

Crystal Structure.

Difference between Crystal and Amorphous Solid: —

The Crystalline and Amorphous Solid differs from one another in the following manner: —

(1) Characteristic Geometry: —

A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in three dimensional space.

But on the other hand Amorphous solids has not any geometrical shape because it is formed by (irregular) disorderly arrangement of molecules or atoms.

It has been found that even, if some orderly arrangement of molecules or atoms exist in a few amorphous solids, it does not extend more than a few angstrom units. Thus unlike crystalline solids (Amorphous solids) do not have a large range order.

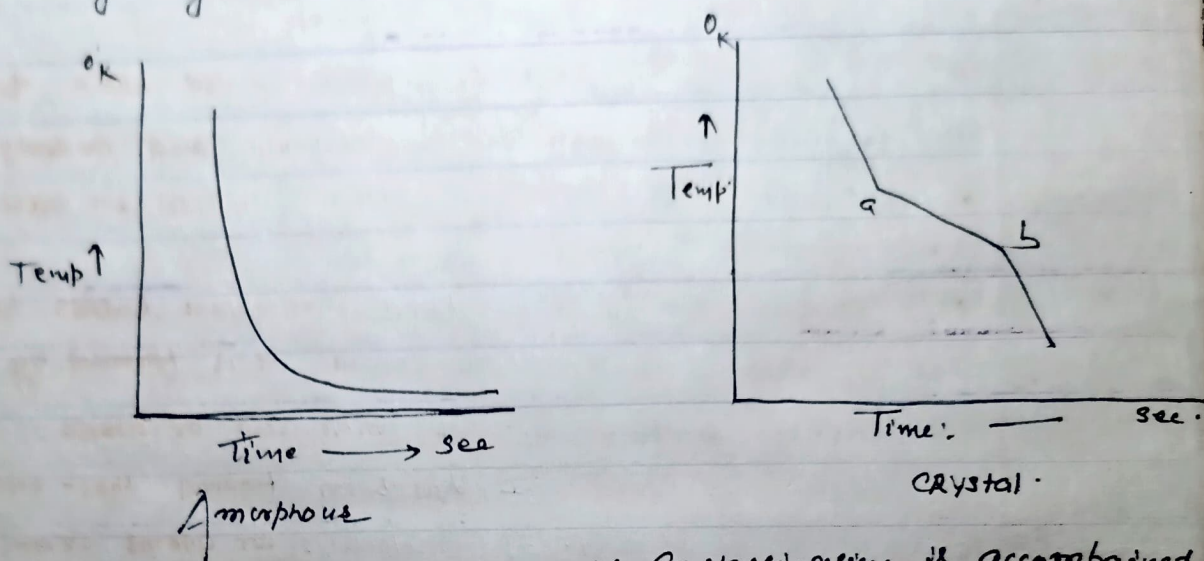
(2) Melting Points — As the solid is heated its molecular vibration is increased and ultimately becomes great the molecules break away from the fixed position.

They now began to move freely, and the solid now changes into liquid state. The temp. at which it occurs is called melting point.

A crystalline solid has sharp melting point i.e. it changes abruptly into liquid state. But amorphous solids does not have sharp melting point. For example, if glass is heated gradually, it softens and then starts to flow, without going under a definite and abrupt change into liquid state.

The amorphous solids are regarded as "Liquid at all temperatures"

- (3) Cooling Curves - Cooling Curve for an amorphous substance is smooth, while the curve for a crystalline substance has two breaks (a & b) which correspond to the beginning and the end of the process of crystallization.



The process of crystallization is accompanied by some liberation of energy which compensates for the loss of heat and causes the temp. to remain constant.

- (4) Isotropy and Anisotropy: - (Isotropy: - Physical Properties are same in all directions)

The amorphous substance has same physical properties (i.e. Electrical Conductivity, thermal conductivity, Mechanical Strength and refractive Index) in all the directions because they are made of irregular and disorderly arrangements of atom or molecules, it means all the directions are equivalent.

