

Solid state ①

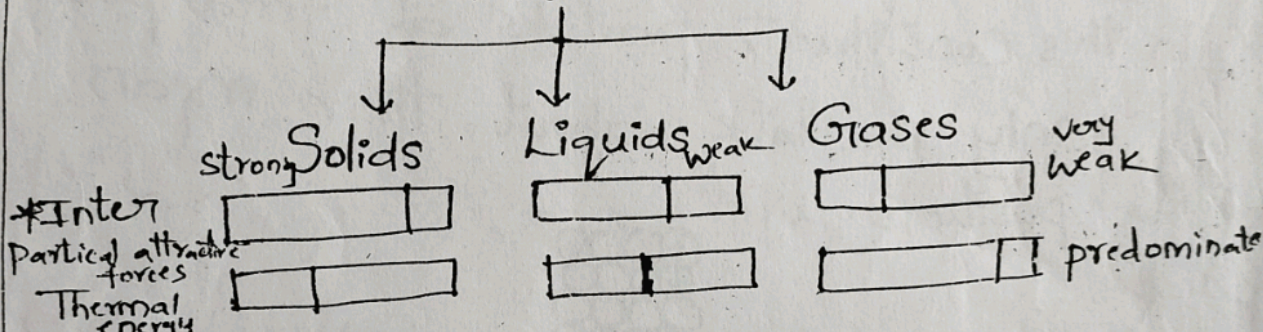
by
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Introduction ::

Matter: Matter refers to anything that occupies space ^{(i) volume} and has mass.

* We always classify matter into three categories such as

Matter



* But whether a substance will exist as a solid/liquid/gas that depends on the net effect of two main opposing factors.

1. Inter particle attractive forces
2. Thermal energy [Thermal energy is the energy possessed by the constituent particles due to temperature.]

Thermal Energy \propto Temperature

* The properties of Solids mainly depends on the nature of

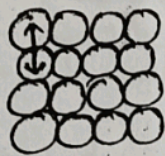
* The constituent particles (2)

* The binding forces (acting b/w the constituent particles)

* Note :- Gases and liquids possess fluidity due to the movement of constituent particles (free to move)

Rigidity :- Solids possess Rigidity,

in this constituent particles at fixed position, only oscillate about their mean positions. i.e.



Solid state

Solid possesses * Definite shapes

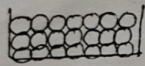
* Definite volumes

Classification of Solids / types of Solids :-

* If you look at diamond and glass both are solids, but we look at them at microscopic level

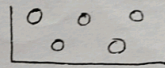
Diamond particles are arranged in orderly fashion

Crystalline Solids



- * Constituent particles are arranged in regular pattern
- * They have definite shape
- * They have sharp Melting points
- * They have long order arrangement
- * They ~~h~~ Crystalline Solids are anisotropic
- * They undergo clean cleavage
- * They have definite M.P & B.P & Heat of Fusion

Amorphous Solids



- * Constituent particles are arranged in irregular pattern.
- * They have indefinite shape
- * They melts over a range of temperature
- * They have short order arrangement.
- * Amorphous Solids are isotropic
- * They undergo irregular cleavage.
- * They do not have definite M.P. B.P &

Laws of Crystallography (4) (1)

Crystallography is the branch of Science which deals with the geometry, properties and structure of crystals and crystalline substances. It is based on three fundamental laws.

1. Law of constancy of interfacial angles.
(Steno's law)

2. Law of Rational indices. (Haüy's law)

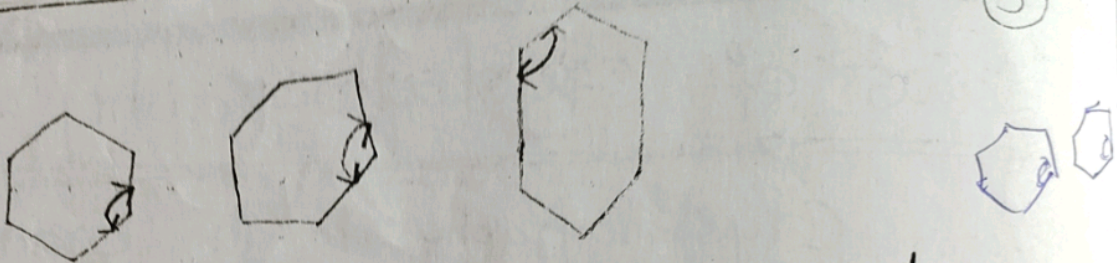
3. Law of constancy of symmetry.

