

## Crystal system and Structural Analysis

1. Seven Crystal System:

⇒ The Crystallographers have been able to divide into 32 point groups and 14 space lattices into Seven Crystal Systems. Some detailed descriptions of these seven crystal systems are,

⇒ Regular (or) cubic system

⇒ Hexagonal system

⇒ Tetragonal or quadratic system

⇒ Rhombic system

⇒ Trigonal or rhombohedral system

⇒ Monoclinic or monosymmetric system

⇒ Triclinic or asymmetric system.

1) Regular or cubic system:

$$a=b=c, \quad \alpha=\beta=\gamma=90^\circ$$

⇒ This system comprises five classes of crystals. Crystals belonging to regular or cubic system are built up on three equal axes at right angles to one another.

⇒ The crystal possesses in all nine planes of symmetry, namely three principle planes at right angles and six secondary planes inclined at  $60^\circ$  to each other.

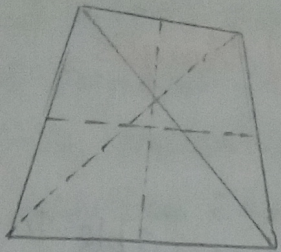


Fig 1.

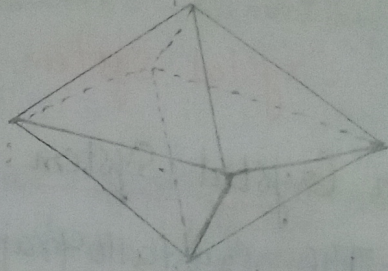


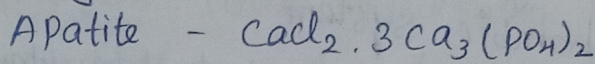
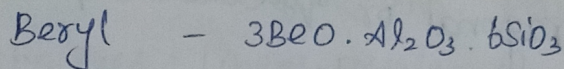
Fig 2.

ii) Hexagonal system:

$$a = b \neq c \quad \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ$$

⇒ This system includes five classes of crystals and is characterised by a crystallographic axis of six fold symmetry which is chosen as vertical crystallographic axis.

Ex:



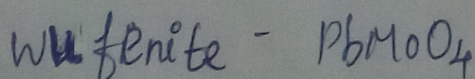
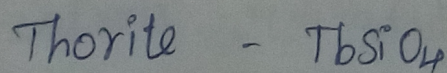
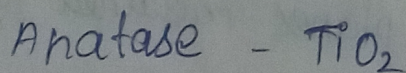
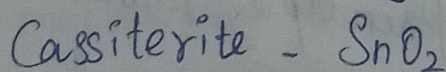
iii) Tetragonal or Quadratic system:

$$a = b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$$

⇒ This system comprises seven classes of crystals each class being characterised by a four fold or tetragonal axis of symmetry, which is chosen for vertical crystallographic axis. Such a crystal is referred to three mutually perpendicular axes, two of which are equal to one another, but not to the third.

Ex:

Metals - ordinary white tin and indium



iv) Rhombic system (or) orthorhombic:

$a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$

(3)

⇒ This system comprises, three classes of crystals.

They are characterised by three rectangular but unequal crystallographic axes at right angles to each other. The vertical axis is one of two fold or diagonal symmetry only.

Ex:  $KNO_3$ ,  $SrCO_3$ ,  $BaCO_3$ ,  $CaCO_3$

Celestine -  $SrSO_4$

Epsomite -  $MgSO_4 \cdot 7H_2O$

Olivine -  $Mg_2SiO_4$

Carnallite -  $KCl \cdot MgCl_2 \cdot 6H_2O$

v) Trigonal or Rhombohedral system:

$a = b = c$ ,  $\alpha = \beta = \gamma \neq 90^\circ$

⇒ It is sometimes referred to as part of hexagonal system. It comprises seven classes having hexagonal axes of reference the vertical axis having only three fold symmetry.

Ex: Quartz, calcite.

vi) Monoclinic or Monosymmetric system:

$a \neq b \neq c$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta \neq 90^\circ$

⇒ This system comprises three classes of crystals, all of which possess three unequal crystallographic axis which one is perpendicular to be other two.

Ex:

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

$Na_2SO_4 \cdot 10H_2O$

$Na_2B_4O_7 \cdot 10H_2O$

Orthoclase -  $KAlSi_3O_8$ , Ceyolite -  $Na_3AlF_6$

vii) Triclinic or Asymmetric system:

$$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$

⇒ Two classes are included in this system. One of which the holohedral class, has a center of symmetry only, whereas the other, the asymmetric class has not even that.

⇒ The system characterised by three unequal crystallographic axes all inclined to each other. none of the angles right angles, there being no axes of symmetry and the crystallographic axes are chosen parallel to three crystal edges.

Ex:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$

Albite -  $\text{NaAlSi}_3\text{O}_8$

Sassolite -  $\text{H}_3\text{BO}_3$

2. Symmetry properties:

⇒ "All crystals of one and the same substance have the same symmetry."

⇒ There are various type of symmetry known as element of symmetry in a crystal, the common types being.

i) centre of symmetry

ii) axis of symmetry

iii) plane of symmetry.

i) centre of symmetry:

⇒ It is a point. Any line drawn through this point will intersect the surface of the crystal at equal distances on either side. Under such conditions, the crystal is said to exhibit centre of symmetry.

## ii) Axis of symmetry:

⇒ It is an imaginary line. If the crystal is rotated about this line, the crystal presents exactly the same appearance as it had before rotation. Only the inclination of the faces and not the sizes are of consequence.

⇒ If the crystal presents the same appearance  $n$ -times in one complete revolution, the axis is said to be one of  $n$ -fold symmetry.

⇒ The only values of  $n$  can be 2, 3, 4 and 6 when the symmetry will be known as di-, tri-, tetra- and hexagonal axes of symmetry. The angles between pairs of axes of symmetry are  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$  and  $90^\circ$ .

⇒ The axis of symmetry is always perpendicular to a possible crystal face and parallel to a possible interfacial crystal edge.

## iii) Plane of symmetry:

⇒ It is an imaginary plane. This plane divides the crystal in two symmetrical halves such that one is the mirror image of the other.

