SOLID STATE

B.Sc. III (Semester–VI)

Poonam Rana and Anamika Mahajan
B.Sc. III
PGGCG-42
Chandigarh

Difference between crystalline and amorphous solid

Property	Crystalline solid	Amorphous solid
• **Shape**	Crystalline solids have sharp edges and well defined planes.	Amorphous solids do not show regularity in their external form.
• **Melting point**	They have sharp melting point I.e they change abruptly into liquid at a fixed temperature	They do not have sharp melting point. They gradually soften over a range of temperature.
• **Symmetry**	Main property of crystal.	Do not have any symmetry.

Anisotropy	They are anisotropic and have different physical properties in different directions.	They are isotropic and have same physical properties in all directions.
Order in arrangement of constituent particles	They have regularity in arrangement of constituent particles. They exhibit long range order.	They do not have sharp melting point . They gradually soften over a range of temperature.
Cleavage property	Crystalline solids show clean cleavage when cut with a sharp edged tool.	Amorphous solids undergo irregular cleavage.
Heat of fusion	They have characteristic enthalpy of fusion	They do not have characteristic enthalpy of fusion.

Law of constancy of interfacial angles

- According to this law, the angle between the corresponding faces of the crystal called the interfacial angles are always the same for a given substance and are independent of the shape and size of the crystal.

- Bigger crystals are obtained if cooling is carried out slowly so that the atoms, ions or molecules get sufficient time to settle down at proper planes in the lattice. Similarly the presence or absence of other substances also affects the crystallisation process. The shape and size of the crystal depends on the condition s of crystallisation.

The interfacial angles can be measure 'd' with an instrument called goniometer.

A simple form of goniometer is shown in figure. This method is applicable only for large crystals having clear cut faces. For more accurate measurements and for small crystals, the optical instrument called reflecting goniometer is used. X-rays goniometer gives the highest precision for measurement of interfacial angles.
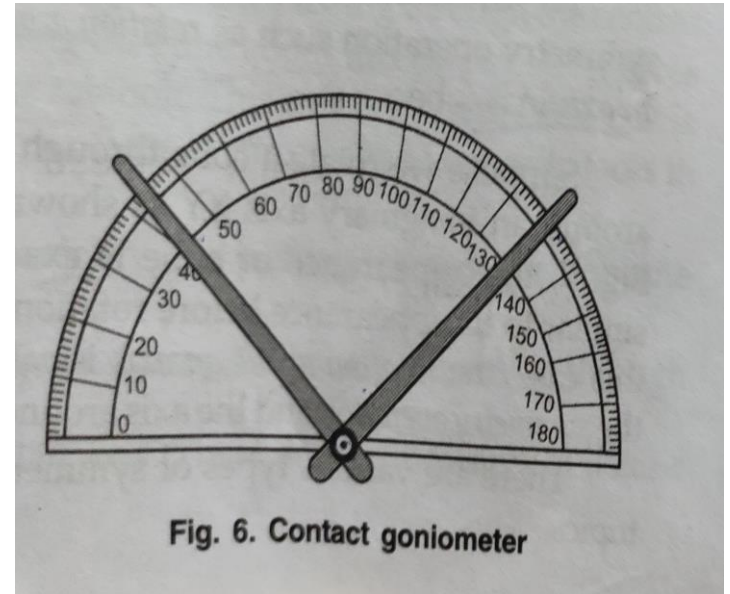

Fig. 6. Contact goniometer

The Law of symmetry

This law states that the crystals of the same substances always possess same elements of symmetry.
For example, a cubic crystal always possesses 23 elements of symmetry. These are as follows :

I.   Rectangular planes of symmetry =3
II.   Diagonal planes of symmetry=6
III. four fold acid of symmetry=3
IV. three fold axis of symmetry=4
V.   two fold acid of symmetry=6
VI. centre of symmetry=1
Total elements of symmetry=9+13+1=23

