Dr. Suryawanshi V.S.
Dept. of chemistry
SCSCO.

SOLID STATE

Contents :

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Introduction :-

Solid are forms q matter which are rigid and have definite shape and volume. Intermolecular forces which are weaker than chemical bonds, acts among the molecules to organise them into large structure q solid and liquid states.

Solid shows following general characteristics......

01) Definite shape and volume.

02) High density and low Compressibility - This is observe in solid due to close Packing q molecules which ellminates free space between molecules.

03) Very slow diffusion :- The diffusion q solid is negligible or very slow as Particles have Permanent Position from which they donot move easily.

04) Vapour Pressure :- The Vapour Pressure q solid is generally much less than the vapour Pressure q liquids at definite temperature.

Crystallography is the science q crystals which is devoted to the study q their development and growth, their external form, internal structure and Physical Properties.

For a long time crystallography was regarded as a Part q mineralogy. Crystals, or more Precisely crystalline substances are very widespread. The majority q bodies and objectes surrounding us have a Crystalline structure.

Crystals have highly diversified specific Properties. The Internal form q solid is very much necessary to understand the chemical Point q view. and external form is a topic q interest for the crystallographers.

Firstly Abbe R. J. Haily (1784) studied the regularity q the Crystal growth. and observed that crystal is made up q a very large number q identical Units which are Called as "Space Lattice." ie space lattice describes three dimensional arrangement of atoms, molecules or ions in crystal Lattic

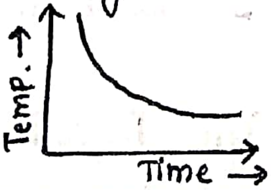
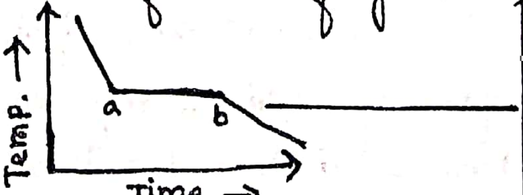
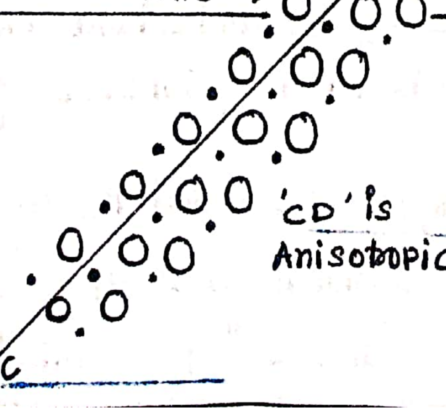
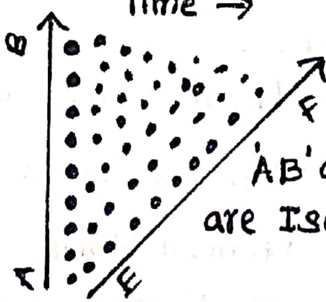
Classification of solids :-

Solid substances are frequently classified as either
- crystalline or
- Amorphous.

Crystalline solids are characterised by a regular, ordered arrangement of Particles e.g. ice, KCl, NaCl etc. crystalline solids have same geometry and regularity of crystal lattice. atoms are closely Paced.

However a small class of non crystalline solids known as amorphous solids, has no well defined ordered structure. e.g. Rubber, amorphous sulphur etc. Glasses are sometime called amorphous solids and sometimes supercooled liquids of high viscosity.

