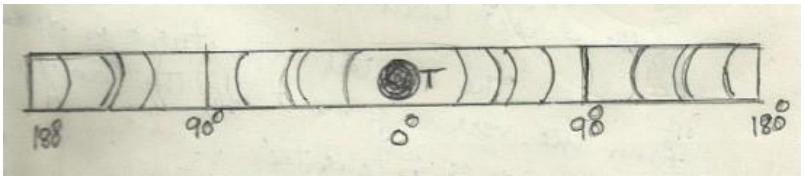


Figure 8.4 : The circular rings of powered photograph on a flat photographic plate.



(a)



(b)

Figure 8.5(a) & (b) : cylinderic film and traces of photographic film in the powdered crystal method

The material to be investigated is ground into a fine powder which is then stuck on a hair by means of gum. It is then suspended vertically in the axis of a cylindrical camera which enables sharp lines to get recorded. The photographic film fits round the inner surface of camera covering practically the whole circumference in order to collect beams diffracted upto nearly 180^0. The x-rays after falling on the powdered sample passes out of the camera through a hole cut in the film, in order to minimize the fogging produced by the scattering of the direct beam.

The crystal structure is deduced from the arrangement of the traces and their relative intensities .Taking Bragg's equation $2d\sin\Theta = n\lambda$.

Differentiating this equation leads to:

$$\Delta d.\sin\Theta + d\cos\Theta.\Delta\Theta = 0; \qquad n \text{ and } \lambda \text{ being constants}$$

Or, $$\Delta\Theta/\Delta d = -\tan\Theta/d$$

When the angle of incidence Θ approaches 90^0, $\Delta\Theta/\Delta d$ becomes very great which means that small variations in d produce large variations in Θ.

8.1.3 Measurement of Bragg Angles Θ and Interplanar spacings d

In order to find d values, it is required to measure Θ values. To do this the film is placed flat on a viewer with a linear scale fitted thereon. The film with diffraction lines is placed on the viewer which has illuminated background. The position of the diffraction lines are noted starting from one end along a line passing through centres of the entry and exit holes. There are two ways in which one can make measurements. One way is to note the reading R_1 and R_2 of the two arcs corresponding to a diffracted cone. $(R1 - R_2)$ is then the linear distance between arcs corresponding to one set. This gives the linear distance 2 R from which Θ is calculated. The second way is to measure R directly. This is done by locating the centre of the direct beam which coincides with the centre of the exit hole and so corresponds to $\Theta = 0^0$. Position of each arc from this point provides us the value of R. We know the radius r of camera, having determined the linear distance R through measurement, Bragg angle Θ can be calculated by using the relation:

$$4\Theta = 2R / r$$

Or, $$\Theta = R/2r \text{ radians},$$

$$= R\{180/2\pi r\} \text{ degrees}$$

The above relation is easily derivable from the diagram shown in figure 8.6

This method is applicable to any kind of crystalline matter. Since it does not require single crystals, it is very valuable and of great use in the investigation of metals and alloys, ceramics and any material in the polycrystalline state.

In the equation $\Theta = R\{180/2\pi r\}$, the term $180/\pi = 180x7/22$ which may be taken as 57.3. So, if a camera of diameter 2r = 57.3 mm is used for recording powder pattern data, 1^o in angle Θ would correspond to 1mm in R. This way, the geometric conversion of R into Θ is simple and straightforward.