Elements of symmetry in a cubic crystal

Rectangular planes of symmetry

Diagonal planes of symmetry

(a) 4-fold axis of symmetry

(b) 2-fold axis of symmetry

(c) 3-fold axis of symmetry

(d) Centre of symmetry

Fig. 12. Elements of symmetry in a cubic crystal.
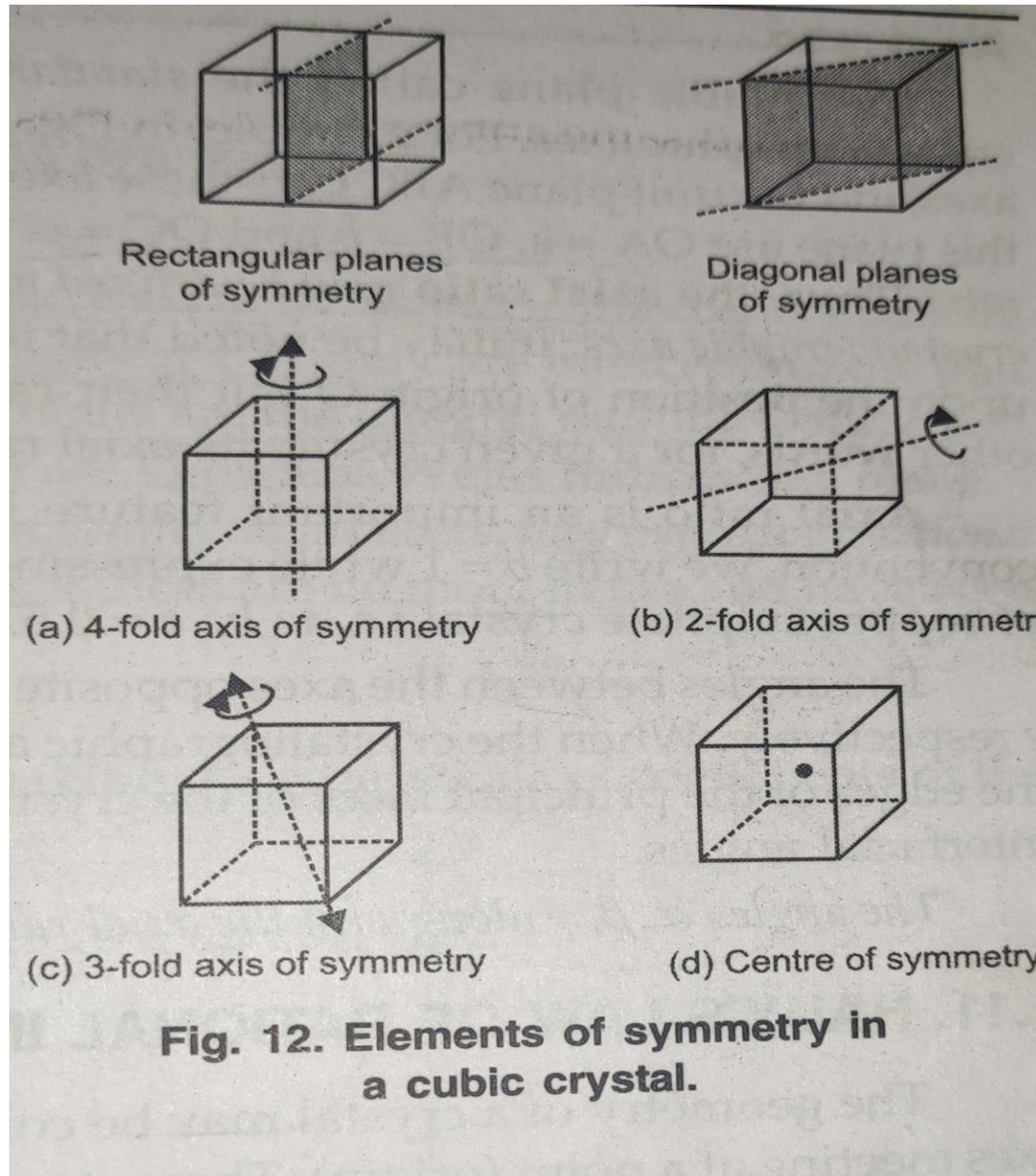
Law of rational indices

- **According to hauy law of rational indices, the intercepts of any plane or face of a crystal on the crystallographic axes are either :**

- **Equal to the unit intercepts (a, b, c)**

- **Some simple whole number multiple of them are simple integers like 1 , 2,3**

- **One or two intercepts may be infinity, when the crystal planes are parallel to one or two axes.**

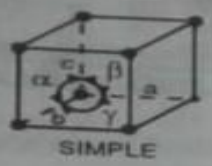Fig.14. Intercepts made by the faces of a cubic crystal.
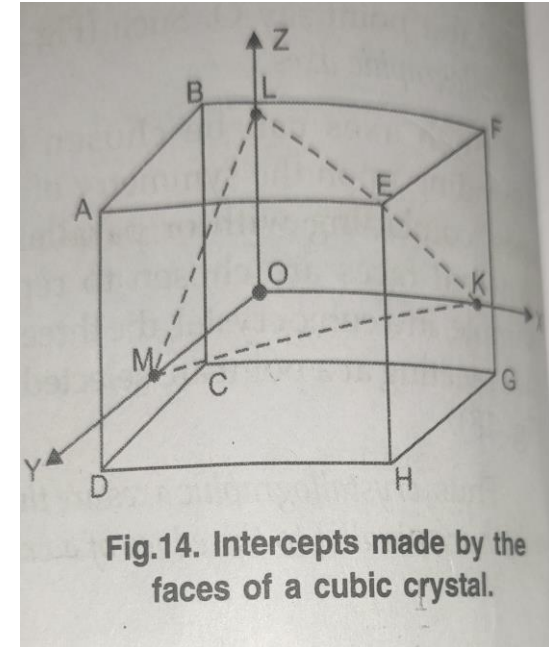
7 CRYSTAL SYSTEM

The external geometry of the crystal can be expressed in terms of axial ratios and angles, hence based on external geometry of the crystal they have been classified into seven groups called crystallographic systems.
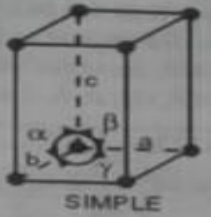
Table 3. Seven Crystal Systems

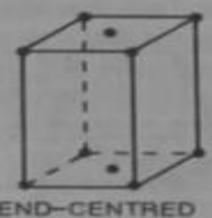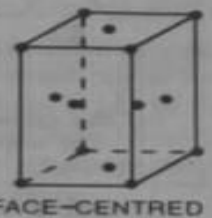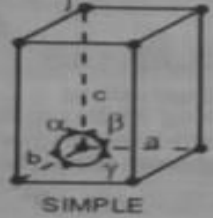| Crystal System	Axial characteristics	Maximum Symmetry	Point groups	Examples
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Planes of symmetry = 9 Axes of symmetry = 13	5	NaCl, KCl, diamond, alums.
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	Planes of symmetry = 5 Axes of symmetry = 5	7	TiO_2, Sn(White), SnO_2
Ortho rhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Planes of symmetry = 3 Axes of symmetry = 3	3	S(rhombic), KNO_3, K_2SO_4, $BaSO_4$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	Planes of symmetry = 1 Axes of symmetry = 1	3	$CaSO_4 . 2H_2O$, $Na_2SO_4 . 10H_2O$ S (monoclinic)
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	Planes of symmetry = 0 Axes of symmetry = 0	2	$CuSO_4 . 5H_2O$, $K_2Cr_2O_7$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°$	Planes of symmetry = 7 Axes of symmetry = 7	7	SiO_2, graphite, ice, Mg, Zn, Cd, ZnO
Trigonal Or Rhombo-hedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	Planes of symmetry = 7 Axes of symmetry = 7	5	$CaCO_3$, ICl, Calcite, $NaNO_3$, As, Sb, Bi.