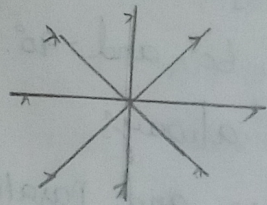
⇒ It must be noted that plane and axes of symmetry constitute the elements of symmetry, while the centre of symmetry is not an element of symmetry.

Furthermore, a crystal may have one or more than one planes or axes of symmetry, but it cannot have more than one centre of symmetry.

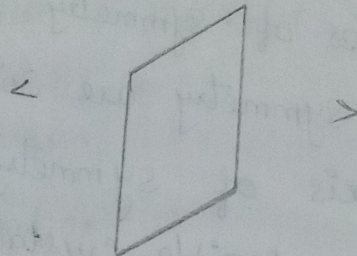
### 3. Symmetry operation:

⇒ A symmetry operation is movement of a body, such that after the movement has been carried out, every point of the body is coincident with an equivalent point (or perhaps the same point) of the body in its original orientation.

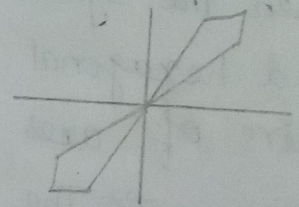
⇒ There are four principle operations for repeating figure. (a) Translation operation, (b) Rotation operation, (c) Reflection operation across a line in two dimensions or plane in three dimensions and (d) Inversion through a point (Fig 2)



Rotation



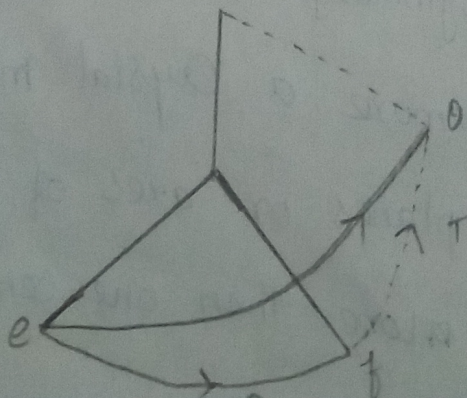
Reflection



Inversion

### Screw axis:

⇒ It is possible to combine proper rotation with a translation parallel to the rotation axis. The operation is shown in fig. where a rotation from  $e$  to  $f$  by an amount  $\theta$  combined with a translation from  $f$  to  $g$  by an amount  $\tau$  is equivalent to a screw motion from  $e$  to  $g$ . The symmetry element that corresponds to such a motion is called Screw axis.



⇒ After  $n$  rotations through an angle  $\theta$  and  $n$  translations  $T$  along the screw axis, the cumulative translation distance in the direction of the axis must equal some multiple of the lattice translation  $mt$ .

In other words.

$$nT = mt \text{ where } n \text{ and } m \text{ are integers}$$

$$T = mt/n$$

### Glide Planes:

⇒ It is possible to combine a reflection with a.

### A. Bravais Lattice:

⇒ Bravais gave the concept of lattice in which the small units could be replaced by small particles situated at the centres of the solids. Such a geometrical construction is known as space lattice which can, therefore, be defined as "an array of points showing how all molecules or atoms are arranged at different sites in three dimensional space."

⇒ A space lattice is an infinitely extended regular distribution of points in space. Each point is so chosen that its environment in space is the same as that of any other point. These points are so arranged as to form a series of cells, all consisting of parallelepipeds.

⇒ Bravais (1848) showed that all possible three dimensional space lattices are of fourteen types, i.e., there are only fourteen different ways of arranging similar points in a regular, or continuous three dimensional order.

Therefore  $h, k,$  and  $l$  are again small whole numbers. These are known as Miller indices. The use of  $(hkl)$  reciprocal intercepts as indices to define a crystal face was proposed by Miller in 1839.

The procedure for determining the Miller indices for a plane is as follows:

1) prepare a three column table with the unit cell axes at the tops of the columns.

2) Enter in each column the intercept of the plane with these axis.

3) Invert all numbers

4) clear fractions to obtain  $h, k$  and  $l$ .

Ex:

1)  $2a, 3b, c$

	$a$	$b$	$c$
Intercepts	- 2	3	1
Reciprocal	- $\frac{1}{2}$	$\frac{1}{3}$	1
clear fractions	- 3	2	6

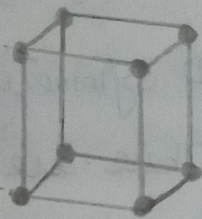
2)  $6a, 3b, 3c$

	$a$	$b$	$c$
Intercepts	- 6	3	3
Reciprocal	- $\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$
clear fractions	- 6	2	2

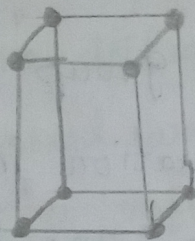


$\Rightarrow$  The Symmetry of these lattices related to the seven crystalline system discussed above. Each system is associated with certain definite types of lattice. To generate a complete space lattice, each of the representation in figure must be repeated in all directions without limit.

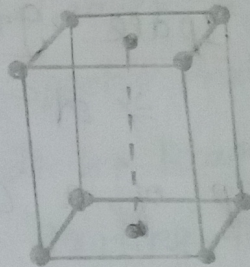
$\Rightarrow$  The point in a space lattice can be arranged in number of ways in a series of parallel and equidistant planes called the lattice planes. The principal planes of symmetry of a crystal which contain atoms are called the plane of crystals. The plane is explained by miller indices.



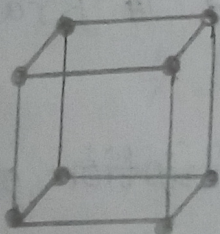
1) Triclinic



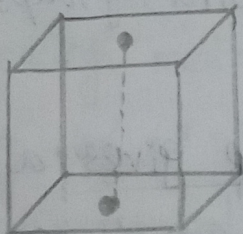
2) simple monoclinic



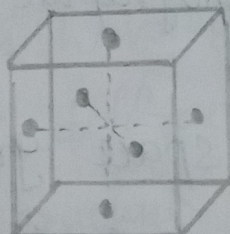
3) side centered monoclinic.