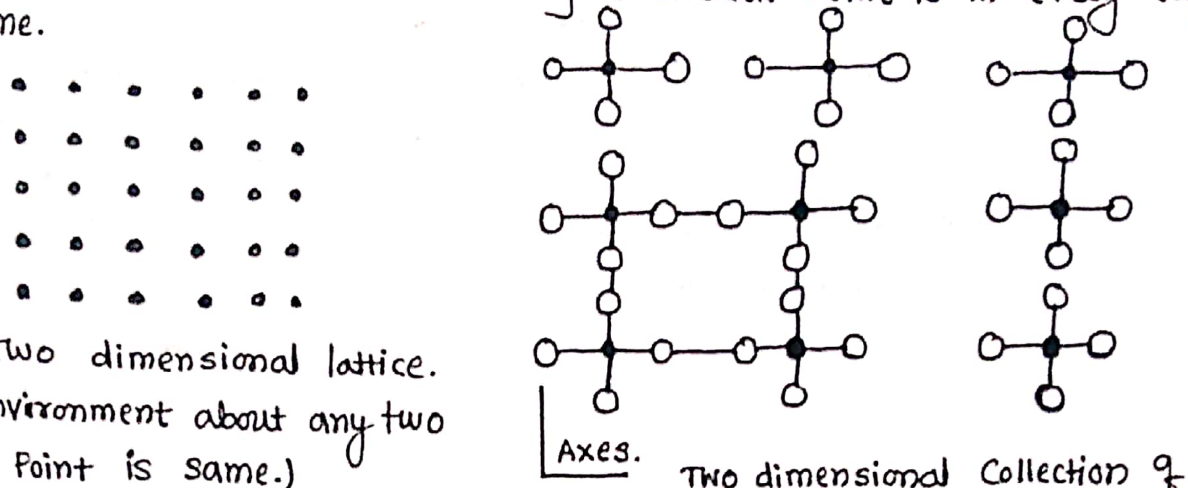
Difference between Crystalline and Amorphous solid.

Sr. Nos.	Crystalline solids	Amorphous solids.
01	Definite and regular geometry with flat faces and sharp edges.	No definite geometrical shape.
02.	It break up into smaller crystals of same geometrical shape.	Broken Pieces are not generally flats.
03.	sharp melting Point	No sharp melting Point.
04.	They are Anisotropic ie Physical Properties are diff. in different directions.	They are Isotropic. ie Physical Properties are same in all directions.
05.	cooling curve is smooth. 	Cooling curve has two breaks (a & b) which corresponds to beginning and end of Process of Crystallization 
06.	 'CD' is Anisotropic.	 'AB' and 'EF' are Isotropic.

Space Lattice :- or Lattice :-

The regular pattern of Points which describes the three dimensional arrangement of Particles (atoms, molecules or ions) in a crystal structure, is called the space lattice or crystal lattice.

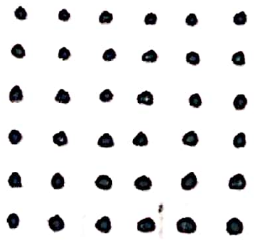
In another way it may be defined as, space lattice is one in which a three dimensional collection of Points is Present Provided that the environment about any Particular Point is in every way same.



Two dimensional lattice. (environment about any two Point is same.)

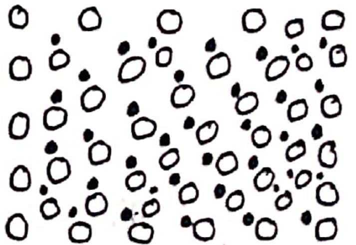
Two dimensional Collection of Points but not a Lattice.

A) Fig. Crystal Lattice.



B) crystal Lattice.

Basis. (C)



(D) Crystal structure.

fig (B) – Arrangment of Points in which any Point is completly equivalent to any other Point in the structure.

Fig (C) – A particular arrangement of three ions denoted by solid dot, smaller hollow (खोखला) circle and bigger circle which represents the basis.

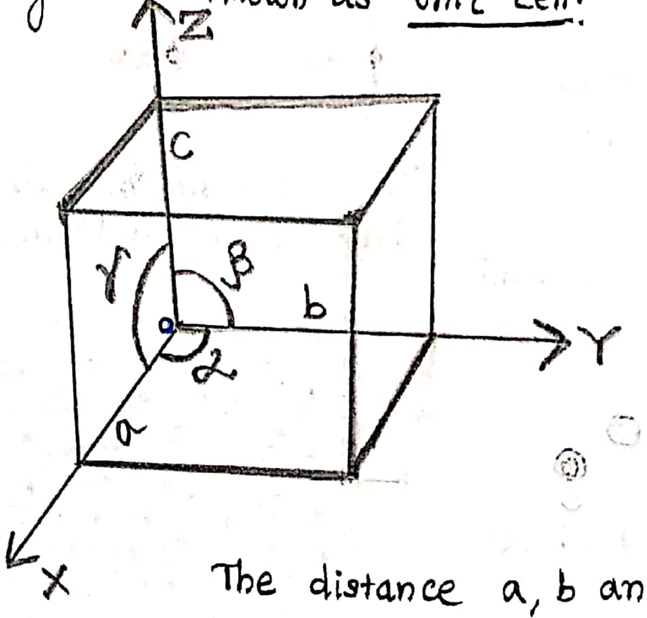
fig (D) :- Basis is attached to every Point of the Lattice called as crystal structure. All this has been shown in two dimension and is equally applicable to the three-dimensional Crystals.