1. CUBIC
$$\left\{ \begin{array}{l} \alpha = \beta = \gamma = 90° \\ a = b = c \end{array} \right\}$$

SIMPLE   FACE-CENTRED   BODY-CENTRED

2. TETRAGONAL
$$\left\{ \begin{array}{l} \alpha = \beta = \gamma = 90° \\ a = b \neq c \end{array} \right\}$$

SIMPLE   BODY-CENTRED

3. ORTHORHOMBIC
$$\left\{ \begin{array}{l} \alpha = \beta = \gamma = 90° \\ a \neq b \neq c \end{array} \right\}$$

SIMPLE   FACE-CENTRED   END-CENTRED   BODY-CENTRED

4. MONOCLINIC
$$\left\{ \begin{array}{l} \alpha = \gamma = 90° \neq \beta \\ a \neq b \neq c \end{array} \right\}$$

SIMPLE   BODY-CENTRED

SIMPLE   SIMPLE   SIMPLE

5. TRICLINIC
$$\left\{ \begin{array}{l} \alpha \neq \beta \neq \gamma \neq 90° \\ a \neq b \neq c \end{array} \right\}$$
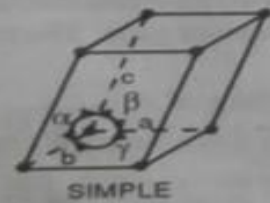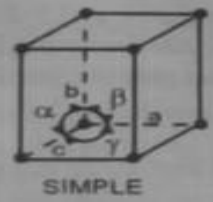
6. RHOMBOHEDRAL
$$\left\{ \begin{array}{l} \alpha = \beta = \gamma \neq 90° \\ a = b = c \end{array} \right\}$$
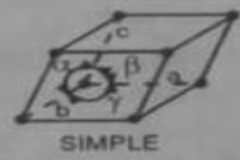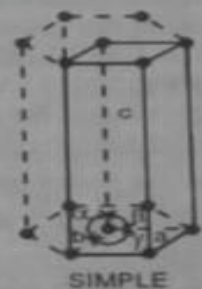
7. HEXAGONAL
$$\left\{ \begin{array}{l} \alpha = \beta = 90°, \gamma = 120° \\ a = b \neq c \end{array} \right\}$$

FIGURE 5.21.

Bravais lattices corresponding to seven crystallographic systems.

The fourteen bravais lattices

❑ **Bravais showed that there are fourteen basic arrangements possible for arranging similar points in regular three of lattices called bravais lattices. The crystals exhibit four types of bravais lattices depending upon shape of unit cell**

1. **Simple or primitive unit cell:** It has point at all corners of unit cell. A primitive cubic cell is shown in fig. Since each atom at the corner is shared by 8 unit cells, therefore the number of atoms per unit primitive or simple cubic unit cell is (8×1/8) = 1.

2 **Body centered unit cell (bcc) :** The unit cell with points all the corners and at the center of the unit cell is known as body centered cell. A body centered cubic unit cell is shown in fig. There are 8 atoms at the corners each atom shared by 8 unit cells and one at the center. Therefore, the number of atoms per unit cell is (8×1/8) +1=2.

3 **Face centered unit cell (fcc) :** In this type of unit cell, the points are located at the corners as well as centre of each face of the cell. Therefore, the number of atoms per unit is (8×1/8) +(6×1/2) =4

4 **End centered unit cell:** In the end centered unit cell, are points at the corners and at the centers of two end faces. For example, in orthorhombic unit cell fig. , there are eight points at the corners and two points at the end faces. The number of atoms per unit cell is (8×1/8) +(2×1/2) =2.
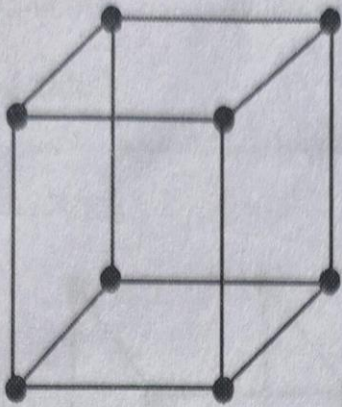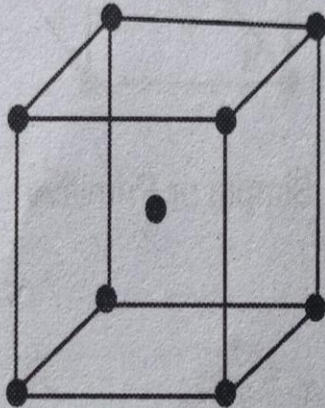
Fig. 22 (a) Primitive cubic unit cell.

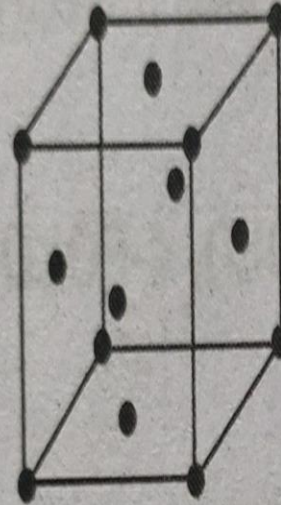Fig. 22 (b) Body centred cubic unit cell.
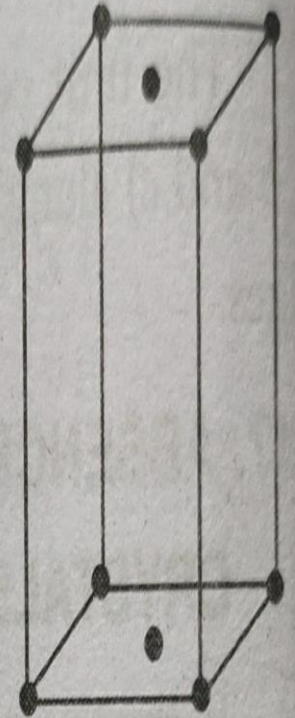
Fig. 22 (c) Face centred cubic unit cell.

