SOLID STATE

Introduction

A substance can exist in three physical states. Viz.,

1) solid state,
2) liquid state and
3) gaseous state

Depending on the temperature at which the substance is present. With increase in temperature solid converts into liquid and liquid converts into gas.

A solid is a nearly incompressible state of matter with well-defined state, rigidity and a definite volume. In solid state the atoms or molecules or ions making up the solid are in close contact and are in fixed positions.

CHARACTERISTICS OF SOLIDS:

- They have definite volume irrespective of the size of the container.
- They are rigid and have definite shape.
- They are almost incompressible.
- They are mostly crystalline in nature.
- They have relatively higher densities than liquids or gases.
- They diffuse very slowly, when compared to liquids and gases.
- Most of them melt on heating and become liquids.

CLASSIFICATION OF SOLIDS:

All the solids can broadly be classified into two types.

i) Crystalline solids

ii) Amorphous solids.

Crystalline solids:

Crystalline solid is a solid which possesses a large number of small crystals each of them having a definite characteristic geometrical shape the arrangement of constituent particles (atoms, molecules or ions)are perfectly ordered.

They consist of long-range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal .

For example -NaCl ,MgO ,Quartz etc.

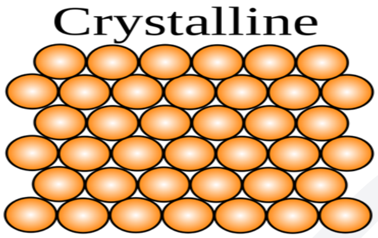
Amorphous solids.

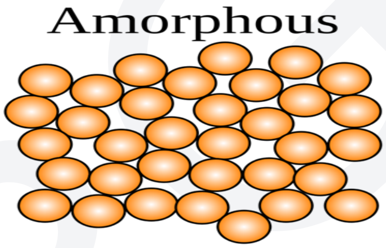
Amorphous solids are the solids which consist of particles of irregular shape, the arrangement of constituent particles (atoms, molecules or ions) in such solid has only short-range order.

The word amorphous is derived from Greek language amorphous which means no form.

Examples: rubber, plastic etc.

In crystalline solids certain physical properties like, refractive index, density etc., have definite values in different directions (anisotropic) while in amorphous solids those certain properties have the same value in all the directions (isotropic).





Laws of crystallography:

CRYSTALLOGRAPHY:

The study of geometry, properties and structure of crystalline substances is known as crystallography.

It is based on three fundamental laws which govern the whole crystallography.

(i) The law of constancy of interfacial angles
(ii) The law of symmetry and
(iii) The law of rational indices.

(i) The law of constancy of interfacial angles

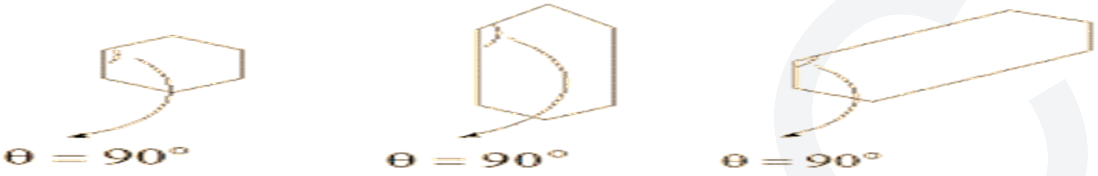
Interfacial angle may more generally be defined as the angle between any two adjacent faces of a crystal.

In crystallography, however, the interfacial angle of a crystal is the angle subtended between the normal drawn on the two faces concerned.

This law states that “the angle between the adjacent corresponding faces is the interfacial angles of the crystal of the particular substance is always constant inspite of having different

shapes and sizes and mode of growth of the crystal”. The size and shape of the crystal depend upon the conditions of the crystallization.
This law is also called Steno's Law.

For example, the interfacial angles in all the NaCl crystals are found to be the same i.e., 90° irrespective of the size and shapes of faces. Depending on the interfacial angles of a crystal we can easily predict the type of crystal. The instrument used to measure the interfacial angles is called a goniometer. The measurement of crystal angles is important in the study of crystals.



Different shapes of crystals of the same substance with same interfacial angle

(ii) The law of symmetry:

The crystals of a particular substance always possess the same elements of symmetry and crystals of different substances exhibit different elements of symmetry. This is known as the “law of symmetry”.