ie Lattice + Basis ═ Crystal structure.

⊙ Unit Cell :

Crystal of Calcite ($CaCO_3$) can be broken into a large number of small rhombus which have original shape. on the basis of this observation, Havy suggested that a Crystal is made up of number of set of smaller crystals, even if it again broken, a point would be reached at which the smallest crystal would exists.

When it is further broken down, the crystal would Produce the molecules or other Particles which made up of Crystals. The smallest unit of the arrangement of atoms in a crystal is known as Unit cell.



The distance a, b and c are lengths of the edges of the unit cell and angles α, β and γ are angles between three imaginary axes OX, OY and OZ.

The unit cell has eight Corners and at each Corner eights cells meets.

There are three types of unit cells.

A) Simple unit cell :- atoms, ions or molecules are Present only at the Corner of the unit cell.

B) Face Centered :- Besides the Corner, there is a Point Present in the Centre of each face.

C) Body Centered :- There is a Point at the Centre within the body of the unit cell.

Weiss indices and Miller indices :-

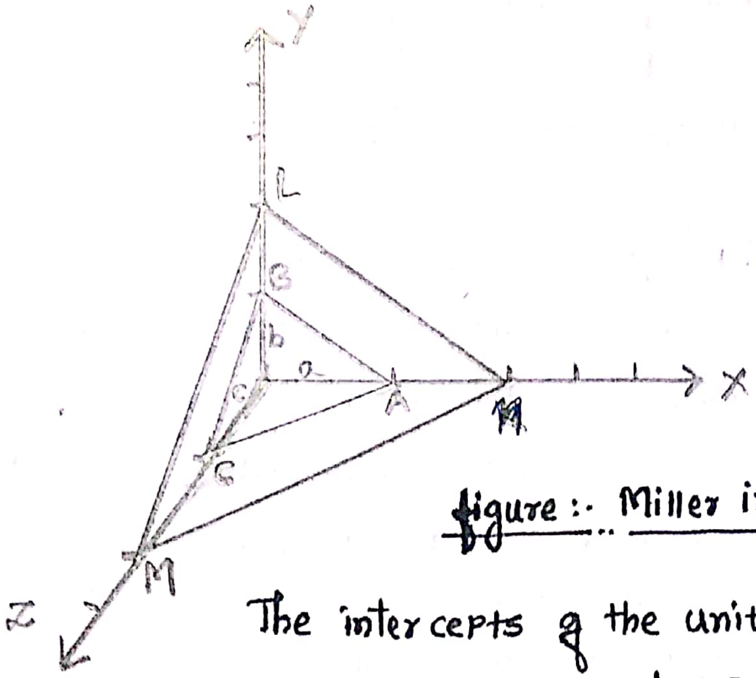


figure :- Miller indices.

The intercepts of the unit or standard plane along crystallographic axes OX, OY and OZ are a, b and c respectively. These are known as unit or standard intercepts. If a plane or face parallel to the standard plane face cuts the above axes with intercepts x, y and z. Respectively then accroding to the law of rational intercepts,

$$x = la \;;\; y = mb \text{ and } z = \text{[redacted]}.nc.$$

The coefficients or multiplies l, m and n are called weiss indices of the plane. These number characterises and represents any plane of the crystal. The corresponding plane is designated as (lmn) plane.

Weiss indices are generally small whole number and may be fractions of whole numbers as well as infinity.

Miller indices of a plane are the reciprocals of the distance from the origin at which a given face intersects, the three axes. Miller indices obtained by takeing the reciprocals of the weiss coefficients and multiplying by the smallest number that will express all the reciprocals as integers.