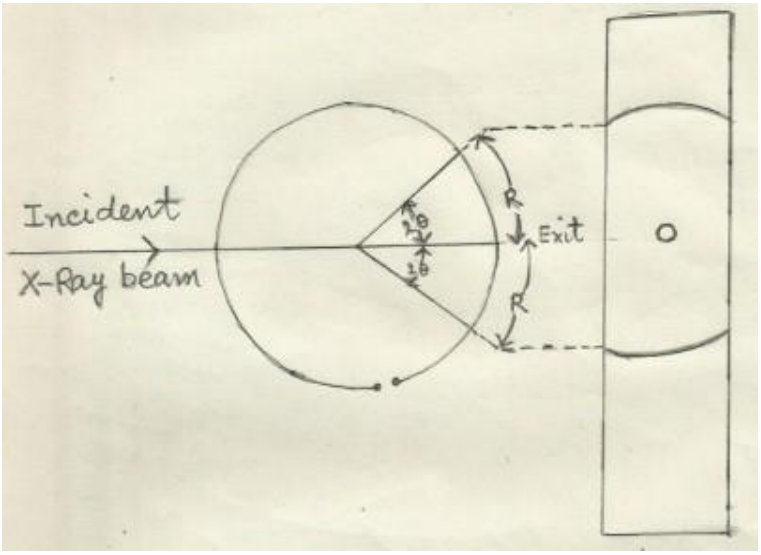


Figure 8.6 : Conversion of linear distance on the film into Bragg angle

It is important to bear in mind that while making measurement of linear distances and then converting them to Θ values, a distinction is required to be made between low-angle diffraction lines and the high-angle diffraction lines. Scattering of radiation from the air in the camera results into the background intensity. This background intensity is maximum near Θ = 0 which corresponds to centre of the exit hole of the camera. Because of this the film near the low angle side has more of background blackening. The second distinguishing feature of low-angle diffraction lines concerns the resolution of lines corresponding to say $k\alpha_1$ and $K\alpha_2$ components of the k_α doublet for Cuk_α radiation which is generally employed for powder diffractometry. Cuk_α is composed of Cu$k\alpha_1$ with wavelength λ = 1.54050 Å and Cu$k\alpha_2$ with wavelength λ =1.54434 Å. As a result of this, every diffraction line is a doublet corresponding to these components of $k\alpha_1$ and $K\alpha_2$ wavelengths. For a camera of diameter 57.3 mm, the doublet appears as a pair of two closely spaced lines which can hardly be resolved and as such appear as one thick line. The situation is different in case of cameras with larger diameters. The two components arising from $k\alpha_1$ and $K\alpha_2$ wavelengths get better resolved only at the high angle side where the separation between the two Bragg angles is wider and so the doublet can be easily identified.

Once the Bragg angle Θ is found out, application of equation $2d \sin\Theta = \lambda$ yields d values (interplanar spacing). The Interplanar spacings are related to the lattice constants a, b, c through Miller indices h, k, l by the equations given in quadrant VI section 6.3.1 for various crystal systems. We shall take the example of a powder photograph of a cubic crystal taken on a camera of 57.3 mm diameter with Cu$k\alpha$ radiation (λ =1.54 Å). From $2d\sin\Theta = \lambda$, we have $\sin^2\Theta = \lambda^2/4d^2$.
For a cubic crystal:

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

$$\text{Sin}^2\Theta = (\lambda^2/4a^2).(h^2 + k^2 + l^2).$$

Put $h^2 + k^2 + l^2 = N$, where N is an integer.

Therefore, $\text{Sin}^2\Theta = (\lambda^2/4a^2).N$ or, $\sin^2\Theta/N = \lambda^2/4a^2$

The linear distances of the diffraction lines are measured and Θ values determined for every line. From these Θ values, we determine the $\sin^2\Theta$ values. Division of $\sin^2\Theta$ by different values of integers gives the possible N-values. A list of possible N-values is prepared and the values of $\sin^2\Theta/N$ determined which should have a common factor $\lambda^2/4a^2$ as per the above equation. Suppose that common factor turns out to be σ . Substituting for λ = 1.54 Å(say), one is able to get the approximate value of lattice parameter a . This procedure is adopted for a few low angle lines and then for high angle lines.