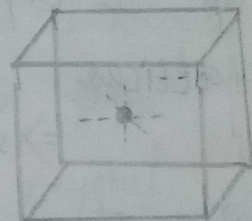
4) simple orthorhombic



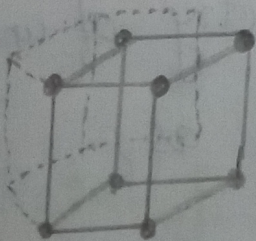
5) End-centered orthorhombic



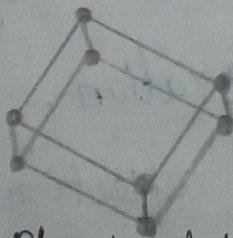
6) Face centered orthorhombic



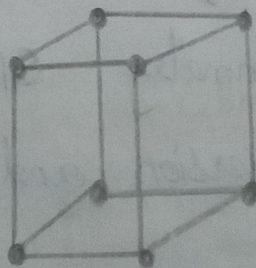
7) body centered orthorhombic



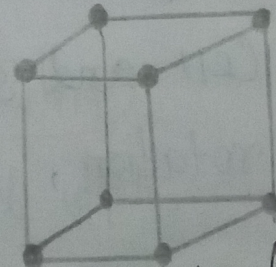
8) Hexagonal



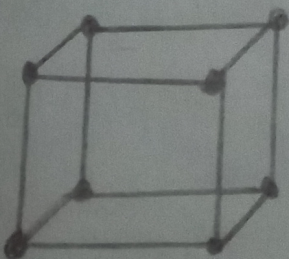
9) Rhombohedral



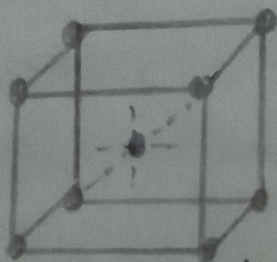
10) simple & Tetragonal



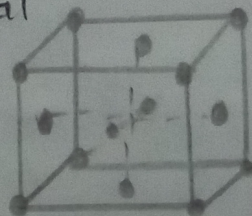
11) Body centered Tetragonal



12) Simple cubic



13) Body centered cubic

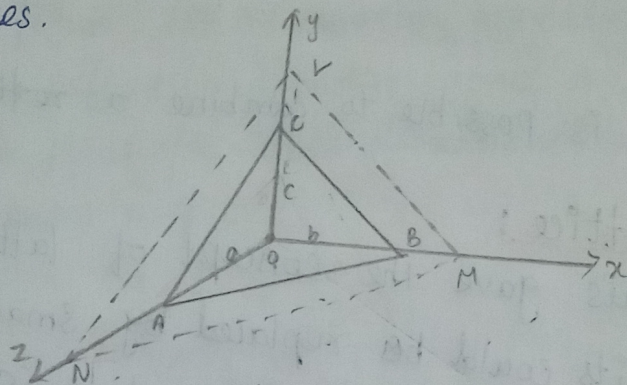


14) Face centered cubic

## 5. Miller Indices:

⇒ The plane of the crystal is explained by Miller indices.

⇒ Miller indices are a set of integers  $(h, k, l)$  which are used to describe a given plane in crystal. The Miller indices of a face of a crystal are inversely proportional to the intercepts of the face on the various axes.



⇒ Let, ABC be the unit crystal and LMN be the face of the crystal under consideration.

$$OA = a, \quad OB = b, \quad OC = c$$

also suppose that the intercepts of plane LMN on the three axis is be,

$$OL = Ha, \quad OM = Kb, \quad ON = Lc$$

where, H, K and L are simple integers eg: 1, 2, 3, etc.

⇒ Let us now describe any particular face LMN in terms of crystallographic axes and axial ratios. For, doing this we shall take the relationship between axial ratios and intercepts of that face on the axes into,

$$= \frac{a}{KL} : \frac{b}{LH} : \frac{c}{HK}$$

$$= \frac{a}{h} : \frac{b}{k} : \frac{c}{l}$$

$\Rightarrow$  Therefore  $h, k,$  and  $l$  are again small whole numbers. These are known as Miller indices. The use of  $(hkl)$  reciprocal intercepts as indices to define a crystal face was proposed by Miller in 1839.

The procedure for determining the Miller indices for a plane is as follows:

1) prepare a three column table with the unit cell axes at the tops of the columns.

2) Enter in each column the intercept of the plane with these axis.

3) Invert all numbers

4) clear fractions to obtain  $h, k$  and  $l$ .

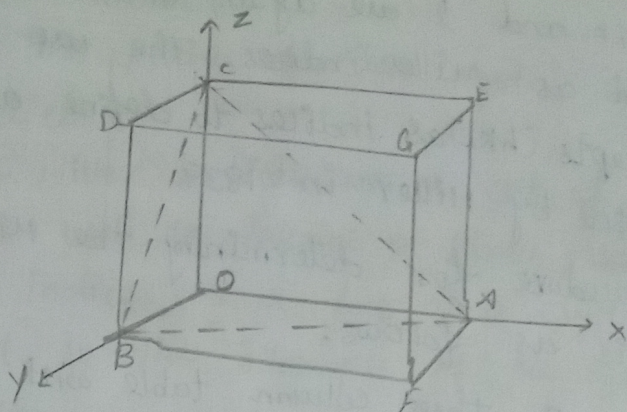
Ex:

1)  $2a, 3b, c$

	$a$	$b$	$c$	
Intercepts	-	2	3	1
Reciprocal	-	$\frac{1}{2}$	$\frac{1}{3}$	1
clear fractions	-	3	2	6

2)  $6a, 3b, 3c$

	$a$	$b$	$c$	
Intercepts	-	6	3	3
Reciprocal	-	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$
clear fractions	-	6	2	2



⇒ Three planes are shown in fig. These are face GEAF, face CEFB and face ABC.

⇒ The axes of the space lattice are  $OX$ ,  $OY$  and  $OZ$  with  $O$  as the origin.

face GEAF: along the axis  $OX$ , the face is placed at a definite position cutting of the intercept  $OA$ .

The face is parallel to the axes of  $Y$  and  $Z$ . When a face is parallel to an axis, its intercept on that axis is infinite.