The three important elements of symmetry are

- **Plane of symmetry**
- **Centre of symmetry and**
- **Axis of symmetry.**

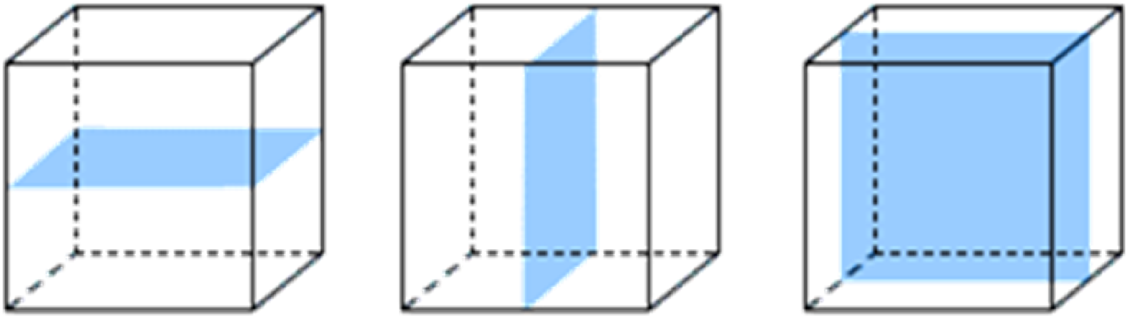
I.Plane of symmetry

An imaginary plane passing through the crystal, which can divide the crystal into two parts such that one is the exact mirror image of the other, is called “plane of symmetry”. The planes of symmetry are also called mirror planes.

A cubic crystal like sodium chloride possesses two types of planes of symmetry. They are
a)Rectangular planes of symmetry
b)Diagonal planes of symmetry.

a) Rectangular planes of symmetry:

The planes which are situated midway and parallel to the opposite faces are called regular planes of symmetry. As a cubic crystal has six faces, it has three rectangular planes of symmetry
Total faces-06
Total opposite face pairs-03
Therefore Rectangular Plane of symmetry= 3

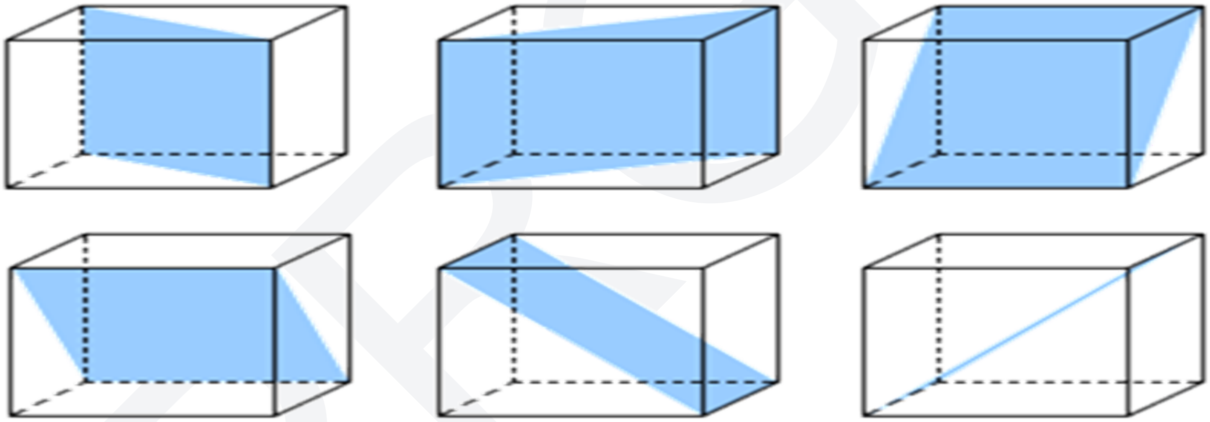


b)Diagonal planes of symmetry:

These are the planes touching the opposite edges. As they lie on the diagonal of the opposite faces these are called diagonal planes of symmetry.

In a cubic system, there are 12 edges or six pairs of opposite edges.

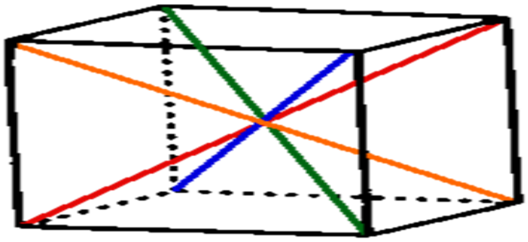
Therefore, a cubic crystal has 6 diagonal planes of symmetry



II.Centre of symmetry:

It is defined as an imaginary point within a crystal such that any line passing through this point intersects the opposite faces of the crystal at equal distances.

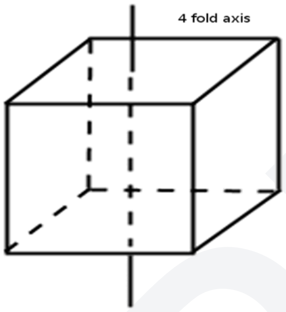
- It is also called the centre of inversion.
- It's passing from the body centre.
- Only one centre of symmetry is possible.