For crystallographic characterization of any material, it is extremely important to determine lattice parameters very accurately. That is done by taking measurements on the diffraction line corresponding to $\Theta = 90^\circ$. However, $\Theta = 90^\circ$ corresponds to diffracted beams which are directed back into the incident x-ray beam, making its recording impossible. So, one tries to make measurements as close to $\Theta = 90^\circ$ as possible or extrapolate the measured d values to $\Theta = 90^\circ$.

The parameters required to be determined are the lattice parameters and the indices of various lines. While it is relatively simple for crystals of higher symmetry, it is quite complicated for the crystals of other systems.

8.1.4 Indexing of powder photograph.

The procedure of indexing of the powder pattern is based on the type of crystal classes that one is dealing with. It depends on the following:

1. Substances whose unit cell is known
2. Substances whose unit cell is not known.

For substances in category 1, indexing is rather simple whereas for the category 2, indexing is not that simple. For the latter type, trial and error methods are adopted for assigning indices to the powder lines. Let us first know very briefly about the method of indexing powder lines of those substances whose unit cell is known. There are two approaches-analytical approach and the graphical approach. In analytical method for substances whose unit cell is known, the assignment of the indices is done by comparing observed Θ values with those of the calculated ones.

From the powder pattern values of $\sin^2 \Theta$ are found. On the other hand, $\sin^2 \Theta$ corresponding to various (hkl) indices from the known unit cell parameter is calculated. Through comparison of the observed values of $\sin^2\Theta$ and the calculated values of $\sin^2\Theta$, the values that tally correspond to the hkl indices. Taking simple cubic crystal as an example, the interplanar spacing d is given by:

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

$$2d\sin\Theta = \lambda, \text{ \& so } \sin^2\Theta = \lambda^2/4d^2$$

$$\text{Therefore, } \sin^2\Theta = (\lambda^2/4a^2)(h^2 + k^2 + l^2) = \frac{\lambda^2 . N}{4a^2}$$

All possible values of N are used to calculate set of $\sin^2\Theta$ values from this expression . The possible values of $N = (h^2 + k^2 + l^2)$ for the cubic lattice are provided in the literature. It may be of interest to know that certain possible values of N (like 7, 15, 23, 28, 31 and so on) are forbidden. If the substance does not belong to any of the cubic systems, one has to adopt a different procedure.

For example, in case of tetragonal system, the following equation between $\sin^2\Theta$ and hkl indices is used:

$$\text{Sin}^2\,\Theta_{hkl} = (\lambda^2/4a^2)(h^2 + k^2) + (\lambda^2/4c^2)\,l^2$$

Put $\lambda^2/4a^2 = A$ & $\lambda^2/4c^2 = B$

$$\text{Sin}^2\,\Theta_{hkl} = A(h^2 + k^2) + B(l^2),$$

To calculate various values of $\sin^2\Theta_{hkl}$ for different sets of (hkl) indices , a table with two sets of values , one for the first term containing possible values of A and the other for the second term containing possible values of B. Tables giving possible values of $\sin^2\Theta$ are available in the literature. A particular $\sin^2\Theta_{hkl}$ value is obtained by suitable addition of the values from the two sets. The calculated $\sin^2\Theta_{hkl}$ values are then compared with the experimentally determined values and those which match are taken for assignment of indices h, k, l to the observed lines.

Similar procedure is followed for indexing the lines in the powder pattern of trigonal and orthorhombic systems. The equations to be used in case of hexagonal and rhombohedral systems are:

$$\sin^2\Theta_{hkl} = \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + (\lambda^2/4c^2).(l^2)$$

For orthorhombic system, the equation to be used is:

$$\sin^2\Theta_{hkl} = (\lambda^2/4a^2)\,h^2 + (\lambda^2/4b^2)\,k^2 + (\lambda^2/4c^2)\,l^2$$

For monoclinic and triclinic systems it is convenient to use expressions in terms of the reciprocal lattice parameters a* , b* , c* and α*, β*, γ* instead of direct lattice parameters and the expressions for monoclinic and triclinic systems are respectively given as follows:

Monoclinic system: $1/d^2 = h^2 a^{*2} + k^2 b^* + l^2 c^{*2} + 2lh\, c^* a^* \cos\beta^*$; the unit cell having been defined such that b-axis is perpendicular to the a and c axes.