⇒ The three axis are  $OY$ ,  $OX$  and  $OZ$ . ( $OX = OX$ )

The reciprocal of these intercepts known as miller indices, will be,

$$\frac{1}{\infty} : \frac{1}{1} : \frac{1}{\infty} \quad (\text{or}) \quad 0 : 1 : 0$$

face DGFB:

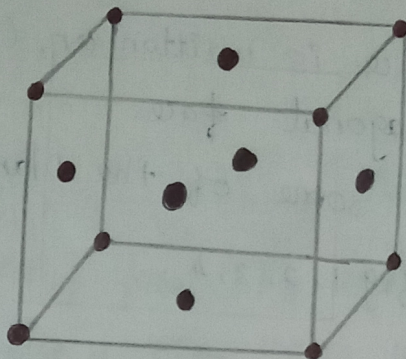
⇒ The intercepts  $OB : \infty : \infty$  taking the axes in the order  $OY, OX, OZ$ . The miller indices will be  $1 : 0 : 0$

face CEFB:

⇒ The intercepts along axes  $OY, OX$  and  $OZ$  are  $OB, \infty$  and  $OC$ , the plane is parallel to  $OX$ ; so,  $OC = OB$   
Miller indices are,  $1 : \infty : 1$  (or)  $1 : 0 : 1$

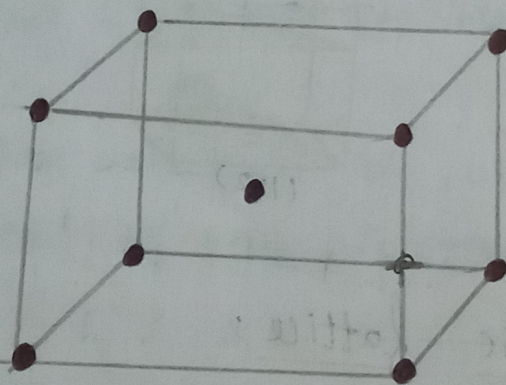
ii) Face centered cubic lattice:

When one unit is situated at each corner and one at the centre of each of the faces then it is known as face centered cubic lattice, as shown in fig. (13)



iii) Body centered cubic:

In a body centered cubic lattice, one unit is situated at each corner and one at the centre of the cube as shown in fig.



Type of lattice	$d_{100}$ ; $d_{110}$ ; $d_{111}$
Simple cube	$1$ ; $\frac{1}{\sqrt{2}}$ ; $\frac{1}{\sqrt{3}}$
Face centred	$1$ ; $\frac{1}{\sqrt{2}}$ ; $\frac{2}{\sqrt{3}}$
Body centred	$1$ ; $\frac{2}{\sqrt{2}}$ ; $\frac{1}{\sqrt{3}}$

## 7. Point group & Space group:

### i) point group:

⇒ The crystallographic point group is a set of symmetry operations that leave at least one point unmoved. In point group symmetry operations one central point in the object is kept unmoved while moving other faces of the object to the positions of features of the same kind.

⇒ There are 32 point groups.

⇒ The symmetry operations used in the point group detection are rotation and reflection.

### ii) space group:

⇒ A space group is the 3D symmetry group of a configuration in space. There are 230 space groups. These 230 space groups are a combination of 32 crystallographic point groups and 14 Bravais lattices.

⇒ A space group gives a description of symmetry of a crystal. Space groups are combinations of translational symmetry of unit cell and symmetry operation, such as, rotation, inversion and reflection.

## 8. X-rays:

⇒ X-rays which are known to be light of extremely short wave length could be used to investigate the internal structure of crystals.

The X-ray method is capable of telling us what the chemical composition of the various planes is and in short, the mode of distribution of the various atoms composing the crystal.

⇒ Laue (1912) first suggested that X-ray can be used in determining the structure of crystals by passing a beam of X-rays through a crystal and examining the diffraction spectra produced.

⇒ Further advanced was made by Bragg's to use the crystal as a reflection grating the resulting spectra being much simpler.

⇒ Following methods have been developed for the study of X-ray diffraction for ascertaining the internal structure of crystal.

1) Rotating crystal method.

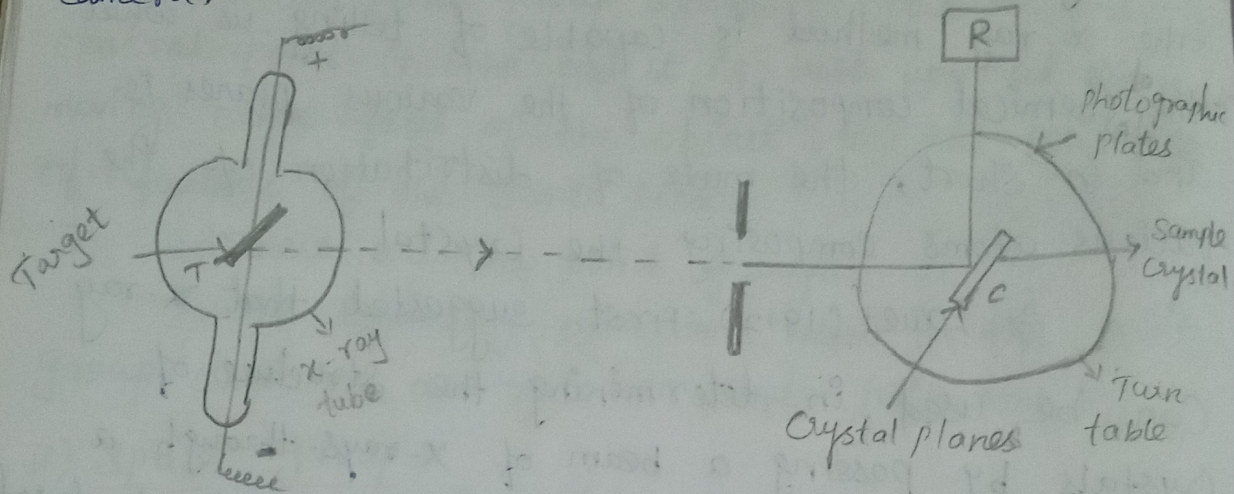
2) Powder method.

### 1. Rotating Crystal Method: (Schiebold-1919)

⇒ He developed this method with photographic recording of the diffraction pattern. It is the most widely used technique.