Miller indices are expressed as (h, k, l) there h, k and l refers to reciprocals of the intercepts and expressed in units of the lattice distance.

$$h = \frac{a}{\text{intercept of Plane along 'x' axis}}$$

$$K = \frac{b}{\text{intercept of plane along 'Y' axis.}}$$

$$\ell = \frac{c}{\text{intercept of plane along 'z' axis.}}$$

larger the value of miller index smaller will be the value of the intercept of that plane along the given axis and when it is zero (The intercept is infinity ∞), Plane is Parallel to that axis. Two parallel planes in a crystal have the same miller indices.

To find out miller indices —

1) Write the intercepts as multiples of a, b, c. say la, mb & nc.

2) Take reciprocals of weiss indices ie l, m and n.

3) Clear the fractions to get whole numbers h, k, l.

4) Miller indices of the plane are (h, k, l).

Laws of Crystallography :-

There are three laws of crystallography which deals with interfacial and rational indices.

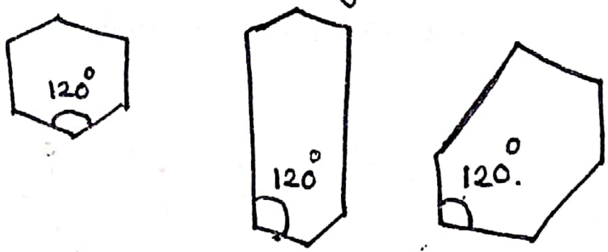
01) Law of constancy of interfacial angles :-

The crystals of the same substance can have different shapes. It depends on number and sizes of faces but the angle between the corresponding faces remains always equal. This law is known as first law of Crystallography.

The size and shape of a crystal of a Compound Varies with Conditions of crystallisation. but the angle between the faces remains Constant.

for e.g. The following crystals forms are shown during the Process of crystallisation.

It has hexagonal symmetry with the interfacial angle of 120°. The interfacial angle remains constant.



02) The law of symmetry :-

It states that, "All crystals of the same substance possess the same elements of symmetry."

Symmetry in the crystal may be due to a plane, a line or a point. On basis of this law there are three types of symmetry.

01) Plane of symmetry.
02) Axis of symmetry.
03) Centre of symmetry.

03) Law of rational indices (Havy Law) :-

This is the second law of Crystallography.
It states that," The ratio between the intercepts on the axes for the different faces of the crystal can always be expressed by rational numbers.

Such a ratio of three intercepts of any plane is given by la : mb : nc where l, m and n are small whole numbers and a, b and c are the intercepts made by unit plane along the crystallographic axes.

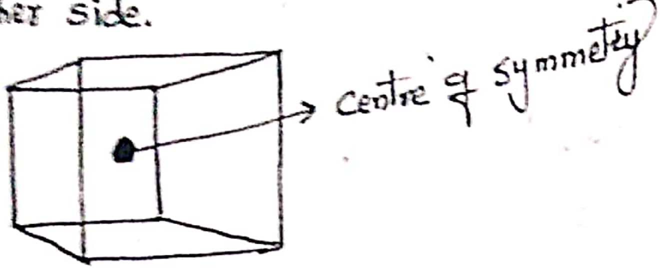
Elements of Symmetry :-

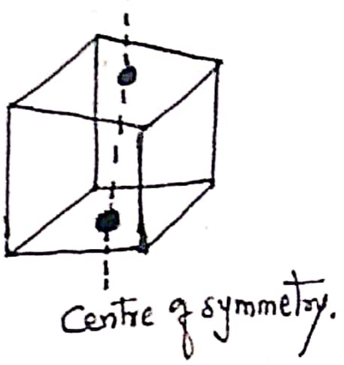
The large number of crystals are formed by different substances, depending on the condition of crystallization, each substance having a characteristics crystalline form or forms.

The study of geometrical structures reveals that there are variety of more than 200 crystal forms, so there is problem to classify them, but on basis of elements of symmetry they can be grouped into small number as diff. classes.

A) Centre of symmetry :- i

It is a point that any line drawn through it will meet the surface of the crystal at equal distances on either side.