Fig. 22 (d) End centre orthorhombic unit cel

1. **Weiss indices:** In this method, the orientation of a plane is described in terms of the intercepts made by the plane on three crystallographic axes. The coefficients of a, b and c are intercepts of the unit plane, then the intercepts na, n'b and n"c made by a plane are the integral multiples of a, b and c. The coefficients of a, b, c(n, n'b, n") in this case are known as Weiss indices of a plane. It may be noted that the Weiss indices are not always integral numbers, they may have fractional values as infinity (which is an indefinite quantity)

2. **Miller indices:** Miller indices my be defined as the reciprocals of the coefficients of the intercepts of a face on the crystallographic axes expressed as intergers. For example, consider a lattice plane KLM in a crystal as shown in fig.The plane has intercepts OK, OL and OM along X, Y And Z axis at distances 2a, 4b and 3c respectively. Thus. Miller indices of a face or a plane may also defined as the intergers which give the ratio of the intercepts of the unit plane to those of the given plane i.e(a/ha: b/kb : c/IC) expressed as intergers.

Fig. 15. The intercepts of a crystal plane.
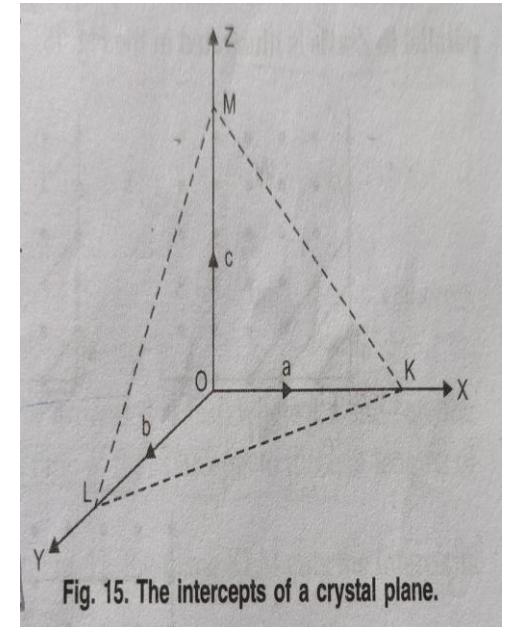
PRINCIPLE & BRAGG'S LAW DERIVATION...

➢The monochromatic radiation directed towards the sample produces constructive interference when condition satisfies Bragg's law.

Consider incident ray AX on atomic plane PP' and ray BY on plane QQ' with interatomic spacing "d". We get constructive interference if path difference between AXD and BYE (i.e. GYH) equals n times λ.

FIGURE 5.23.

Reflection of X-rays by equidistant parallel atomic planes.
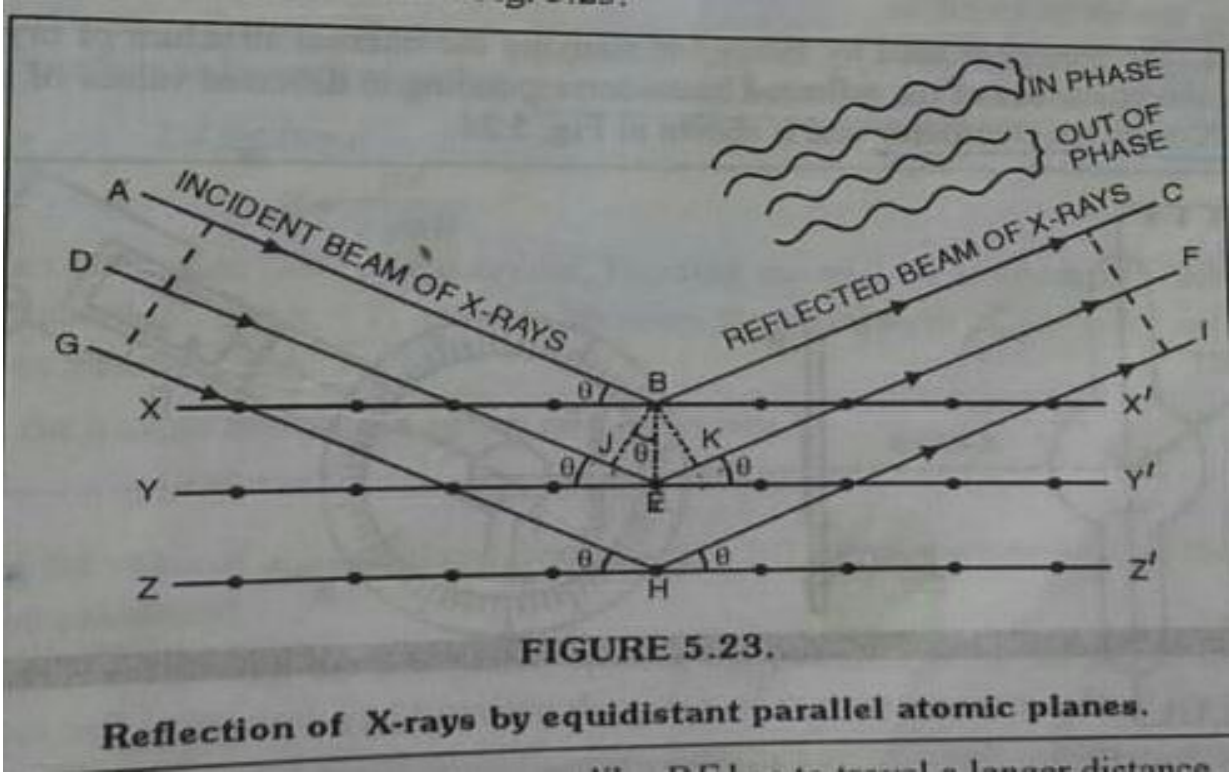
We thus have,

$$\text{distance } GYH = n\lambda \quad \ldots\ldots(1)$$

Where n is integer i.e. 1,2,3,etc. "d" is the distance between sucessive atomic planes.

$$GY = YH = d \sin\theta \quad \ldots\ldots\ldots(2)$$

So that $\qquad GYH = 2d \sin\theta$

equating (1) & (2) we get:

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

This is Bragg's Equation. It gives the condition underwhich reflected beam will have maximum intensity for monochromatic X-Ray and λ is constant.

respectively. The reflected beams like BC, EF, etc., then undergo interference with each other. If these reflected rays are in phase (i.e., in the reflected rays, crests fall over the crests and troughs over the troughs), they reinforce into each other and the intensity of the reflected rays is maximum. On the other hand, if the reflected rays are out of phase (i.e., crests fall over the troughs), the intensity of the reflected beam is very low. If a photographic plate is placed to receive the reflected rays, *diffraction pattern* is obtained.