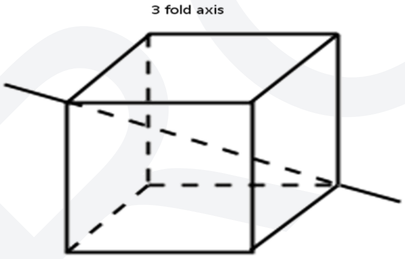


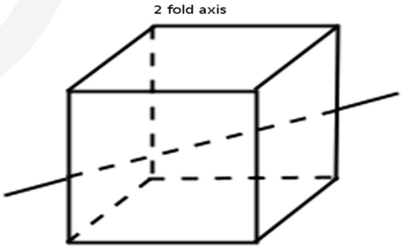
III.Axis of symmetry.

It is an imaginary line or axis passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution i.e. in a rotation through 360^0

Suppose the same appearance of the crystal is repeated on rotating it through an angle of 360°/n around the imaginary axis, the axis is called an n-fold axis of symmetry, where n is called order of axis.







a) Axis of Four fold symmetry (C_4):

If a cube is rotated about an axis passing perpendicularly through the centre, so that the similar appearance occurs **four times** in one revolution then axis is called a four-fold axis (tetrad axis).

It is Passing from the centre of two opposite faces.

Total faces-06

Pairs of opposite faces-03

Θ= 90 degrees (rotation angle)

b) Axis of three fold symmetry (C_3):

If the original appearance is repeated **three times** in one revolution i.e., rotation after 120°, the axis is called the threefold axis of symmetry or triad axis.

It is Passing from two opposite corners along with body diagone.

Total corners-08

Pairs of opposite corners-04
Θ= 120 degrees (rotation angle)

c) Axis of two fold symmetry (C_2):

If similar appearance occurs **twice** in one complete revolution, i.e., after 180° the axis is called a two-fold axis of symmetry or diad axis.

It is Passing from two diagonally opposite edges.
Total edges-12
Pairs of opposite edges-06
Θ= 180 degrees (rotation angle)

Types of Elements of Symmetry					
Plane of symmetry		**Axes of Symmetry**		Centre of symmetry	
Rectangular plane of symmetry	3	Four fold axes of symmetry	3	Centre of symmetry	1
Diagonal plane of symmetry	6	Three fold axes of symmetry	4		
		Two axes of symmetry	6		
Total	**9**		13		1

(iii) The law of rational indices:

This law was proposed by Hauy. According to him if the intercepts of any face of the crystal on the three axes are measured, the following generalization is observed, this is called the law of rational indices.

The intercepts made by any face of the crystal on the crystallographic axes are either:

- same as those of the unit plane.(or).
- simple whole number multiples of those of the unit plane (or).
- one or two intercepts may be infinity, if the face is parallel to one or two axes i.e., the face does not cut one or two axes.

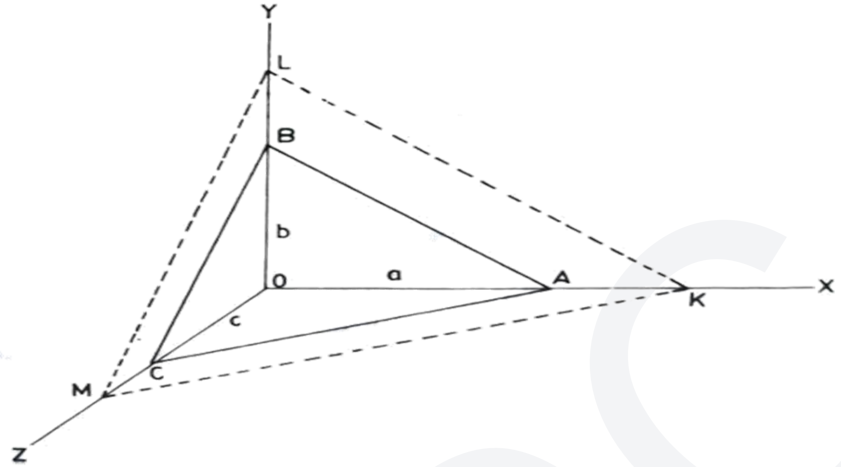
Explanation of law of rational indices

Consider a crystal plane intersecting the x, y, z axes at A, B, C respectively such that OC = a,OB = b and OC = c, as shown in figure

The ratio of the intercepts is $a : b : c$.

Considering one and half times larger crystal, the same plane intersects the x, y, z axes at K, L, M respectively, such that OK = 2a, OL = 2b and OM = 3c.

Therefore OK: OL : OM = 2a : 2b : 3c.
Hence the ratio of the intercepts, OK : OL : OM for larger crystal is the same as the intercept of a smaller crystal on the three coordinate axes.



Miller Indices:

a) Weiss Indices

The Weiss parameters, introduced by 'Weiss' (1817) are the ancestors of the Miller indices. These indices give an approximate indication of a face orientation with respect to the crystallographic axes and are used as a symbol for the face.

According to the law of rational indices, the intercepts of any face of a crystal along the crystallographic axes either equal to the unit intercepts *a, b, c* or their simple whole number multiples.