⇒ In this method crystal used is small but well formed. It is usually in the form of needle.

a mm long and half mm wide. The crystal is  $(110)$  mounted with a well defined axis and perpendicular to the beam which bathes it in x-ray radiation. The photographic plates is placed in a cylindrical camera.



⇒ The x-ray generated in the tube 'T' are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal 'c' mounted on the turn table. The crystal is rotated gradually using turn table, so as to increase the glancing angle at which the x-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on photographic plates.

⇒ The angles for which reflection are maximum give the value of  $\theta$ . The process is carried out for each plane of the crystal. The lowest angle at which the maximum reflection occurs to  $n=1$ . This is called first order reflection. The next higher angle of reflections  $n=2$ . This is second order reflection, and soon.

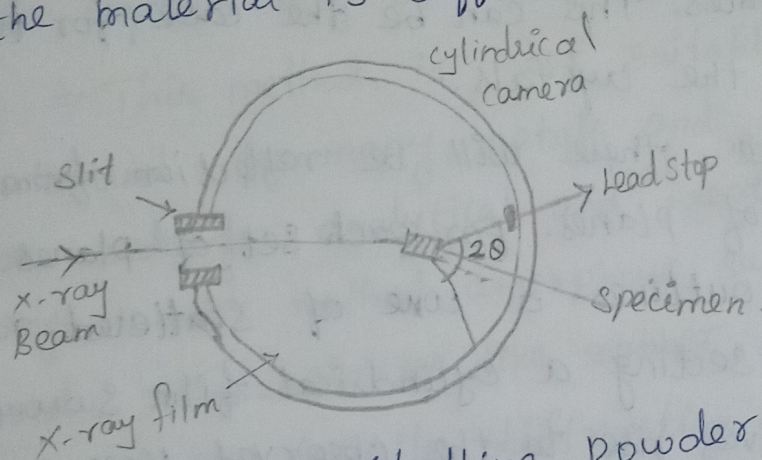


⇒ Applying the Bragg's equation and knowing (17) that 'n' and 'λ' the distance  $\alpha$  between successive planes can be calculated.

## 2) Powder Method:

⇒ Powder method is the simplest method for obtaining x-ray diffraction. It was first used by P. Debye and Scherrer.

⇒ In this method, the crystal sample need not be taken in large quantity but as little as mg, of the material is sufficient for study.



⇒ The crystalline powder is contained in a thin walled glass capillary, poly (so small) crystalline metals are studied in the form of fine wires.

⇒ A beam of monochromatic x-rays falls on the powdered materials. The diffracted rays and the undeviated beam record themselves on a photographic plate which is bent in the form of a circular arc surrounding the powdered crystal.

⇒ Since in the powdered specimen, there are random orientations of the small crystals hence there will be some at the proper angle for x-ray reflection from each set of planes.

⇒ The direction of the reflected beam is (12) limited only by the requirement that the angle of incidence equals to the angle of reflection.

⇒ If the angle of incidence is  $\theta$ , then the angle of reflection be  $2\theta$ . It is likely that a certain number of small crystals have their (100) faces at such an angle with respect to the incident beam that a first order reflection will occur similarly, there will be other crystals in such a position so as to give a second and third order reflection from (100) faces. This can be the case for (110) and (111) faces of the crystals.

⇒ Hence, there will be reflection from many different set of planes. For, each set of planes the reflected beam outlines a cone of scattered radiation. The cone intersecting a cylindrical film surrounding the specimen, gives rise to the observed lines. On a photographic plates, the observed pattern consists of series of concentric circles.

⇒ After obtaining the powder diagram we index the lines assigning each to the responsible set of planes. The distance 'l' of each lines is measured from the central spot, usually by having the distance between the two reflections on either side of the centre.

⇒ If the film radius is 'r', the circumference  $2\pi r$  corresponds to a scattering angle of  $360^\circ$ .

Then,  $\frac{\lambda}{2\pi r} = \frac{2\theta}{360^\circ}$  (or)  $\theta = 360^\circ \times \frac{\lambda}{4\pi r}$  (19)

⇒ Once the value of  $\theta$  is known, we can calculate the value of 'd' from Bragg's equation,

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

⇒ For indexing the reflections, we must know the crystal systems to which the specimen belongs. This can usually be done by microscopic examinations. Powder diagrams of monoclinic, orthorhombic and triclinic crystals may be almost impossible to index.

⇒ This method is most suitable for cubic crystals and for many metals and alloys. It can also be used for analytical and identification purpose. By using powder method amorphous substance are also analysed. As substances like rubber, cellulose, asbestos gives definite diffraction patterns, hence it can be concluded that they possess a definite structure.

⇒ This method also helps us to distinguish allotropic modifications of the same substance we can also find the transition from one form to another by cooling the powder.

E.g.  $\alpha$  and  $\beta$ -iron have a body centred lattice while iron has face centred lattice.

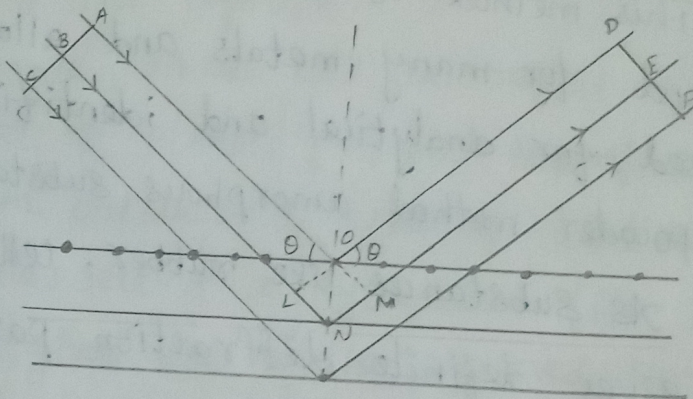
## 9. Bragg's Equation:

(20)

⇒ Bragg equation pointed out the unlike reflection of ordinary light, the reflection of x-rays can take place at certain angles which are determined by the wave length of x-rays and distance between the planes in the crystal.

⇒ The fundamental equation which gives a simple relationship between the wave length of x-ray, the inter planar distance in the crystal and the angle of reflection, is known as Bragg's equation.