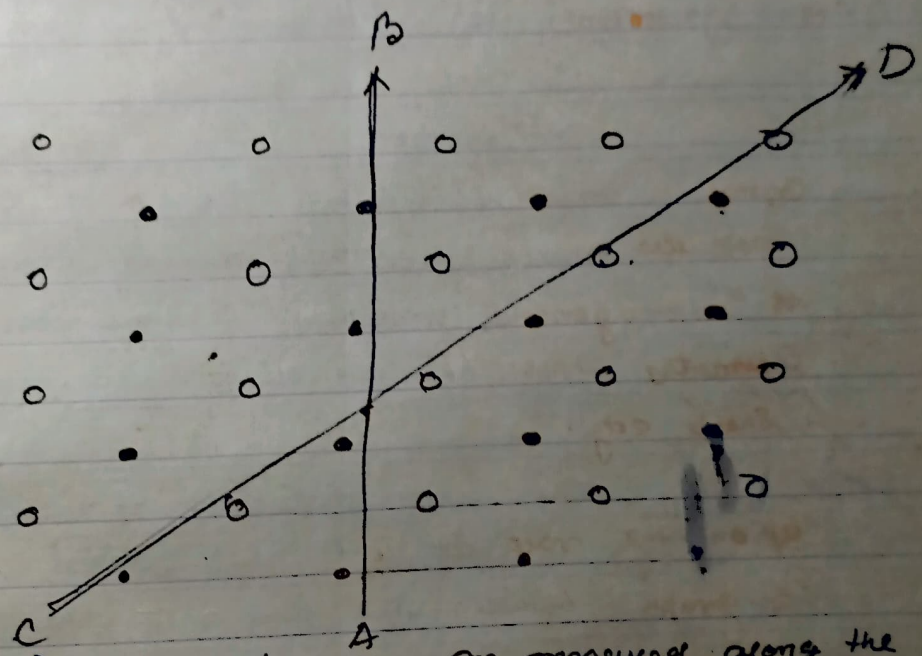
Amorphous Solids are said to be Isotropic, (The liquid and gases are also isotropic)

Crystalline Solids on the other hand are anisotropic because their Physical Properties are different in all directions.

Let us consider on the crystal of Sulphur iodide, the coefficient of thermal expansion is positive in one direction and negative in other direction.

Another example is that, when the velocity of light passing through a crystal varies with the direction in which it is measured. The phenomenon of Anisotropy offers a strong evidence for the presence of ordered molecular arrangement in the crystal. It may be shown on reference of fig.

For which the simple two dimensional arrangement of only two different kinds of atom is depicted.



If the physical properties are measured along the slanting line CD, these physical properties differs to those physical properties measured along vertical line AB.

The reason is describe as follows. In the first case (along CD) each row is made of alternate type of atoms. But in the 2nd case (i.e. along AB), each row is made of same type of atoms only.

But in Amorphous Solid or in liquid and gases, atom or molecules are arranged in a random or disorderly manner, so the all directions are identical, therefore all the properties are similar in all the direction.

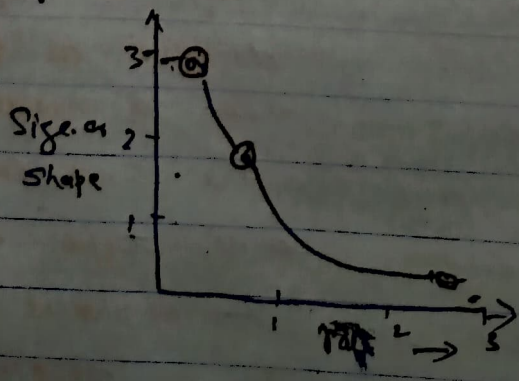
(5) Plane fracture: — Crystalline solids often have plane fracture (Broken parts have similar structure).
 Where as amorphous solids have conchoidal fracture.
 The existence of ordered molecular arrangement in crystalline solids gives rise to the following characteristic properties.

- (1) Characteristic Geometries
- (2) Sharp melting point
- (3) Two breaks in cooling curve
- (4) Anisotropy (5) Plane fracture.

✓ CRYSTALS: —

Crystal is made up of large number of small (units) atoms molecules or ions in orderly manner. Crystal is also defined as "Homogeneous anisotropic substance having a definite geometry shape bounded with surface. (usually plane and sharp edge).

The shape and size of a crystal depends upon the rate at which it is formed. If we draw a graph between size and rate. We found faster the rate smaller the shape and smaller the rate bigger the shape.

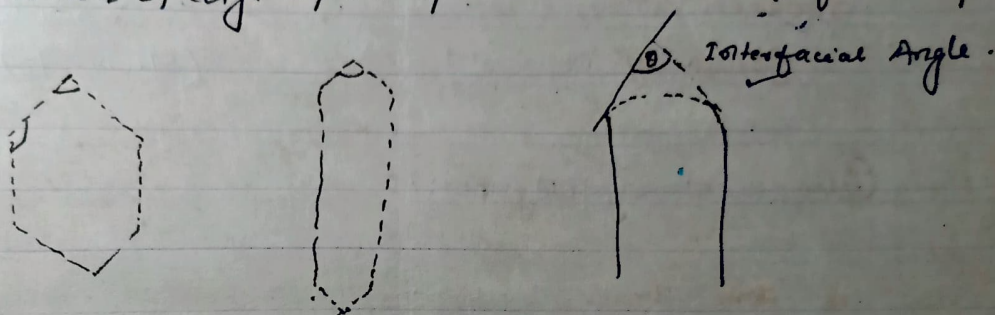


1. **FACE:** - Crystals are bounded by surfaces which are usually planes are called face of the crystal.