As shown in the figure the plane has intercepts at distances of 2*a*, 2*band* 3*c* on X, Y and Z axes respectively. The coefficients of a, b and c, namely 2, 2 and 3 respectively are known as the **Weiss indices** of a plane. Further, the Weiss indices may not always be an integral number. They may contain fractional values including infinity.

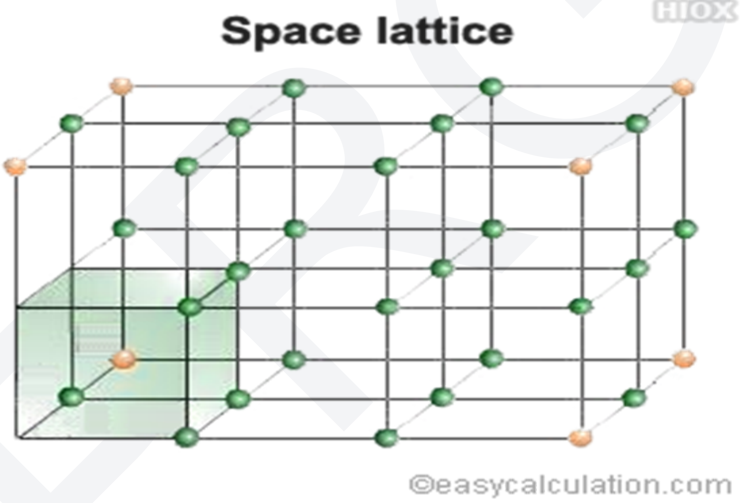
b) Miller Indices:

Miller indices are the set of integers (*h, k, l*) which are used to describe a given plane in a crystal. The Miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes. So Weiss indices have been replaced by 'Miller indices'. Miller indices of a plane are obtained by taking the reciprocals of Weiss Indices and then multiplying throughout by a smallest number to make all these reciprocals as integers.

For illustration, consider that a Weiss notation is given by $\infty a : 2b : c$ then the Weiss indices of the plane are ∞, 2 *and* 1. The Miller indices of the plane may be calculated as reciprocals of the coefficients of Weiss indices and multiplying by 2 in order to get whole numbers 0, 1 and 2. Thus, the Miller indices of the plane are 0, 1 and 2 and the plane is designated as (012) plane i.e., $h = 0$, $k = 1$ *and* $l = 2$.

Space lattice, Lattice points, Unit cell:

Space lattice:

- The arrangement of geometrical points in a definite pattern in space is called lattice.
- If the constituents of a crystal viz., atoms, molecules or ions are denoted by points, then the lattice is regarded as an infinite set of points, repeated regularly through space.
- The lattice may be one dimensional, two dimensional or three dimensional.
- 

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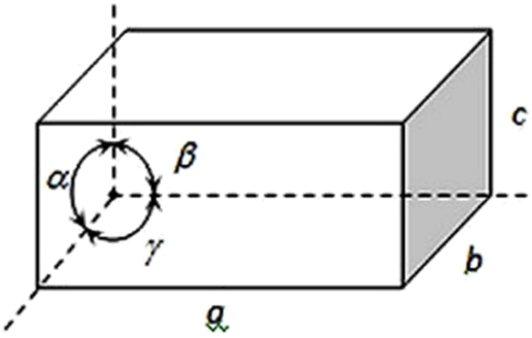
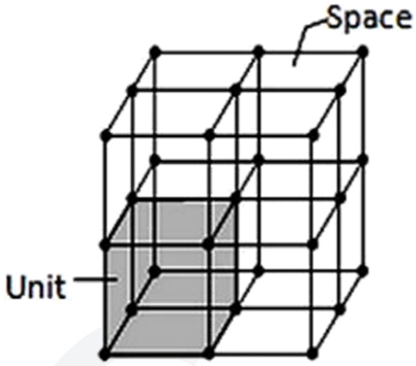
Unit cell:

- The basic units of the space lattice are called unit cells.
- Thus, a unit cell is the smallest repeating unit in the space lattice, which when repeated over and over again produces a crystal of the given substance.
- It possesses all the structural properties of the given crystal.
- So, it is an essential feature of the crystal structure.



Unit cell



Space lattice & unit cell

The unit cells are of two types.

They are:

i) primitive or simple unit cells

ii) centered unit cells.

Primitive unit cells

- Those unit cells in which constituent particles are present only at the corners of the unit cells are called primitive unit cells. Every crystal system has one primitive unit cell.

Centered unit cells

- Those unit cells in which the constituent particles are not only present at the corners but also present at other positions of the unit cells are called centred unit cells. These are of three types.