### Derivation:



⇒ consider, the diagram the horizontal lines are parallel planes in the crystal structure separated from one another by the distance  $d$ .

⇒ Suppose a beam of x-rays falls on the crystal at glancing angle  $\theta$ . Some of these rays will be reflected from the upper plane at the same angle  $\theta$ . While some others will be absorbed and get reflected from the successive layers. Let, the planes ABC and DEF be drawn  $\perp$  to the incident and reflected beams.

⇒ The waves reflected by different layers (d) planes will be in phase with one another only if difference in path lengths of the waves reflected from the successive planes is equal to an integral number of wave length.

⇒ Drawing OL and OM perpendicular to incident and reflected beams. The difference in the path lengths (S) of the waves reflected from the first two plane is given by,

$$S = LN + NM$$

⇒ This should be equal to a whole number multiple of wave length  $\lambda$ ,

$$LN + NM = n\lambda$$

⇒ Since, the triangles OLN and OMN are congruent hence,  $LN = NM$

$$2LN = n\lambda$$

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

⇒ This is Bragg's equation. knowing  $\theta$ ,  $n$ , and  $\lambda$ , 'd' can be calculated.

## 8. Fourier synthesis of Electron density in a Crystal:

$\Rightarrow$  X-rays are scattered by the electrons in a crystal, the ultimate goal of x-ray crystallography is to determine the electron density  $\rho(xyz)$  as a function of the coordinates  $x, y, z$ . Since, the number of electrons and the size of the atomic orbitals both vary from atom to atom, different atoms have different scattering efficiencies. The scattering factor of an atom is defined as,

$$f = 4\pi \int_0^{\infty} \rho(r) \frac{\sin kr}{kr} r^2 dr \quad \Rightarrow (1)$$

$\rho(r) \Rightarrow$  spherically symmetric electron density (no. of  $e^-$ s per unit volume) of the atom.

$$k = (2\pi/\lambda) \sin \theta$$

where,

$\lambda \Rightarrow$  wave length of the x-rays.

$\theta \Rightarrow$  scattering angle.

$\Rightarrow$  The wavelength of the x-rays used for recording the x-ray diffraction pattern is of the size of the atom, the scattered waves from different regions of an atom interfere constructively.

$\Rightarrow$  The integral in eqn. (1) takes this interference into account through the factor  $(\sin kr)/kr$ . Before proceeding further we shall prove an important result that the scattering factor of an atom in the direction  $\theta \rightarrow 0$  is equal to the number of electron ( $N_e$ ) in the atom,

$$\lim_{\theta \rightarrow 0} f = N_e \quad \Rightarrow (2)$$

$\Rightarrow$  Here,  $\theta \rightarrow 0$  implies that the x-rays pass straight through the atom. If  $\theta = 0$ , then  $k = 0$  and the term  $(\sin kr)/kr$  in equ (1) is indeterminate. Hence, to evaluate the integrand, we evaluate the limit  $(\sin kr)/kr$ .

We know from the result of the power series that,

$$\lim_{\theta \rightarrow 0} \frac{\sin \theta}{\theta} = \lim_{\theta \rightarrow 0} \frac{\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \dots}{\theta} = 1 - \frac{\theta^2}{3!} + \frac{\theta^4}{4!} - \dots = 1$$

Hence,  $\lim_{kr \rightarrow 0} (\sin kr)/kr = 1$  so that,

$$f = 4\pi \int_0^{\infty} \rho(r) r^2 dr = Ne \quad \Rightarrow (3)$$

$\Rightarrow$  Since, the integrand is the product of electron density and the spherical volume element  $4\pi r^2 dr$ , which upon integration yields the total number of electrons in the atom.

$\Rightarrow$  Let, us now return to the electron density  $\rho(xyz)$   $dx dy dz$  is the number of electrons in the volume element  $dx dy dz$ , since the electron density is a periodic function, it can be expanded by a Fourier series;

$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) \exp \left[ -2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] \quad \Rightarrow (4)$$

where,

$V \Rightarrow$  volume of the unit cell,

$x, y, z \Rightarrow$  Co-ordinate of the point in the unit cell.

$a, b, c \Rightarrow$  Unit cell dimensions.

$(hkl) \Rightarrow$  Miller indices

(24)

$F(hkl) \Rightarrow$  Fourier coefficient which are also referred to as structure factors.

$\Rightarrow$  Each structure factor is associated with a particular reflection from the  $(hkl)$  planes. Through the triple summation in Eqn. (4) is over all the values  $(-\infty$  to  $\infty)$  of  $h, k, l$ , in practice all the terms need not be included in the summation although the more the terms included, the higher is the resolution of  $P(xyz)$ . The structure factors contain all the information about all the atoms in a unit cell.

The structure factor  $F(hkl)$  is defined as,

$$\text{where, } F(hkl) = \sum_j f_j \exp \left[ 2\pi i \left( \frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right) \right] \Rightarrow (5)$$

$f_j \Rightarrow$  scattering factor of the  $j$ th atom in the unit cell and the summation is over all the atoms in the unit cell.

$\Rightarrow$  To account for the above expression for  $F(hkl)$ , we recall that when the Bragg law is satisfied for a given reflection, the amplitude of the wavelet scattered from an atom in one unit cell of the crystal is in phase with the amplitudes of the scattered wavelets from the corresponding atoms in the millions of the other unit cells of the crystal.

$\Rightarrow$  However, the wavelet scattered by one atom may, in general, not be in phase with the wavelet scattered by another atom within the same unit cell with



the result that the intensity  $I(hkl)$  of reflection (25) will depend upon the extent to which amplitudes of the wavelets reflected from different atoms (denoted by  $f_i$ ) are in phase with one another. It is known that,

$$I(hkl) \propto |F(hkl)|^2 \Rightarrow (6)$$

$\Rightarrow$  The intensities of the x-ray diffraction patterns from the  $(hkl)$  planes of the crystal are proportional to the square of the modulus (absolute value) of  $F(hkl)$ .