It is obvious that in order that the reflected rays, BC and EF may be in phase, the extra distance JEK traversed by the ray DEF should be an integral multiple of the wavelength λ of the X-rays, i.e.,

$$\text{Distance } JEK = n\lambda \qquad \text{...(1)}$$

where n is an integer, i.e., 1, 2, 3, 4, etc. If d is the distance between the successive atomic planes, it is obvious from Fig. 5.23 that

$$JE = EK = d \sin \theta$$

so that

$$JEK = 2\,d \sin \theta \qquad \text{...(2)}$$

Putting this value in equation (i), we get

$$\boxed{2\,d \sin \theta = n\lambda} \qquad \text{...(3)}$$

This equation is called **Bragg's equation.** It gives us the conditions under which the reflected beam will have maximum intensity. Using monochromatic X-rays, λ is constant. Also for a particular crystal when a particular face is facing the X-rays, d is constant. Hence n will be integer only for certain values of the angle θ. Thus by gradually increasing the value of θ, a number of positions are observed corresponding to n = 1, 2, 3, 4 etc., where the reflected beam will have maximum intensity. For other values of θ lying in between, the reflected beam will have intensity less than the maximum. Thus a diffraction pattern will be obtained in which the various maxima correspond to n = 1, 2, 3 etc. These are respectively called diffraction maxima of the first order, second order, third order etc.

Measuring the

APPARATUS

❑For the measurements of the intensities of the reflected beam to corresponding different angles θ , an instrument called Bragg's X-Ray Spectrometer is used.
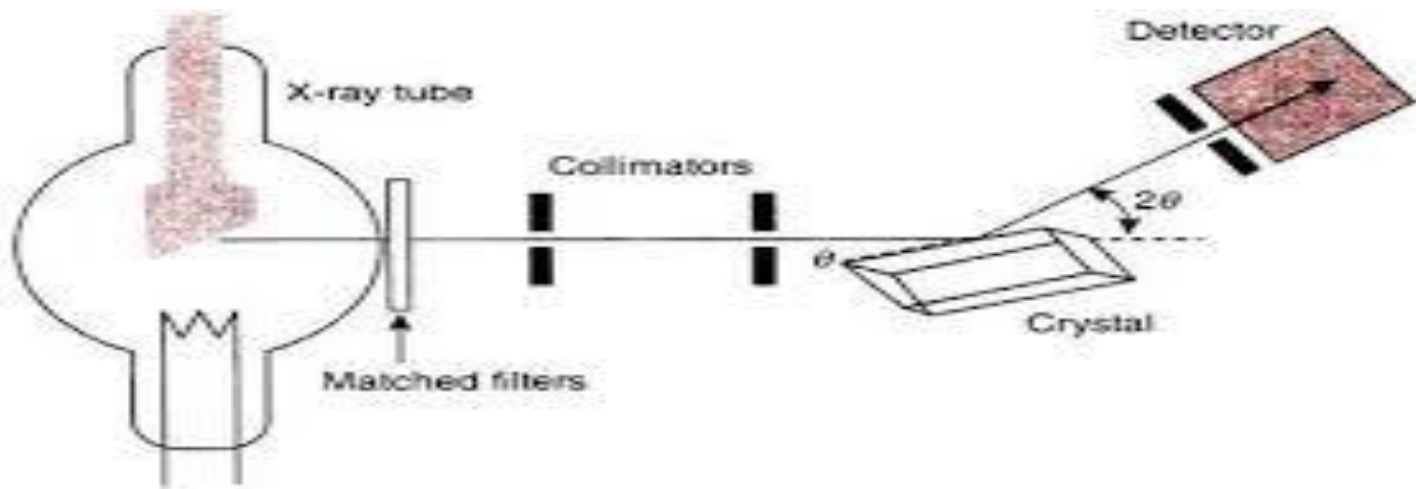

Figure 3.20 XRD spectrometer.

EVIDENCES & CALCULATIONS

X-rays are generated in the X-ray tube A. These are made monochromatic by passing through the absorbing screens B. Then they are passed through the leads slits L, to obtain a fine beam. This beam is then allowed to fall on some particular face of the single large crystal C which is mounted on a turn-table T. The turn-table can be moved over a circular scale S. The reflected beam is passed into the ionization chamber D which is connected to an electrometer E. The ionization chamber can also be moved on the circular scale S independent of the turn table T. The chamber contains some easily ionizable gas such as sulphur dioxide (SO_2). Greater is the intensity of the reflected beam, greater is the ionization produced in the gas and larger is the reading on the electrometer. When the crystal face is rotated by rotating the turn-table, the direction of the reflected beam changes. To receive the reflected beam into the ionization chamber every time, the ionization chamber is rotated through double the angle through which the crystal face is rotated. From these plots, the angles corresponding to the first, second, third maxima etc. are noted and the value of d calculated using Bragg's equation ($viz.$, $2\,d \sin\theta = n\,\lambda$).

Evidence in favour of Bragg's equation. For sodium chloride crystals, for the face (100), the 1st, 2nd, 3rd maxima occur at angles $5.9°$, $11.85°$ and $18.15°$ using X-rays produced from palladium target. The sines of these angles are 0.103, 0.205 and 0.312 which are very nearly in the ratio $1:2:3$. This proves that the 1st, 2nd, 3rd maxima occur for $n = 1, 2, 3$, respectively. Hence the correctness of the Bragg's equation is confirmed. (The small hump on the left of each maxima is due to the β radiation accompanying the X-rays used).