  (i) face centered

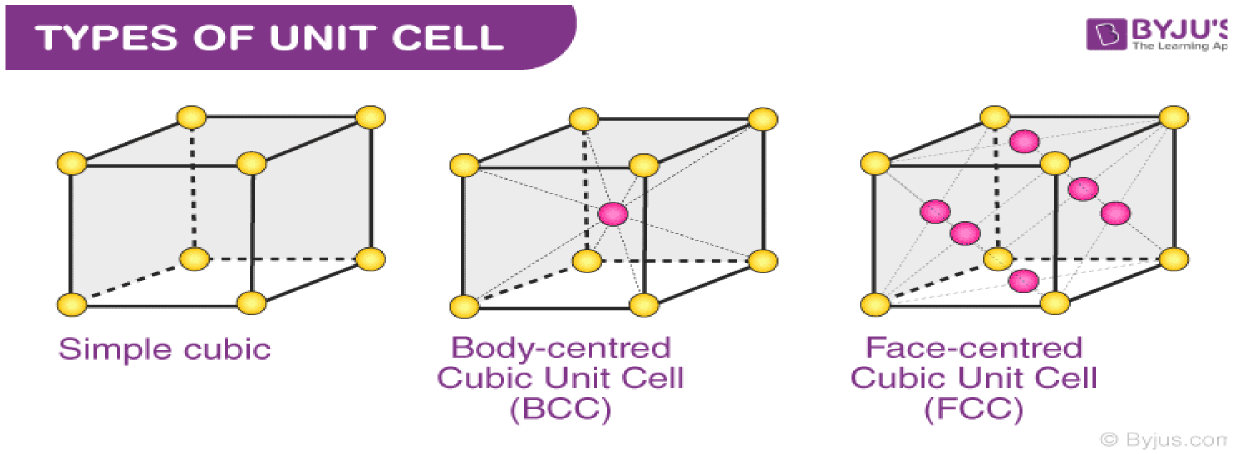
  (ii) body centered and

  (iii) end centered unit cells.

(i)**. Face centered unit cells:** In these unit cells, the constituent particles are present at all the corners and centres of all the faces.

(ii)**.Body centered unit cells:** In these unit cells constituent particles are present at all the corners and one constituent particle at its centre.

(iii)**.End centered unit cells:** In these unit cells constituent particles are present at all the corners and centre of any two opposite faces.



Lattice points

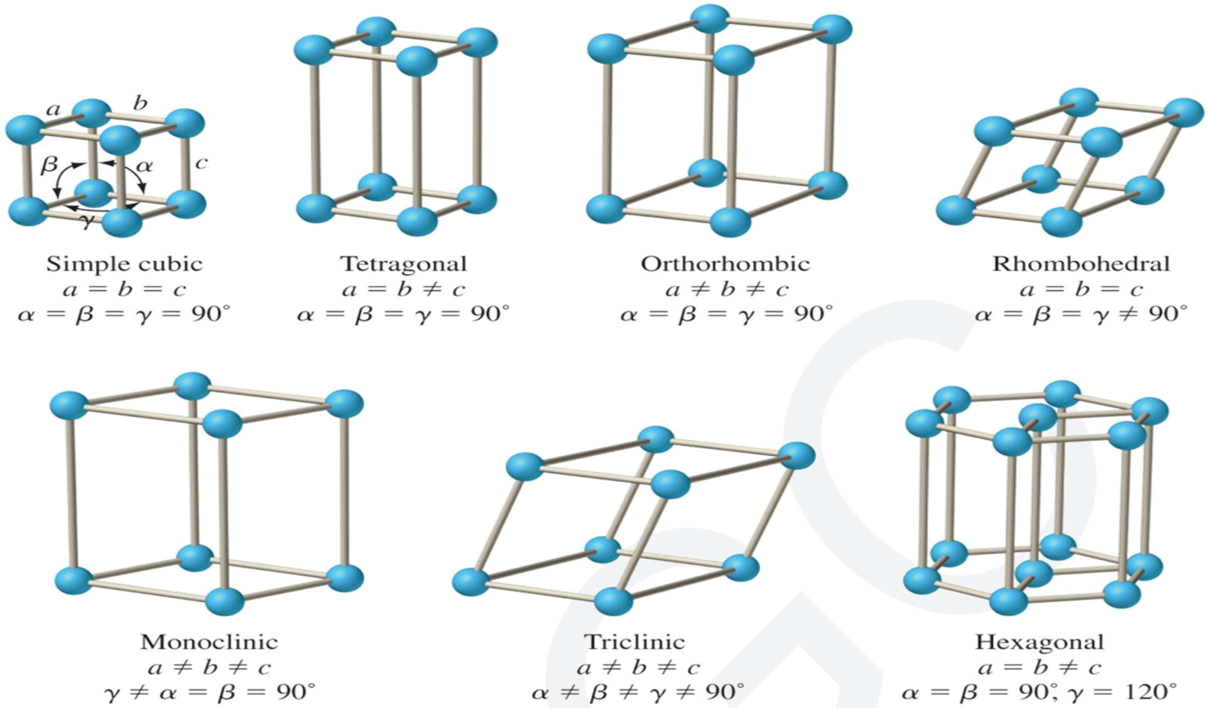
- The points representing the atoms or molecules or ions in a unit cell are known as lattice points.
- They include the corners, face centers, body centre of the unit cells.
- The lattice point that lies at the corner is shared by eight other unit cells.
- So, the contribution of corner points to each unit cell is 1/8.
- The lattice point that lies at the edge centre is shared by four other unit cells.
- So, the contribution to each unit cell is ¼.
- The lattice point that lies at the face centre is shared by two unit cells.
- So, the contribution of the face centered point to each unit cell is ½.
- The lattice point at the centre of the unit cell is independent as it is not shared by any other unit cells.