$\Rightarrow$   $I(hkl)$  can be determined from the densities of spots on the photographic film. From the values of  $I(hkl)$ ,  $|F(hkl)|^2$  can be determined. But, the crystallographer needs  $F(hkl)$  rather than  $|F(hkl)|^2$  to calculate  $\rho(xyz)$  with the help of equ. (4). Since,  $F(hkl)$  is a complex number, we can write,

$$F(hkl) = A(hkl) + iB(hkl)$$

Hence,

$$\begin{aligned} |F(hkl)|^2 &= |A(hkl) + iB(hkl)| |A(hkl) - iB(hkl)| \\ &= |A(hkl)|^2 - |B(hkl)|^2 \Rightarrow (7) \end{aligned}$$

$\Rightarrow$  Since, the values of  $A(hkl)$  and  $B(hkl)$  are not obtained directly, indirect methods are employed to determine these quantities for the evaluation of  $F(hkl)$ . For a centrosymmetric crystal  $F(hkl)$  is of the form,

$$F(hkl) = \pm f_{\text{heavy}} \pm f_{\text{light}}$$

where;

$f_{\text{heavy}} \Rightarrow$  Scattering factors of the heavy atoms

$f_{\text{light}} \Rightarrow$  Scattering factors of the light atoms.

⇒ The  $f_{light}$  are much smaller than  $f_{heavy}$  and their phases are almost random if the atoms are distributed throughout the unit cell. Thus, the heavy atoms dominate scattering. Since, their scattering factors are of the order of their atomic numbers. Since the net result of  $f_{light}$  changes  $F(hkl)$  only slight, it follows that  $F(hkl)$  will have the same sign as that calculate from the location of the heavy atoms. This phase is then combined with the observed  $|F(hkl)|$  obtained from the observed value of  $I(hkl)$  to perform the Fourier synthesis of the entire  $e^-$  density in the unit cell thereby enabling the location of both the heavy and light atoms.

## 11. Neutron Diffraction:

⇒ Diffraction patterns can be obtained by means of electron beams, when they are scattered by molecule. Because of their negative charge and hence between low penetrating power, the electron beams are generally used for the investigation of surfaces and thin films. Neutrons, on the other hand, have a high penetrating power and are particularly useful for structural studies of solids. Neutron diffraction by crystals was demonstrated as early as in 1936 but the method did not become important until the advent of nuclear piles. Fast neutron produced in a nuclear pile are slowed down by collisions with a moderator ( $D_2O$  or graphite) to produce thermal neutrons, neutron for which the range of kinetic energies is determined by the

temperature of the surroundings.

⇒ The wave length of a neutron beam is related to the neutron mass and velocity by de-Broglie relation  $\lambda = h/p = h/mv$

where,  $m_n \Rightarrow$  neutron mass  
 $v \Rightarrow$  velocity.

⇒ The spectrum of the neutron beam emerging from a nuclear pile is continuous, the wave lengths covering several Angstroms. A monochromatic beam which is used for neutron crystallography, is obtained by reflection at a flat crystal surface. wide beams, with cross sectional areas of a few square centimetres, are used in order to obtain a sufficiently high counting rate in the detector. The large size and high cost of neutron spectrometers combined with the need for a nuclear pile have made neutron diffraction a less popular method in crystallography.

⇒ whereas x-rays are scattered by the orbital electrons, the neutrons are scattered by atomic nuclei. The atomic nuclei contribute nothing to x-ray scattering. Neutron diffraction is caused by two additional factors:

- 1) Nuclear scattering due to the interaction of neutrons with the atomic nuclei
- 2) Magnetic scattering due to the interaction of the magnetic moments of neutrons with permanent magnetic moments of atoms or ions.

⇒ The X-ray scattering power increases fairly regularly with the atomic number but there is no regular trend for neutron scattering. The neutron scattering power does not vary greatly while the X-ray scattering power increases from hydrogen atom to the heavy elements by about three orders of magnitude. In uranium hydride, X-ray diffraction has been used to locate the uranium coordinates and neutron diffraction to locate the hydrogen coordinates.

⇒ The difference b/w neutron and X-ray scattering offer great advantages and equally great disadvantages to neutron crystallography. The major advantage is that light elements such as 'H' or 'D', which cannot be located by X-ray diffraction, can be located by neutron diffraction because they are comparable in neutron scattering power to heavy elements. The great disadvantage is that the background scatter is likely to be much more serious because different isotopes of the same element, which would be expected to be randomly distributed among the sites for that element, might differ greatly in their scattering power.

⇒ Neutron, which possess magnetic moment by virtue of having a spin of  $\frac{1}{2}$ , interact with nuclei which have magnetic moments to produce further background scattering for substance for which the nuclear spins are randomly oriented.

⇒ The spin-disorder scattering is so great (29) for hydrogen in comparison with the ordered scattering that deuterated compounds are often used for neutron diffraction studies.

⇒ paramagnetic substances also contribute to the general background scattering because of the interaction of the magnetic moment of neutrons with the randomly oriented orbital magnetic moments of the electrons. The magnetic moments of neighbouring atoms are oriented in the same direction in ferromagnetic substances whereas the magnetic moments of neighbouring atoms are oriented in opposite directions in antiferromagnetic substances.

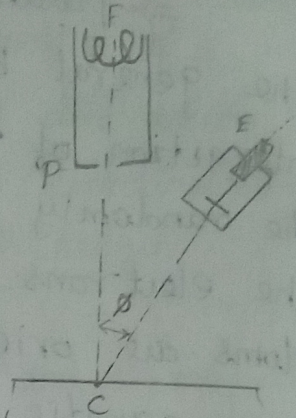
⇒ Neutron diffraction thus offers a tool for the investigation of the magnetically ordered lattices. Neutron diffraction thus reserved for special applications for which it can yield information not obtainable from X-ray diffraction studies. The Canadian physicist B.N. Brockhouse and the American physicist C.G. Shull were awarded the 1994 physics Nobel prize for the development of neutron spectroscopy and neutron diffraction techniques.

## 12. Electron diffraction:

(30)

⇒ The electron waves predicted by de-Broglie was experimentally detected by Davisson and Germer (1927). The experimental arrangement is shown in figure (1).

⇒ Electrons are produced from an electron gun, i.e. from a hot filament  $F$ . These are accelerated through a p.d. of 100 volts and then collimated by suitable openings in the plate  $P$ . When a line parallel narrow beam emerges. This beam is then allowed to fall on a large single crystal of nickel target. This target is capable of rotation about an axis parallel to the axis of the incident beam.