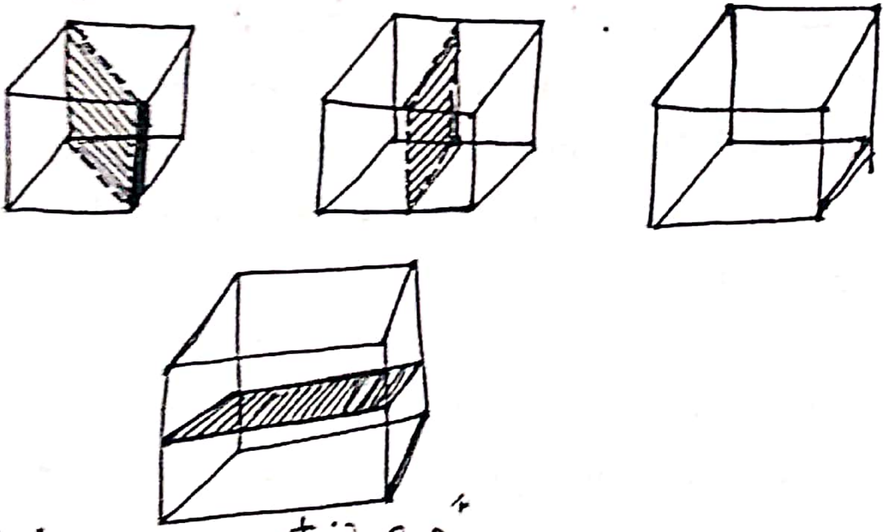




B) Plane of symmetry :- (6)

A crystal is said to possess a plane of symmetry when an imaginary plane passing through the centre of crystal can divide into two parts such that one is the exact mirror image of the other. It is indicated by '6'.

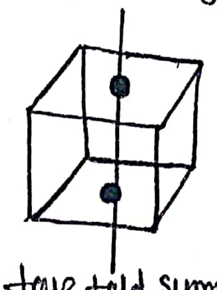
A cubic crystal has in all 3+6 = 9 planes of symmetry.



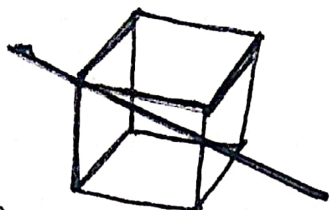
C) Axis of symmetry (C).

It is an imaginary line about which the crystal may be rotated so that it represents the same appearance more than one during a complete revolution. If the equivalent configuration occurs twice, thrice, four and six times ie after rotation of 180°, 120°, 90° and 60°, the axes of rotation are known as two fold (diad), three fold (triad), four fold (tetrad) and six fold (hexad) axes of symmetry respectively. denoted by C_2, C_3, C_4 fold axis of symmetry...

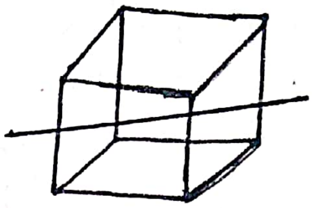
The word two fold is arising 360 because $\frac{360}{180} = 02$. If the self coincidence occurs thrice, one has rotated through 120° ie $\frac{360}{120} = 03$. Called as triad axis.



four fold symmetry



Three fold symmetry



Two fold symmetry

A cubic crystal has in all $3+4+6=13$ axes of symmetry.

The total number of Centres of symmetry, Planes of symmetry and axes of symmetry Possessed by a crystal is termed as elements of symmetry of the crystal.

A cubic crystal Possesses 23 elements of symmetry ie Elements of symmetry = Plane symm + Centre symm. + axis of symm.

$$= 1+9+13$$

$$\boxed{= 23}.$$

X-ray diffraction from crystals :-

The phenomenon of diffraction is the interferance caused by an object in the path of waves and the pattern of varying intensity that result is called the diffraction.

Max Von Laue observed that they might be diffracted when passed through a crystal. The reason for this was that the wavelength of x-rays was of about the same order as the interatomic distances in a crystal. X-rays are more penetrating than the cathode rays. Electric and magnetic field have no influence on x-rays and so they evidently donot consist of charged Particles.

Further Braggs suggested to use the crystal as a reflection grating, the resulting spectra being much simpler and amenable to the theoretical treatment.