Crystal systems

In the space lattice each unit cell is characterized by lengths of the edges a, b and c and angles between the edges α, β and γ These are known as the parameters of the unit cell. On the basis of these parameters there are a total of seven crystal systems.

The seven crystal systems along with edge length and interfacial angles α, β and γ are shown as follows.

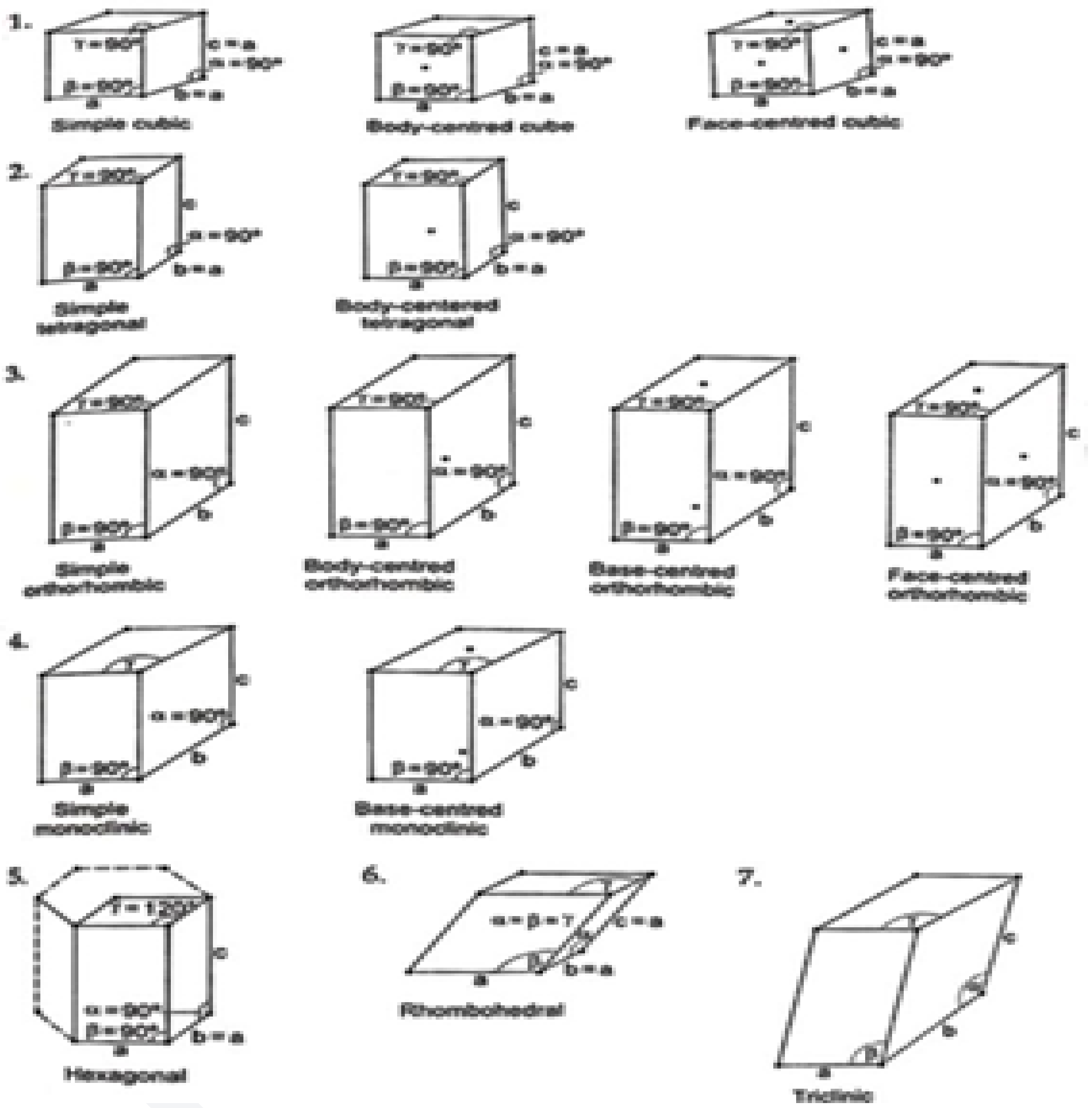
S.NO	NAME OF THE CRYSTAL SYSTEM	EDGE LENGTHS	AXIAL ANGLES	EXAMPLES
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	NaCl, ZnS, Cu
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	SnO_2, TiO_2, White tin
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	$BaSO_4$, KNO_3, rhombic sulphur
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^0$, $\beta \neq 90^0$	$CaSO_4\ 2H_2O$, $Na_2SO_4\ 10\ H_2O$ Monoclinic sulphur
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	$CaSO_4\ 5H_2O$, $K_2Cr_2O_7$
6	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^0$	$CaCO_3$, HgS
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0, \gamma = 120^0$	CdS. ZnO, graphite