(or)
law of symmetry (or) symmetry in crystals.

✓ 1. Law of constancy of interfacial angles :-

⇒ This is also called first law of crystallography.

⇒ According to this law "The angle between the corresponding faces of a crystal of the substance ^(or) ^{interfacial angle} are always the same / constant. irrespective of the size & shape (or) the method of preparation (or) source of the crystal.



Interfacial angles of crystals.

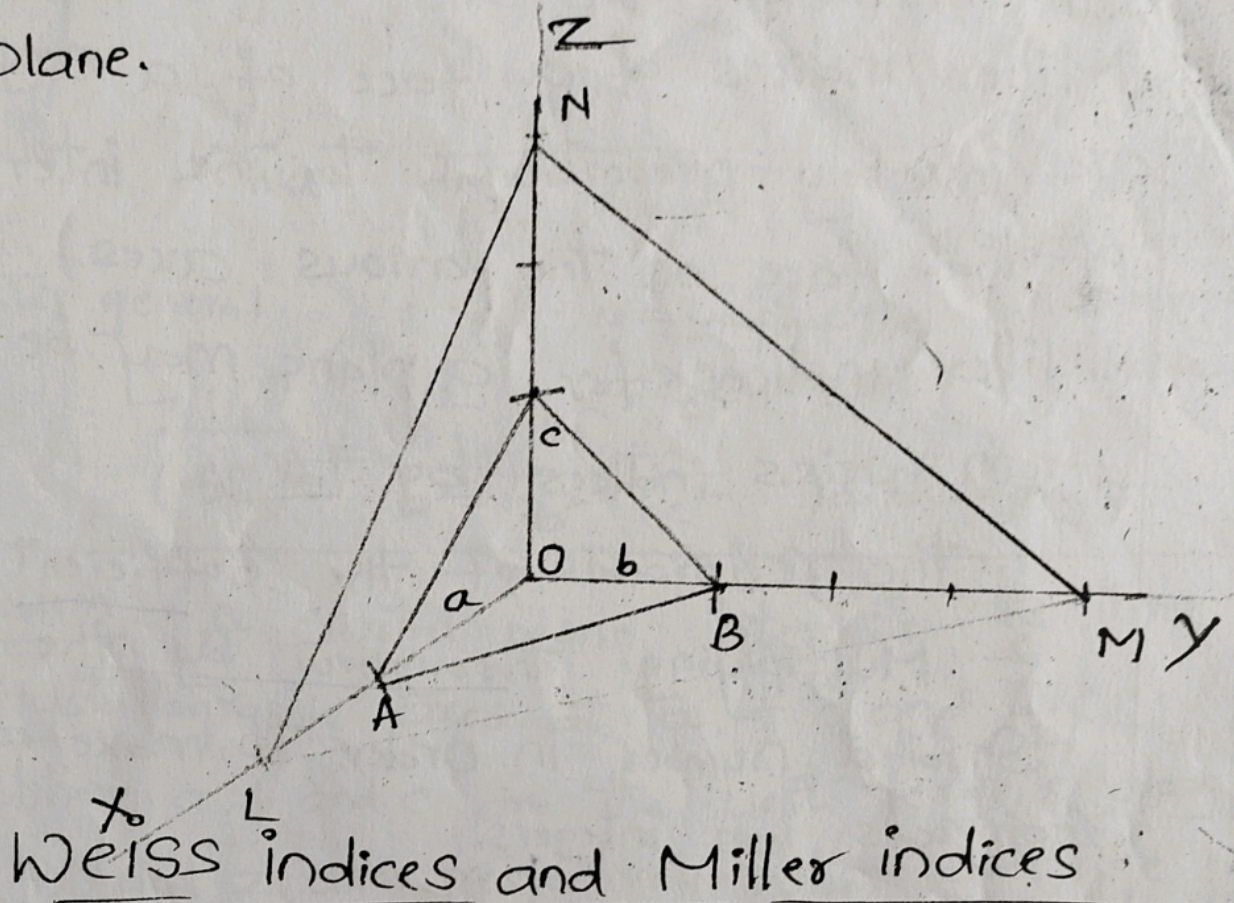
2. Law of Rational indices :- (Haüy's law)

* This law states that "The ratio between the intercepts on the axes for the different faces of a crystal can always be expressed by rational numbers."