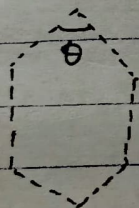
For example: - NaCl, KCl.

But in case of diamond the face is not planes it becomes slightly curved.

2. **Edge:** - Intersection of two adjacent faces are called edge. The position of edge depends upon the position of faces in space.



3. **Interfacial angle:** - The angle between any two faces of a crystal is termed as interfacial angle. This definition assumed that the crystal is perfectly grown. (ideal).



Normally crystals are not as perfect as illustrated above, faces do not meet to angle.

In such cases the angle between the normals to the two intersecting faces is the interfacial angle.

Generally, the angle between two faces of a crystal is termed as the interfacial angle. The relation between plane faces, straight edges and interfacial angle is expressed as,

$$F + C = E + 2$$

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where

F = Numbers of faces.

C = Numbers of Angles.

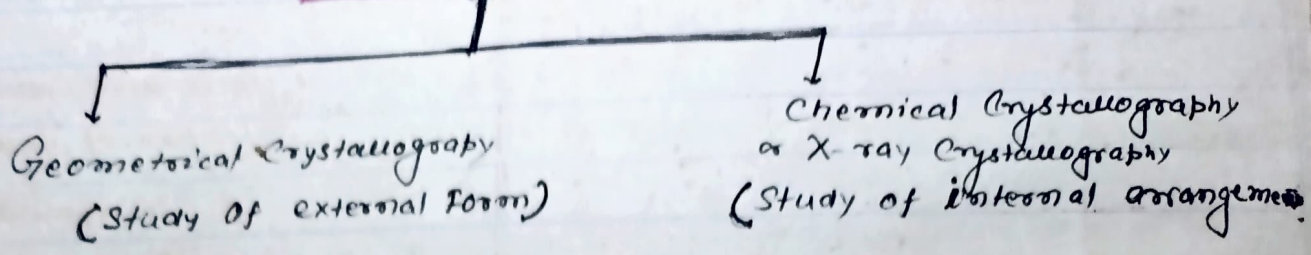
and E = Numbers of edges.

Stero definition for interfacial angle: -

Under the same physical condition (same temp. and same chemical composition) the angle between the corresponding faces on various crystals of the same substance are constant.

Similar the set of similar faces are

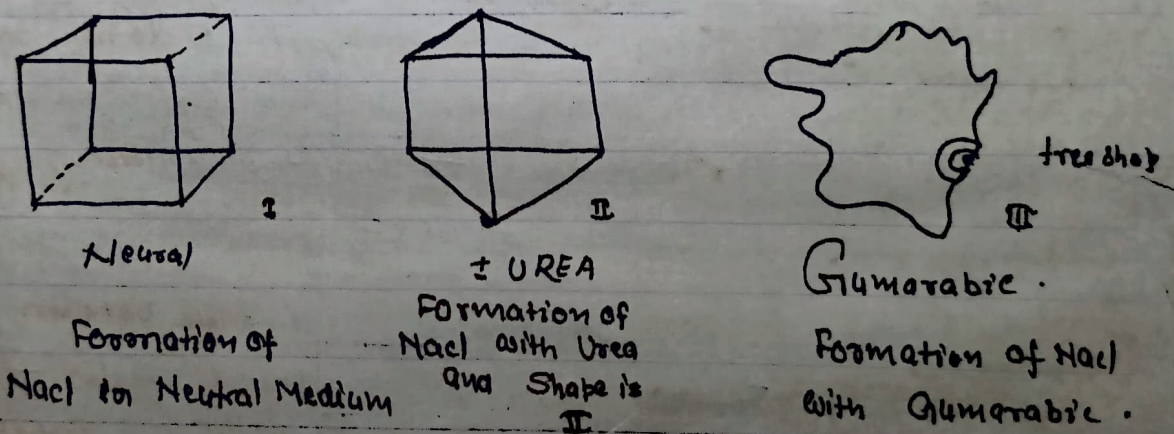
CRYSTALLOGRAPHY:-



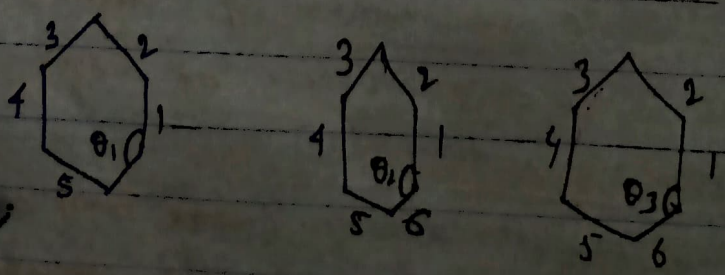
Geometrical Crystallography:-

The studies of Geometrical Crystallography is done by the help of three laws:-

- ① Steno's Law of Constancy of interfacial angles.
- ② Law of Constancy of Symmetry.
- ③ Haüy's Law of rational intercepts.