Triclinic system: $1/d^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^*\cos\gamma^* + 2klb^*c^* \cos\alpha^* + 2lhc^*a^*\cos\beta^*$

The said procedure is the analytical one. However, graphical method is also followed. In this method, curves are drawn between the Interplanar spacings (d spacings) and the cell dimensions for those whose unit cell is known. The experimental d spacings are plotted and compared directly with the theoretical curves. The matching between the theoretical and experimental curves is done and indexing of the powder pattern is achieved.

8.1.5 The Rotating Crystal Method

The powdered crystal method is the most useful and feasible method obtaining information concerning a material which cannot be made available as a single crystal. However, it is not suitable for the determination of internal structure on account of difficulty in indexing. Therefore, the rotation and oscillation techniques are used, provided the material becomes available in the form of a single crystal. This method enables measurement of lattice constants and indexing of reflections quite easily. The intensities of individual reflections are conveniently measured which enables us to determine the crystal structure.

The rotating crystal method was devised by Schiebold and Polanyi. Its principle is based on the fact that if a crystal is rotated slowly about a fixed axis, a large number of planes will successively come into the reflecting positions and the diffracted radiation onto the photographic plate /film in the form of a pattern of spots, popularly called as rotation photograph.

In one type of technique, a photographic plate say 'P' is kept at a distance of a few centimetres from the single crystal C so that its plane is normal to the incident beam. The crystal is then rotated about its pre-determined axis (say c-axis). The beams reflected from all planes parallel to this axis lie on the surfaces of a family of cones whose axes coincide with the axis of rotation and whose vertices are at the crystal. The cones on intersecting the photographic plate positioned parallel to its axis result into a series of hyperbolas. The experimental set-up is shown in figure 8.7

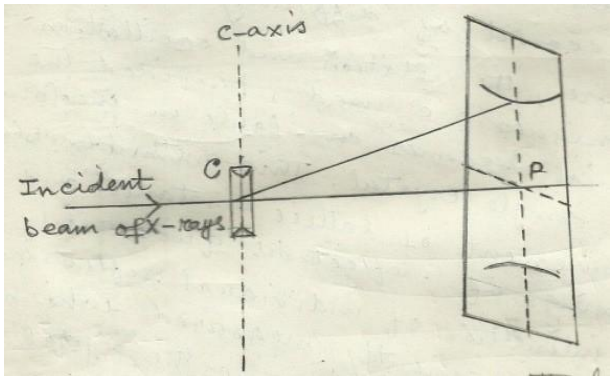


Figure 8.7 : Rotating crystal method

In a slightly modified technique (see figure 8.8 (a)) the reflected beams from crystal C are registered on a photographic film P which is bent in the form of a cylinder whose axis is along the

axis of rotation of the crystal. In this type of set-up the reflections from all planes which are parallel to the axis of rotation lie in a plane normal to the axis. This plane cuts the cylindrical film in a circle. On unrolling this film the reflections are found to get registered on a horizontal line containing the registration of the incident beam. The registration of spots is seen as a series of hyperbolas above and below the horizontal line. These lines have been named as layer lines and look something like shown in figure 8.8(b)