Bravais lattices

With the help of geometrical calculations Bravais showed that there can be 14 different ways in which similar points can be arranged in a three-dimensional lattice. Thus, the total number of space lattices or unit cells possible for 7 crystal systems is only 14.

These 14 space lattices possible for 7 crystal systems are referred to as the Bravais lattices. The 14unit cells /space lattices are shown in following figure



X-ray Diffraction and Crystal Structure

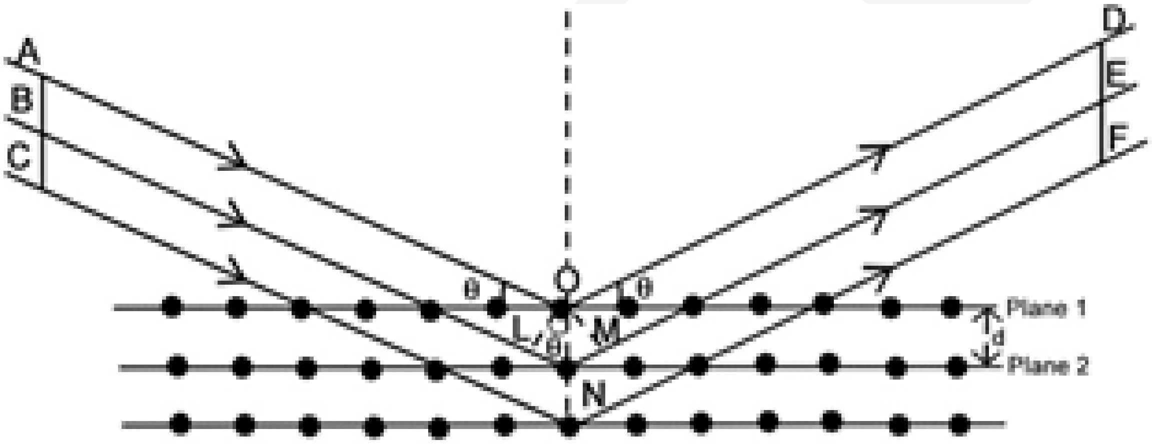
The phenomenon by which X-rays are reflected from the atoms in a crystalline solid is called diffraction. The diffracted X-rays generate a pattern that reveals structural orientation of each atom in a given compound. X-ray diffraction finds the geometry or shape of a molecule using X-rays. This technique is based on the elastic scattering of X-rays from structures that have long range order (crystalline solids).

Bragg's law (Bragg's equation)

Bragg observed that scattering of X-rays by crystals is considered as reflection from successive planes of atoms in the crystal. But, unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles. These angles are determined by the wavelength of the X-rays and the distance between the planes in a crystal.

The fundamental equation which gives a simple relation between the wavelength of the X- rays, the interplanar distance in the crystal and the angle of reflection, is known as Bragg's equation.

This can easily be derived by considering the following figure



From the above the horizontal lines indicate 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 angle θ, as shown in the figure.

Some of these rays will be reflected from the upper plane at the same angle θ while some others will be absorbed and get reflected from the successive layers.

ABC is the plane perpendicular to the incident ray and DEF is that perpendicular to the reflected beam.