FOR FACE (100) OF NaCl CRYSTAL

FIRST MAXIMA

SECOND MAXIMA

THIRD MAXIMA

INTENSITY OF THE REFLECTED X-RAYS

$5°$ $5.9°$ $10°$ $11.85°$ $15°$ $18.15°$ $20°$

ANGLE OF INCIDENCE (θ) →

FIGURE 5.25.

Plot of intensity vs. θ for the face (100) of NaCl.

Calculations from Bragg's equation. According to Bragg's equation

$$2\,d \sin\theta = n\,\lambda \qquad \text{...(4)}$$

or

$$d = \frac{n\lambda}{2\sin\theta} \qquad \text{...(5)}$$

For a particular face (hkl) of the crystal, knowing the angle θ at which the first order diffraction maxima is obtained (so that $n = 1$) and also knowing the wavelength of the X-ray used, the interplanar spacing (d) can be calculated.

Further, for a cubic system, the values of d_{hkl} is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \text{...(6)}$$

Knowing the value of d_{hkl} calculated from equation (ii) above, the length (a) of the edge of the cubic unit cell can be calculated.

Alternatively, knowing the interplanar spacing d_{hkl} (which can be calculated from eqn. (6) if the edge of the unit cell is known), and knowing the value of θ at which first order diffraction maximum is obtained, eqn. (4) can be used to calculate the wavelength, λ of the X-rays used.

Also, knowing λ and d, using eqn. (4), θ can be calculated for a given value of n.

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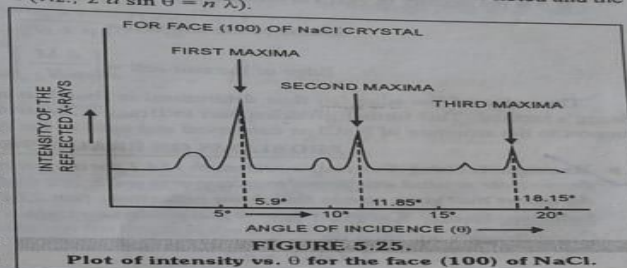
THE POWDER METHOD

In this method the sample is taken in the powdered form In a small thin walled glass tube (capillary tube)and o rotation is required. A beam of monochromatic X-RAYS is focused on the sample and a circular photographic film is placed around it as show In figure (a).In principle, each set of planes will give rise to a diffraction cone originating from the powder. Thus a large number of concentric cones will be produced due to the reflections from different sets of planes and satisfying Bragg's law fig.(b).
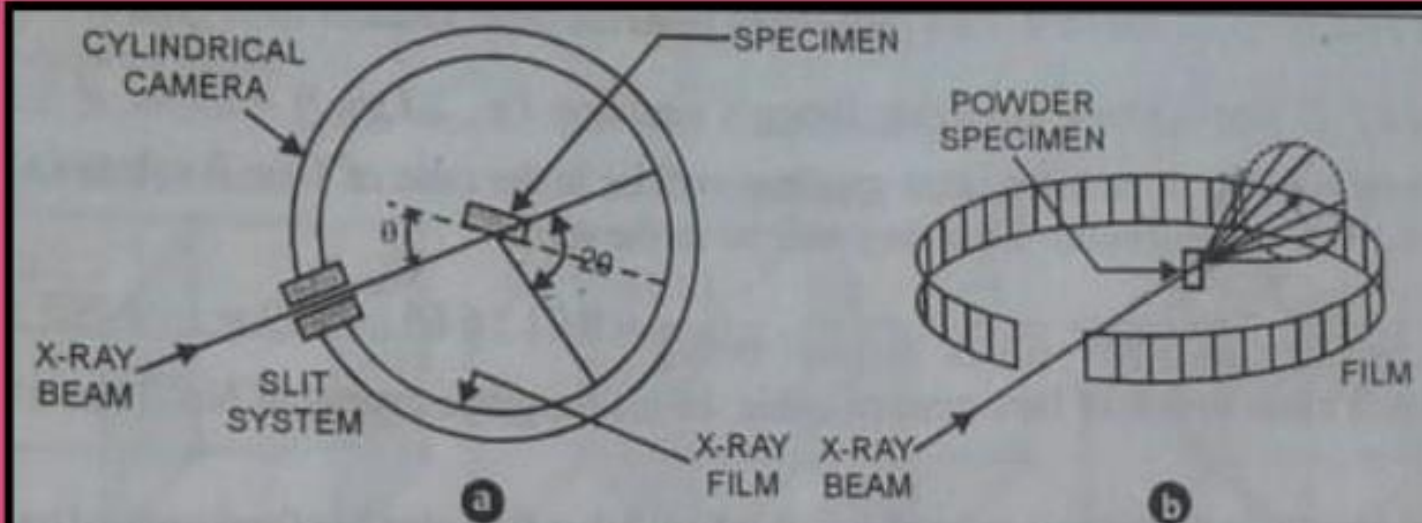

FIGURE 5.27.
Debye-Scherrer method for diffraction of a monochromatic X-ray beam by powder sample.

Each cone will meet the photographic film at two points producing two lines at equal distances from the bright centre spot .Thus a large number of lines will be obtained on the photographic film , each pair of lines being equidistant on the right and left from the centre spot. Further ,if the incident angle is "theta", the reflected beam makes an angle "two theta" with the direction of the incident beam shown In figure.above.

INTERSECTION OF THE
FIRST CONE ON THE FILM

FIGURE 5.28.