⇒ An electrode 'E' is connected to a sensitive galvanometer. The electrons are scattered from the crystal in all possible directions. The galvanometer is set to receive the electrons scattered at any angle, say  $\phi$ . The whole apparatus is enclosed in a highly evacuated vessel, which is also degassed.

current ⇒ The curves shown in fig (2), give the plots of  $I$ , a measure of intensity of diffracted beam of electrons and the angle between the incident beam and the scattered beam. The observations were taken for different voltage electrons.

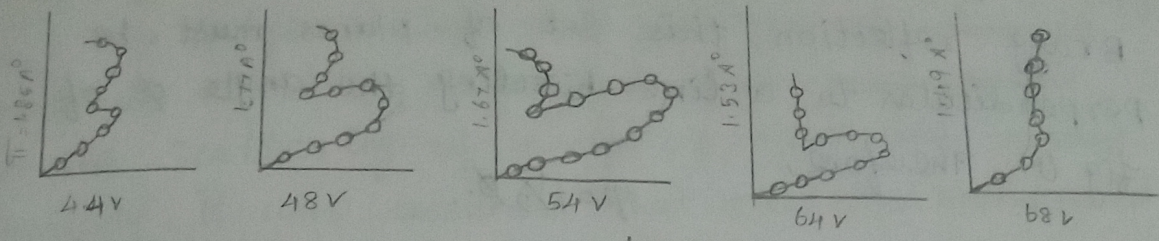


fig 2.

⇒ As the accelerated potential is increased from 44 to 68 volts, a characteristic bump is observed at 44 volts. With increasing voltage the bump moves upward and attains a greatest development in the curve for 54 volts at an angle of  $50^\circ$ . At higher voltages, however, the bump gradually decreases and there is practically no trace at 68 volts.

⇒ Davisson and Germer interpreted the result due to Bragg's reflection - i.e, reinforcement of electron waves reflected from atomic planes within the crystal as shown in fig 3.

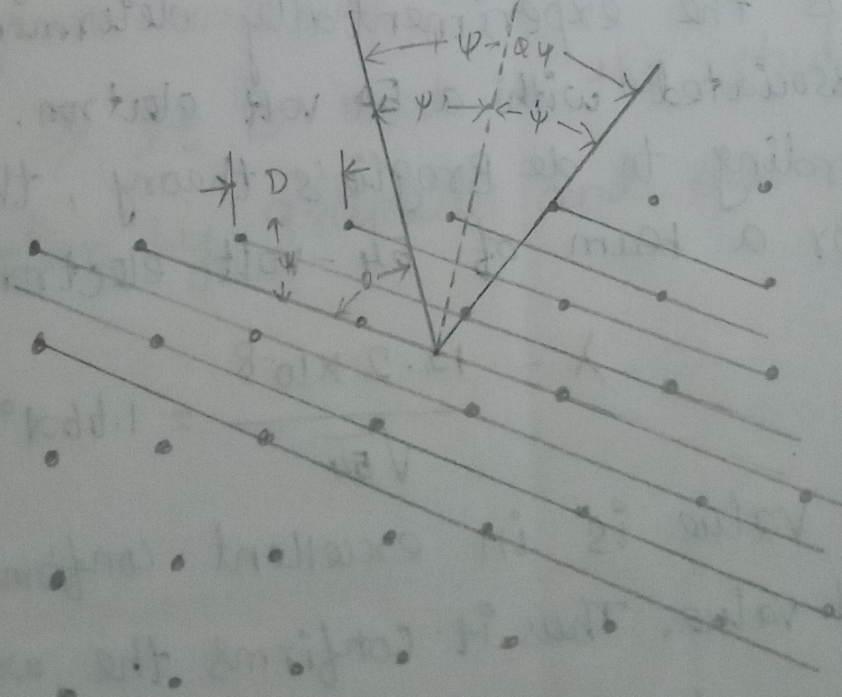


fig 3.

⇒ In order to produce the normal Bragg reflection, this set of planes must be perpendicular to a line bisecting the angle  $\phi$  of fig (1). Therefore,

$$\psi = \frac{1}{2}\phi.$$

⇒ The Bragg angle  $\theta$  occurring in Bragg's equation  $n\lambda = 2d\sin\theta$  is equal to  $(90 - \psi)$  or  $(90 - \phi/2)$ . The spacing  $d$  is the distance b/w planes responsible for reinforcement. From X-ray measurements, the spacing  $D$  between atoms making up of the surface plane of the nickel crystal is  $2.15 \text{ \AA}$ . The spacing  $d$  of these planes causing a reinforcement peak at  $\phi = 50^\circ$  is,

$$d = D \sin \psi = 2.15 \sin 26^\circ$$

So,  $\theta = 65^\circ$ . Hence the wavelength responsible for this first order Bragg reinforcement is,

$$\begin{aligned} \lambda &= 2(2.15 \sin 25^\circ) \sin 65^\circ \\ &= 1.65 \text{ \AA} \end{aligned}$$

⇒ This is the experimentally determined wavelength associated with a 54 volt electron.

⇒ According to de Broglie's theory, the wavelength for a beam of 54-volt electron is given by,

$$\lambda = \frac{12.2 \times 10^{-8}}{\sqrt{54}} = 1.66 \text{ \AA}$$

⇒ This value is in excellent conformity with the experimental value. Thus it confirms the wave like character of beam of electrons.



## uses of electron diffraction:

⇒ Debye showed that positions of atoms in molecule could be determined from measurements on the scattering of x-rays by gases and vapours. Similarly, it was assumed that electrons beams could also be used. Mark and wiersl using electrons of 43,000 volt energy, corresponding to de-Broglie wave length  $0.0578 \text{ \AA}$ , determined atomic arrangements and interatomic distances in a number of gases and vapours such as  $\text{CO}_2$ ,  $\text{Br}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{14}$  etc.

⇒ It is used in the study of surface structure, as well as in investigating the surface layers of unknown compositions. The nature of patterns produced enables us to determine the crystalline structure of the surface.

⇒ It is used in the structural analysis of organic material prepared in thin film.

⇒ It is used in the study of lubrication by graphite and oils.