* The intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercepts (or) some simple whole number multiple of them.

Let ox , oy and oz be the three crystallographic axes and ABC be the unit cell and LMN the plane of the crystal under study. The unit intercepts are 'a' for OA , 'b' for OB and 'c' for OC . For the plane (face) LMN , the intercepts will be $OL = 2a$, $OM = 4b$ and $ON = 3c$. Thus the intercepts for the plane are in the ratio of $2a : 4b : 3c$ where 2, 4 and 3 are

Simple integral whole numbers and are known as the Weiss indices of the plane.



Weiss indices and Miller indices

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 are known as "Weiss indices". It must be noted that it is not necessary that the Weiss indices are always simple integral whole number, they may be fractional number (or) even infinity. Hence these are replaced by "Miller indices" which are always simple integral whole numbers. These are

Represented by h, k and l corresponding to a, b , and c .

* Miller indices of a face of a crystal are inversely proportional to the intercept of that face on the various axes.

* Miller indices for a plane may be obtained from Weiss indices by taking

1. The reciprocals of the coefficient
2. Multiplying throughout by the smallest number in order to make all reciprocals as integers.

* Miller indices of a plane can be expressed as (hkl) where h, k and l are the reciprocals of the intercepts expressed in units of lattice distances. Thus

$$h = \frac{a}{\text{Intercept of the plane along } x\text{-axis}}$$

$$k = \frac{b}{\text{Intercept of the plane along } y\text{-axis}}$$

$$l = \frac{c}{\text{Intercept of the plane along } z\text{-axis}}$$

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The distance between ⁽⁸⁾ the parallel planes ⁽¹⁾ in a crystal are designated as d_{hkl} .

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

In general

a = length of the cube side

$\therefore d_{hkl}$ = interplanar spacing of diff cubes.

$$\frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad a, b, c = \text{lengths}$$

Problem: A crystal plane intercepts the three crystallographic axes at a , $\frac{1}{2}b$ and $\frac{3}{2}c$.

Where a , b and c are the unit lengths along x , y and z axes respectively. What are the Miller indices of this plane?

Sol: From the given data the

Weiss indices are $1, \frac{1}{2}, \frac{3}{2}$ i.e.

a	b	c
1	$\frac{1}{2}$	$\frac{3}{2}$

Taking reciprocals

$\frac{1}{1} \times 3$	$\frac{2}{\frac{1}{2}} \times 3$	$\frac{2}{\frac{3}{2}} \times 3 = \frac{6}{3} = 2$
------------------------	----------------------------------	--

Multiplying by 3

3	6	2
---	---	---

Thus the Miller indices of the plane are $3, 6, 2$ and hence the plane is designated as (362) plane.

3. The law of constancy of symmetry. (9)

(or)
Symmetry in crystals.

Symmetry is the important property of a crystal. The three important symmetries are

1. Plane of symmetry

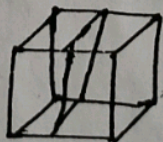
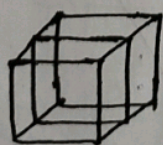
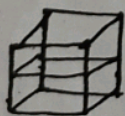
2. Axis of symmetry

3. Centre of symmetry

1. Plane of symmetry: It is an imaginary plane which can divide the crystal into two halves such that one is the mirror image of the other.

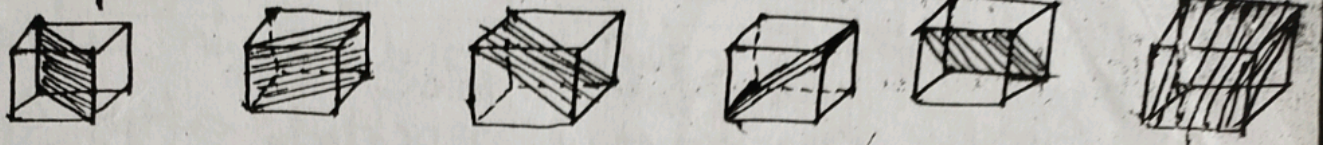
Ex. Cubic crystal has two types of plane of symmetry.

(i) Rectangular plane of symmetry: These are the planes situated midway and parallel to the opposite faces. It is having 3 rectangular planes of symmetry.