(1) N - Steno (~~law~~) formulated that external shape or habit of a crystal of given substance may vary widely with conditions of formation. But the angle between the corresponding faces (interfacial angle) of all the crystal are constant.



Angle between face 146 in each case.
i.e. $\theta_1 = \theta_2 = \theta_3$

(2) Law of Constancy of Symmetry: \rightarrow (Geometrical Operation)

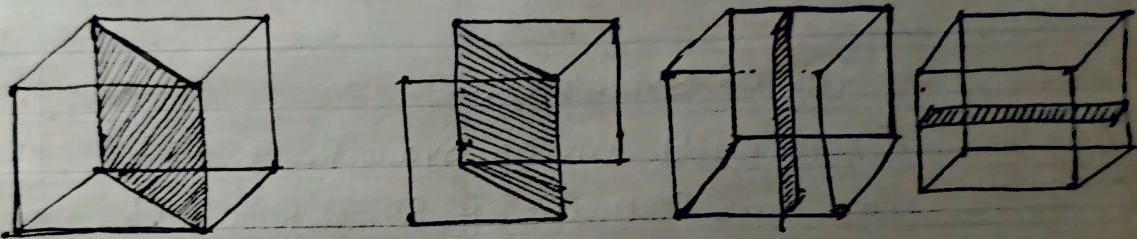
Reflection across a plane — Plane of Symmetry

Rotation along a line: — Axis of Symmetry
(axis)

Rotation along a line (Point): — Centre of Symmetry

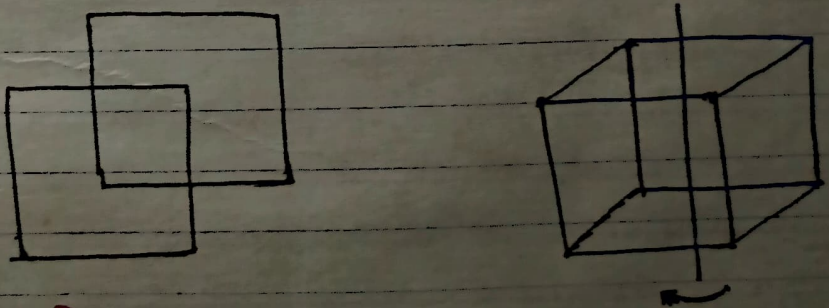
(a) Plane of Symmetry: —

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



(b) Axis of Symmetry: —

It is a line about which the crystal may be rotated so that it represents the same appearance more than one during a complete revolution (Rotating through the angle of 360°).



(c) Centre of Symmetry: \rightarrow

It is an imaginary point in the body of the crystal such that a line drawn through it intersects the opposite identical faces at equal distance in both directions.

Collectively the Plane, axis and Centre of Symmetry are known as elements of symmetry.



Laws: — The law of Constancy of Symmetry is stated as follows: —

"All Crystals of one and of the same substance have the same symmetry."

i.e. Total Number of Elements of Symmetry of a Cubic Crystal (Say NaCl) = 23.