Bragg's equation :-

In 1915 Bragg devised a simple method for the study of crystals by X-rays. He Pointed out that when a beam of X-rays is Passed through a crystal each atom in the path acts as scattering centre and thus emits secondary radiations. However reflection of X-rays can take Place at certain angles when the Path difference of emitted ray from the successive planes is a whole number multiple of the wavelength.

Consider a set of Parallel atomic planes whose spacing is 'd' and let a narrow monochromatic beam of X-rays fall upon these Parallel planes at a glancing angle θ, Each atom in a given layer, according to Huygen's principle, becomes the centre of expanding wavelets whose envelope gives rise to reflected wave front.

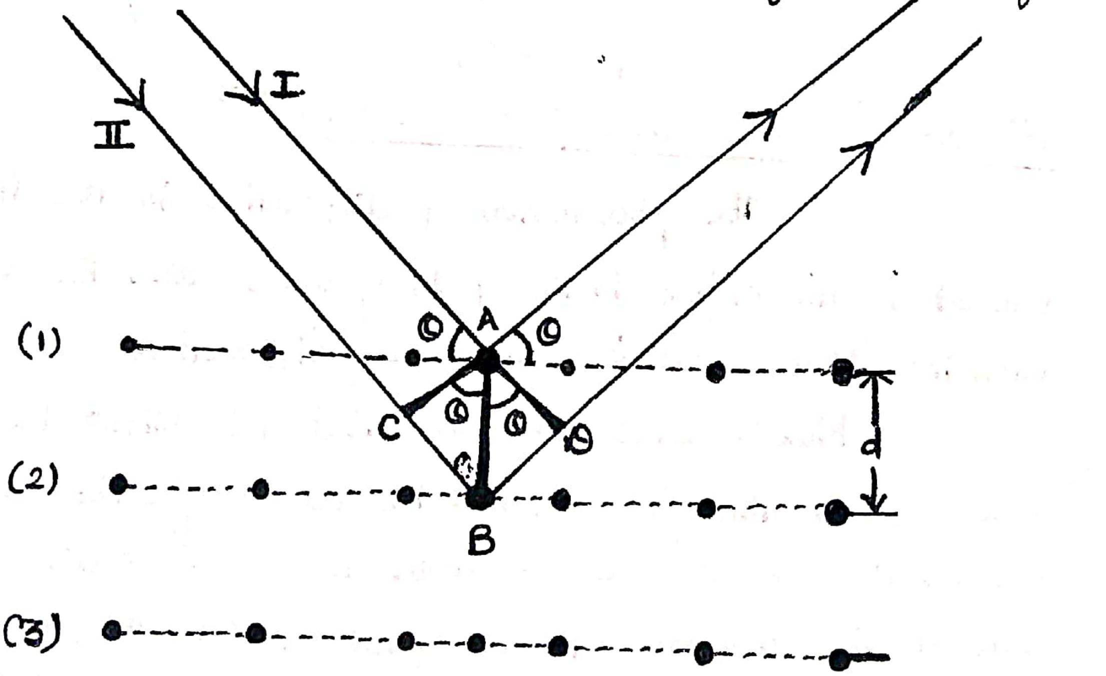


Fig:- Reflection of x-rays from lattice planes of crystal.

As in the case of optical reflection, the reflected wave front will have maximum intencity at an angle θ to this plane. which is equal to the glancing angle. Each Parallel layer in the given set gives rise to the reflected wave front.

The Condition for Constructive interferance between the reflected wave fronts is that the Path difference between the reflected ~~wavelength~~ wavefronts from one layer and that from the next must be equal to an exact wavelength or an integral multiple of it.

In fig. two Parallel rays I and II are reflected by two atoms 'A' and 'B'. The ray reflected from 'B' travels a longer distance than that reflected from 'A'. Draw AC and AD perpendicular to the direction of the incident and the reflected rays. Each of these lines makes an angle 'θ' with 'AB' whose length is equal to the spacing 'd'. Further $CB = BD = AB \sin\theta = d \sin\theta$. The additional path travelled by the ray reflected from the second layer is equal to (CB + BD) Thus, the condition for Constructive interferance between two rays is,

$$CB + AD = n\lambda$$

or $$\boxed{2d \sin\theta = n\lambda} \text{ - - - - } ①$$

where 'n' is an integer. This is known as Bragg's equation. and gives the Condition which must be satisfied for the reflection of x-rays from a set of atomic planes.