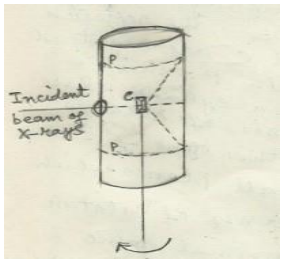


Figure 8.8(a) : Modified rotating crystal method

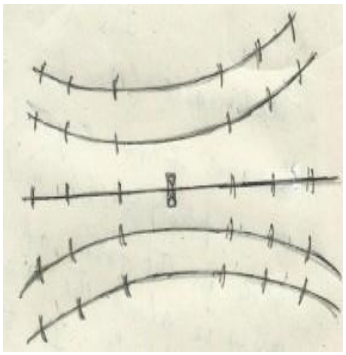


Figure 8.8(b) : Layer lines on the film in rotating crystal method

Production of layer lines in rotation photograph on flat film and cylindrical film is shown in figures 8.9 (a,b).Here, the crystal is rotated about c-axis as shown.Planes which are parallel to c-axis will reflect rays horizontally forming spots along a horizontal row alongwith the central spot. This is called as zero layer line. There will be other reflections which would make an angle with the horizontal row of spots. Accordingly, the lines are named as zero layer line, first layer line and so on as is shown in figure 8.9

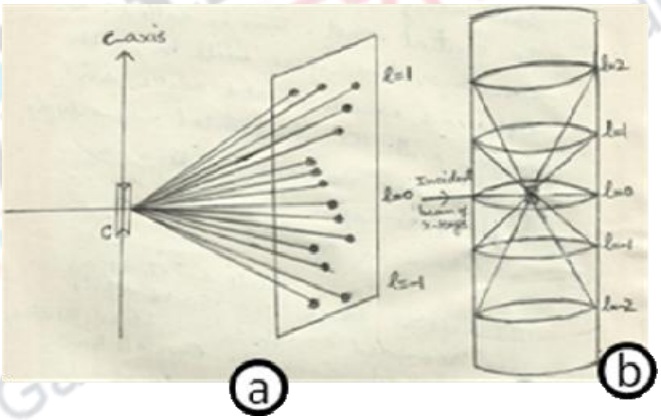


Figure 8.9:layer lines on flat and cylinderical film

With complete rotations of the crystal large numbers of spots are recorded on the film. It is, therefore, customary to rock the crystal back and forth through an angle of only 30^0. It limits the spots on film to those of certain indices. The angular rate of rocking is, however, kept constant.

From the distances between the layer lines the lattice spacing in a direction parallel to the axis of rotation is determined. Taking rotation photographs with rotation of the crystal about all the three axes a, b and c separately, is a method which is helpful in the determination of size of the unit cell.

Weissenberg modified the technique in which the crystal is rotated through $180^0$and back again continuously while the cylindrical camera fitted with the film moves at a constant speed forwards and backwards in the direction of the axis of rotation. The camera motion is so synchronized that its position corresponds to a definite angular position of the crystal as its rotation. It enables to accurately to index the spot on the film by noting its coordinates providing both the angle of reflection and the position of the reflecting plane.A cylinder made of a metal with a suitable and a few millimetres wide slit is placed in between the crystal and the film in a position that allows the spots

corresponding to only one layer to pass through it. In other words, the metal with an annular opening, when suitably adjusted allows only the diffracted beam for the second desired cone to get through while blocking the diffracted beams corresponding to other cones.

The x-ray diffraction technique described above lead to determination of lattice parameters. One also needs to find out the structure i.e., the position of atoms in the unit cell. For the determination of the crystal structure, accurate measurement of the intensities of a large number of Bragg reflections is necessary. Crystallographic measurements are now-a-days done on a computer controlled diffractometer.

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SUMMARY

- In this module we have discussed experimental for X-ray diffraction.
- The methods include Laue Spots Method, Rotating crystal method and powdered crystal method.
- Experimental setup of Laue method is schematically illustrated and described.
- The arrangement of spots as seen in a typical Laue photograph of a simple cubic crystal are schematically illustrated and described.
- Use of Laue diagrams in the determination of symmetry and structure of materials, Orienting single crystals and investigating distortion or polycrystallinity of materials is described.
- The powdered crystal method as a valuable tool particularly for materials which are not available in single crystal form is explained.
- Procedures involved in the measurements of Bragg angle θ and interplanar spacing in crystal are discussed.
- The procedure of indexing of powder photographs both for substances whose unit cell is known as well as substances whose unit cell is not known are described.

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