X-ray diffraction pattern a powder sample
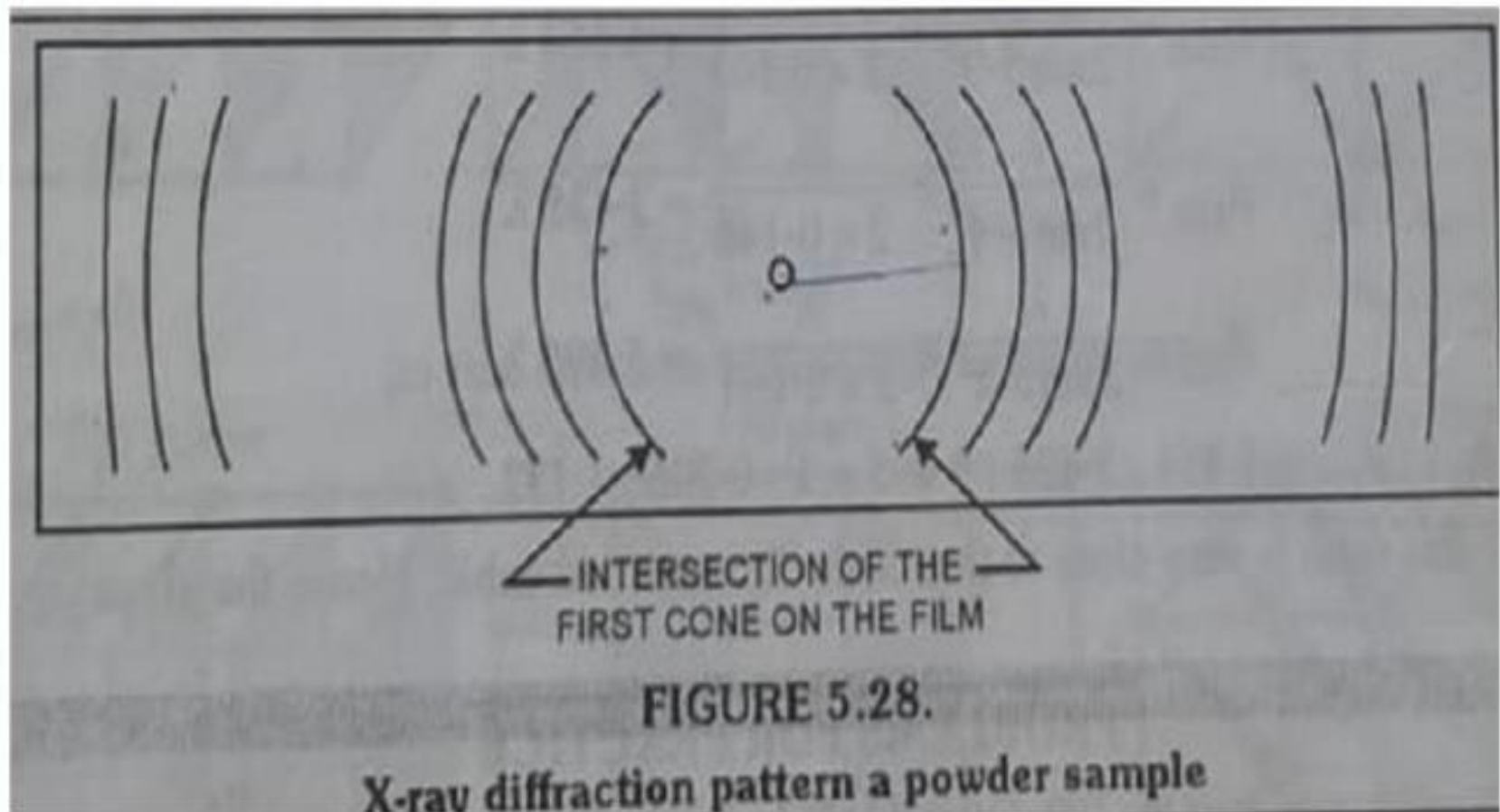
After getting the X-RAYS diffraction pattern of the powder, the next step is the **indexing of lines i.e.** assigning Miller indices to the planes responsible for producing these lines.

IF the radius of the film is 'r', the circumference ,$2\pi r$ corresponds to a scattering angle of 360^0 . This implies that

$$2\theta/360^0 = x/2\pi r$$

Thus θ can be calculated .Knowing θ ,the interplanar spacing can be calculated using Bragg's equation i.e.

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

LAUE'S METHOD

THE LAUE'S METHOD is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal. MAX VON LAUE suggested that *the crystal could act as a three dimensional diffraction grating for incident X-RAYS.*

In the Laue method, continuous spectrum of X-RAYS(**called white radiation**) having a wide range of wavelengths is used (**e.g. from a tungsten target**).
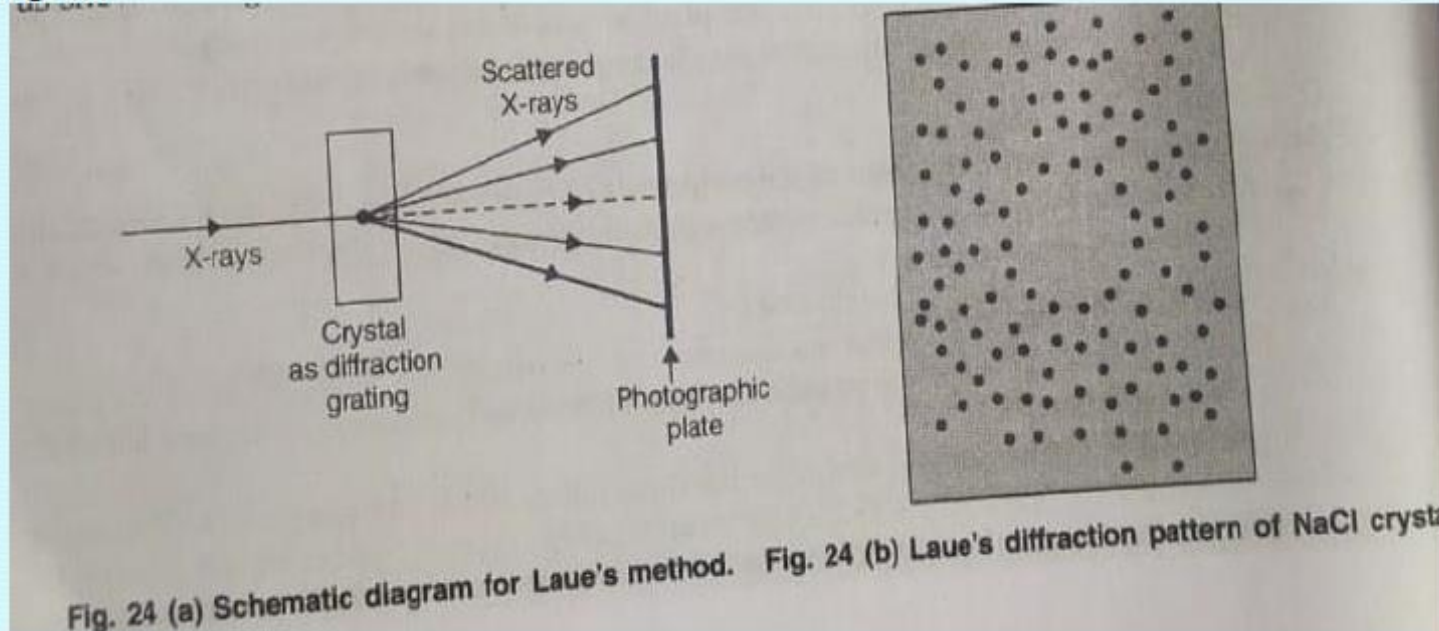