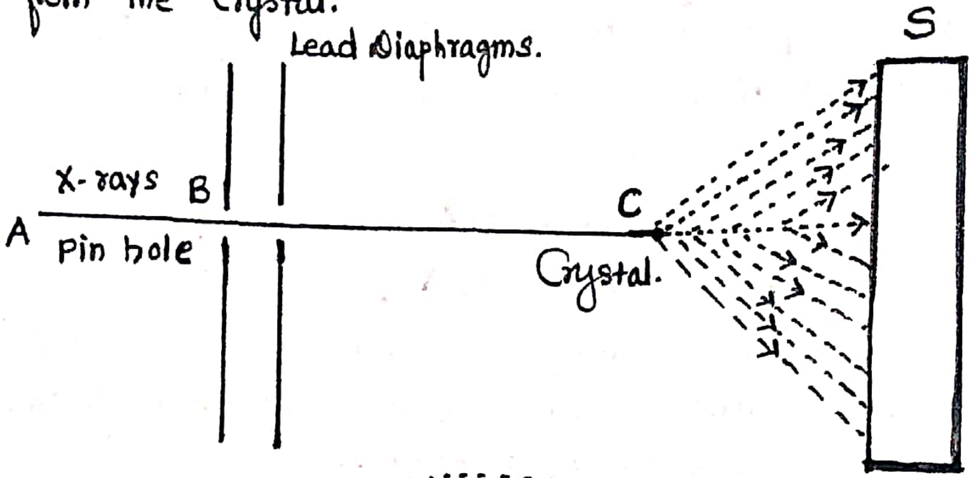
For a given set of lattice planes, 'd' is a fixed value. If homogeneous x-rays of definite wavelength 'λ' are used. then the Possibility of getting maximum reflection, depends on 'θ'. If θ, the angle which the rays make with the plane of crystal is regularly increased. a no. of positions corresponding to n=1, 2, 3 etc. will found at which the reflection will be maximum.

$$\left.\begin{aligned} \theta &= \sin^{-1} 1 \left(\frac{\lambda}{2d}\right) \\ \theta &= \sin^{-1} 2 \left(\lambda/2d\right) \\ \theta &= \sin^{-1} 3 \left(\lambda/2d\right) \end{aligned}\right\} — ②$$

n=1 reflection called first order reflection and so on. from eqn ② that if glancing angle 'θ' are measured for various 'n' of maximum intensity the distance 'd' betn successive lattice planes of given type in crystal can be calculated if value of 'λ' is known.

Laue's Photographic method :-

In 1912 Laue passed x-rays through a crystal to get a diffraction Pattern. He was decided to get the Positions of ions or molecules in a crystal. X-rays were Produced at 60,000 Volt. The beam of x-rays was continuous with different wavelengths. To get a fine beam of one wavelength the Continuous earn was passed through a slit system. The fine beam Coming out of the slit was Passed through a Crystal Placed on a holder. The beam emerging from the crystal was made to fall on a photographic plate. kept few centimeters from the Crystal.



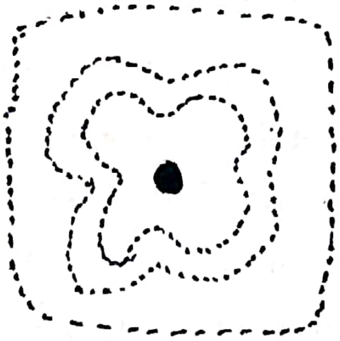


Fig. Diffraction of white X-rays by a single stationary Crystal.

Laue Photograph is obtained, It consists of a central spot which arises due to undiffracted beam. The Central spot is Surrounded by spots which arise from different diffracted beam. The Pattern of spots gives an idea about the Crystal structure.

The mathematics involved in this method for Calculations are highly complex and requires a single Crystal for efficient diffraction Hence simpler method Proposed by Bragg's which is more Popular.