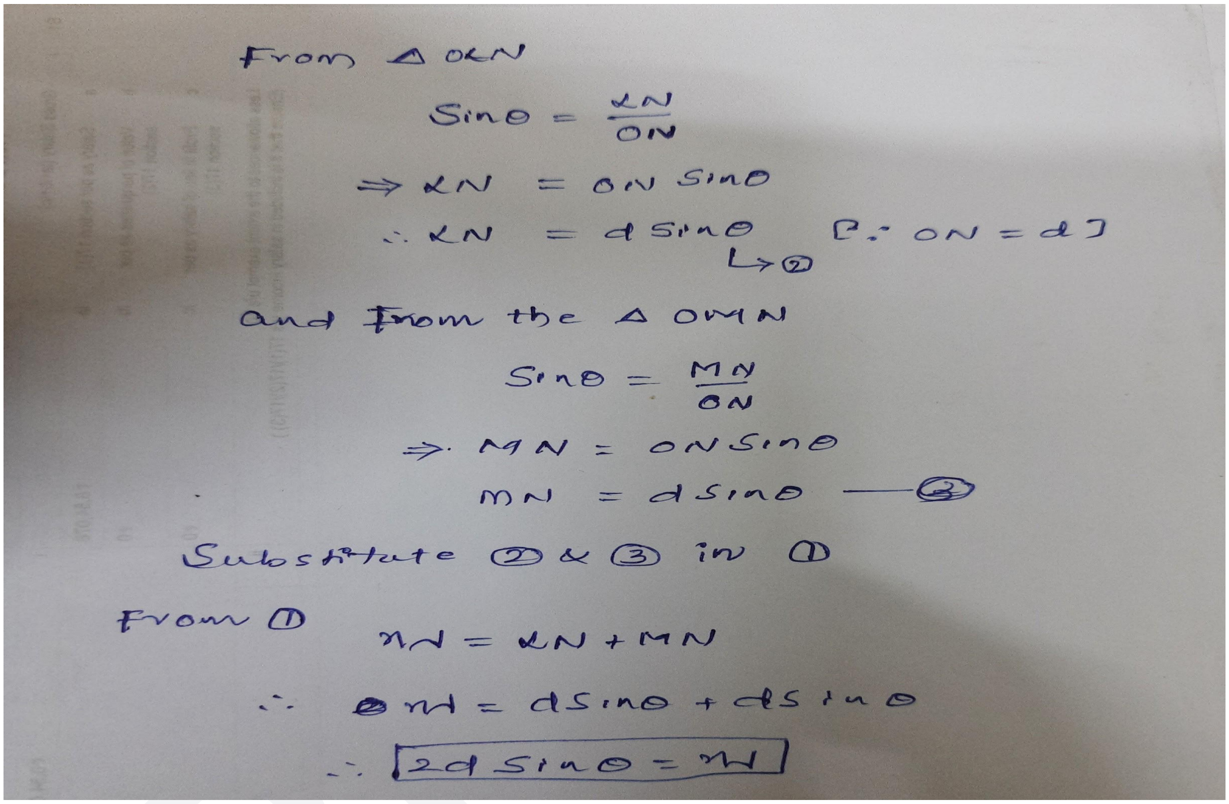
The waves reflected by different layers in a crystal will be in phase with each other only if the difference in the path lengths of the waves reflected from the successive planes is equal to an integral number of wavelengths.

By constructing OL and OM perpendicular to incident and reflected beams it is observed that the difference in path length (assume, **δ**) of the waves reflected from the two planes is given by

$$\delta = LN + NM$$

The value of d is equal to a whole number multiple of wavelength λ , i.e.,

$$n\lambda = LN + NM \text{ ---------- } (1)$$



From Δ OLN

$$\sin\theta = \frac{LN}{ON}$$

$$\Rightarrow LN = ON \sin\theta$$

$$\therefore LN = d \sin\theta \quad [\because ON = d] \rightarrow ②$$

and from the Δ OMN

$$\sin\theta = \frac{MN}{ON}$$

$$\Rightarrow MN = ON \sin\theta$$

$$MN = d \sin\theta \text{ — } ③$$

Substitute ② & ③ in ①

From ① $n\lambda = LN + MN$

$$\therefore n\lambda = d\sin\theta + d\sin\theta$$

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

The above equation is called **Bragg's Equation.**

Where n = 1,2,3.

If n=1, it is called first order difraction,

if n=2 it is called second order difraction and so on.

By knowing the values of θ , *n* and wavelength (λ), the distance between atomic planes *d* can be calculated.

Powder method (Deby – Scherrer – Hull method)

In Bragg's method, a single crystal is required whose size is much larger for experimental purpose. But, in the case of powder method, the crystal sample may not be required in large quantity. For the experimental study, even 1mg of the material is sufficient. The powder method was devised independently by **Debye,Scherrer** and **Hull**.

Powder diffraction is one of the primary techniques used to characterize various materials. This method provides structural information even when the crystallite size is too small for analysis.The powder method is more widely used particularly for crystals with simple structures.

- The crystal under study is powdered and taken in a capillary tube.
- The powder is exposed to a monochromatic X-ray beam of specific wavelength.
- The reflected beam is allowed to fall on a photographic film surrounding the capillary tube like an arc.
- As the powder contains a large number of small crystals and hence there is no need to rotate the capillary tube.
- The powder, in fact, consists of many small crystals which are oriented in all possible directions.
- As a result of this, X-rays are scattered from all sets of planes (e.g. 100, 110, etc). The scattered rays are detected by using an X-ray sensitive film.
- The principle of this method is illustrated in fig.
- The two big spots around the two holes correspond to the incident and out coming beam of X-rays.
- Around each spot, there are lines with specific distances corresponding to a definite angle θ . By using the value of θ, the l value can be calculated from Bragg's equation.