Fig. 24 (a) Schematic diagram for Laue's method.   Fig. 24 (b) Laue's diffraction pattern of NaCl crysta

Such diagrams confirm the definite arrangement of the atoms in a crystal .However their interpretation to know the exact arrangement of atom within the crystal is difficult.

A simple approach based on X-RAYS diffraction from crystals has been put forward by **W.H.BRAGG**.

Structure of Sodium Chloride (NaCl)

- **The salient features of structure of sodium chloride are as follows:**

- **1 X-ray diffraction pattern for NaCl crystal shows that it belongs to the face centred cubic crystal. The values of angle for the first order reflection from the first three planes are found to be 5.9°, 8.4°and 5.2° respectively. The first three planes are 200,220 and 111. The ratio of three planes is: 1 : 0.705 :1:137.**

Cl^-

Na^+
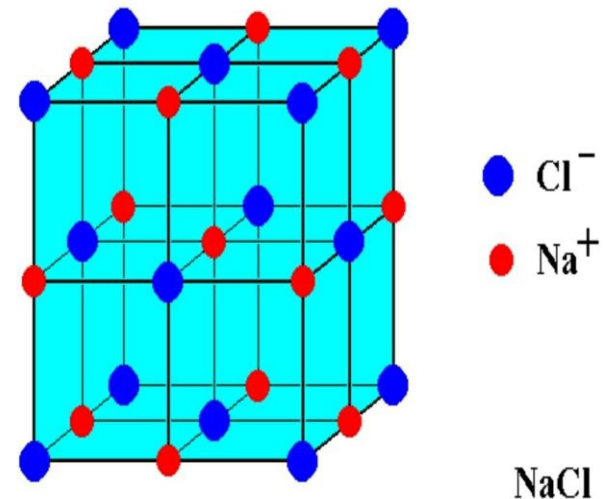
NaCl

- This ratio confirms the face centred cubic crystal system for NaCl. Thus, sodium and chloride ions are arranged in a crystal as face centred cubic lattice.

- The structure composed of only Na ions and Cl ions. Each sodium ion is shared equally by six chloride ions and each Cl ions by six sodium ions.

- Keeping in mind that the contribution made by corners is 1/8, face centres is 1/2 , edge centres is 1/4 and body centre is 1,we can say that a unit cell of NaCl contains 4 Na ions and 4 Cl ions that is 4 NaCl units.

Crystal structure of CsCl

- The diffraction pattern of CsCl shows that it has a body centred cubic lattice.

- There are two simple cubic lattices, one of cesium ions and the other of chloride ions which are interlinked together to give a pseudo body centred lattice.

- As a result, chloride ions occupy corners and cesium ions occupies the body centre within the cell.

- Keeping in mind the contribution of corners equal to 1/8, we can say that the unit cell contains one Cs ion and one Cl ion that is one CsCl unit.

Cs^+

Cl^-

CsCl unit cell
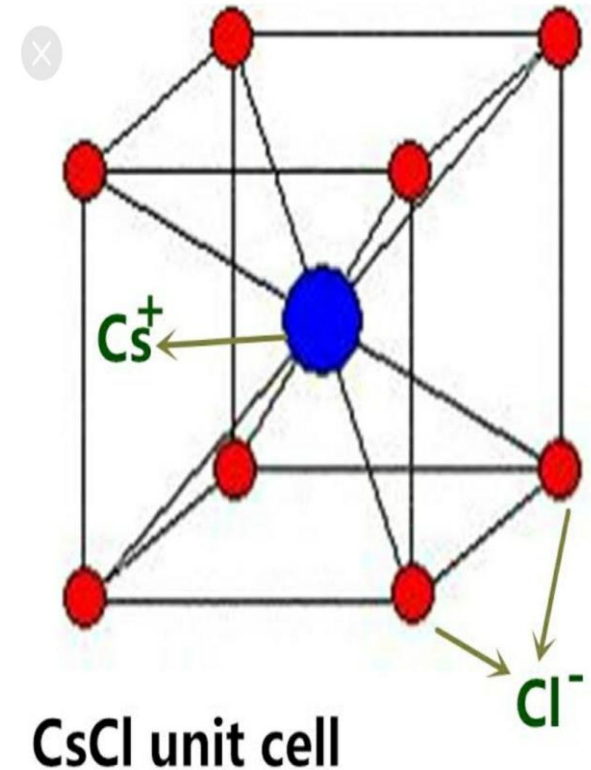
Difference between NaCl and KCl structure

NaCl

- **As in diffraction pattern the x-rays are scattered by electrons.**

- **Therefore, the scattering power of Na ions is less than that of Cl ions. There are less electrons in Na ions than in Cl ions.**

KCl

- **The number of electrons in k+ ions and Cl- ions is equal.**

- **Thus they have same scattering power for x-rays. The ions of KCl appear similar**

THANKS