1. Plane of Symmetry

- (a) Rectangular Plane of Symmetry = 3
- (b) Diagonal Plane of Symmetry = 6

} 9

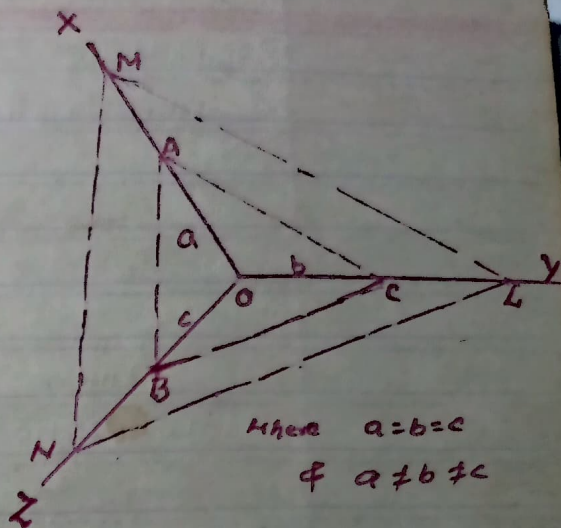
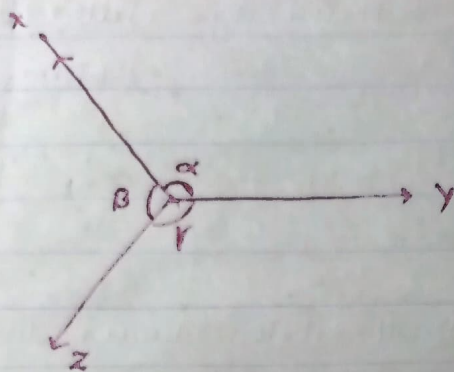
2. Axis of Symmetry: —

- (a) Four Fold axis of Symmetry = 3
- (b) Three Fold axis of Symmetry = 4
- (c) Two Fold axis of Symmetry = 6

} 13

} 9 + 13 + 1 = 23

Hauy's LAW OF RATIONAL INTERCEPT.



Intercept $OM:OL:ON = la:mb:nc$
 where l, m, n are simple integers i.e. 1, 2 or 3.

The law may be stated as:—

The intercept of any face of a crystal along the crystallographic axes are either equal to unit intercepts (a, b, c) or small whole number multiples by them (unit intercept) i.e. la, mb, nc , where l, m, n are simple whole numbers.

WEISS INDICES:— Ratio of intercepts of Plane LMN and Standard Plane ABC is called Weiss indices.

If the intercept of Plane LMN is designated by la, mb, nc and the intercept of Standard Plane ABC is designated by a, b, c ,

$$\text{then, } \frac{la}{a} : \frac{mb}{b} : \frac{nc}{c}$$

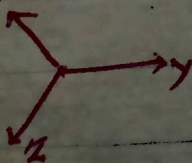
$$l : m : n$$

The Plane LMN is characterised or represented by (l, m, n) Plane.

Other Plane $M'N'$ whose intercept is $2a, 2b, c$

then Ratio of intercept (Weiss indices) is

$$\frac{2a}{a} : \frac{2b}{b} : \frac{c}{c}$$



It should be noted that the Weiss Indices have been completely replaced by Miller Indices.

Weiss Indices

Miller Indices

l	$\frac{1}{l} \cdot x = h$
m	$\frac{1}{m} \cdot x = k$
n	$\frac{1}{n} \cdot x = i$

where x is small whole number used to bring the ratio into whole numbers.

Plane	Weiss Indices	Miller Indices	Miller Index Plane
(2, 1, 2)	2	$\frac{1}{2} \times 2 = 1$	(1, 2, 1)
	1	$\frac{1}{1} \times 2 = 2$	
	2	$\frac{1}{2} \times 2 = 1$	

Miller Indices :->

Any Particular face of a crystal is represented by the reciprocals of the multiples of the unit intercept.

Let us consider on the unit plane ABC, the intercepts a, b, and c are all units. therefore the reciprocals are in the ratio 1:1:1, so the Miller indices of the ABC face are (1, 1, 1). Now we suppose a face cuts only two axes Oy and Oz, intercepts being 2 and 3 multiples of b and c. It does not cut the axis Ox, but being parallel to it. Hence the reciprocal of multiples are $0, \frac{1}{2}, \frac{1}{3}$.

Plane	Reciprocal of Multiples	Miller Index
(0, 2, 3)	$0 \times 6 = 0$	0
Here 2, and 3 are multiples of b and c	$\frac{1}{2} \times 6 = 3$	3
	$\frac{1}{3} \times 6 = 2$	2

Miller indices (0, 3, 2)

So, the Miller indices of any crystal face are inversely proportional to the intercepts of that face on the different axes.

The distance between the Parallel Planes in a crystal are designated as d_{hkl} . For different Cubic lattices, the interplaner spacing (interplaner distance) are given by the General formula.

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

Where 'a' is the length of the cube side. While h, k and l are Miller indices of the plane.

Problem: — How do the spacing of the three planes (100), (110) and (111) of a cubic lattice vary.

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

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

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

(i) Simple Cubic lattice.

$$d_{(100)} : d_{(110)} : d_{(111)}$$

$$= 1 : 0.707 : 0.577$$

(ii) Face Centred Cubic lattices,

$$d_{(100)} : d_{(110)} : d_{(111)} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

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

$$= 1 : 0.707 : 1.154$$

(iii) Body Centred Cubic lattices.

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

$$= 1 : 1.414 : 0.577$$