(ii) Diagonal planes of symmetry: These are the planes touching the opposite edges. As they lie on the diagonal of opposite faces. There are six diagonal planes of symmetry.

are possible in a cubic crystal. (10)



Thus in a cubic crystal, there are 3 rectangular planes of symmetry and 6 diagonal planes of symmetry i.e. $3+6=9$ planes of symmetry

② Axis of Symmetry: It is an imaginary line (or) axis about which the crystal may be rotated so that it presents the same appearance more than once in a complete rotation through 360° .

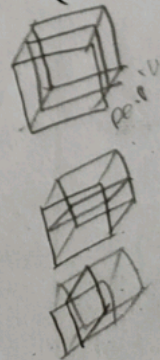
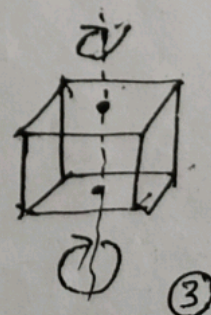
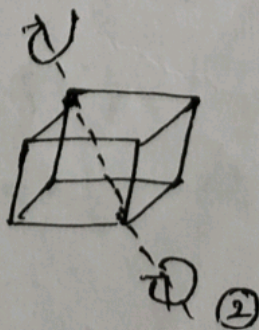
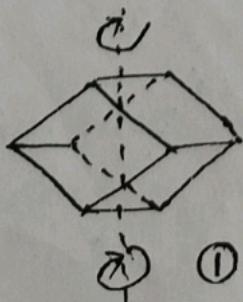
Ex: Cubic crystal it is of three types depending upon the number of times the identical appearance occurs during the complete rotation of 360° .

1. Two fold axis of symmetry: (Diad axis) When similar appearance repeated after 180° angle.

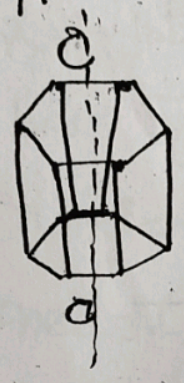
2. Three fold axis of symmetry: (Triad axis) When similar appearance repeated after 120° angle

3. Four fold axis of symmetry: (Tetrad axis)

When similar appearance repeated after 90° angle.

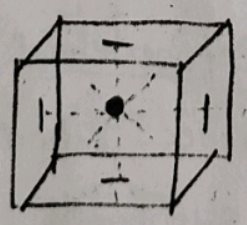


* Six fold axis of symmetry is possible in hexagonal crystals and not in cubic crystals. Similar appearance is repeated after 60° angle.



3. Centre of Symmetry: Centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distances on either side.

* A crystal may have one (or) more planes (or) axes of symmetry, but it never has more than one centre of symmetry which lies at the centre of the cube.



① Definitions of Lattice point. (12)

The points representing the atoms, molecules, (or) ions in a unit cell are known as lattice points. In the various unit cells there are three kinds of lattice points.

(a) Points located at the corners of unit cell

Since such point ~~contribute~~ lies at the corner of a unit cell, it is shared between 8 such unit cells. Thus only $\frac{1}{8}$ th part of each such point contributes to any one cell.

(b) Points located at the centre of a face of a unit cell :-

Since such point is shared between two such cells, only $\frac{1}{2}$ of each such point contributes to any cell.

(c) Points located at the centre of the unit cell.

This point being present entirely within a unit cell, thus the total no of lattice points (number of atoms) per unit cell in the four types of cells are as follows.

$$\text{Simple} \quad \text{---} \quad 8 \times \frac{1}{8} = 1$$

$$\text{Fcc} \quad \text{---} \quad 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Bcc} \quad \text{---} \quad 8 \times \frac{1}{8} + 1 = 2$$

$$\text{End face Centred} \quad \text{---} \quad 8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2$$

Unit cell

13

- * The smallest repeating pattern (unit) from which the lattice is built is known as a unit cell.
- * Unit cells are repeated over and over again in three dimensions and results in to the whole of the space lattice of the crystal.
- * There are different types of unit cells.

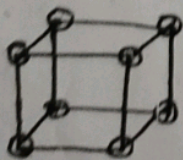
(a) Simple cubic unit cell ∴ (or) primitive.

In this type points i.e (atoms, ions / molecules) are present only at the corners of the unit cell.

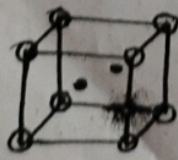
(b) Face centred unit cell ∴ In this type the points are present at the corners as well as ~~at~~ the centre of each of the six faces.

(c) Body centred ∴ points are present at the corners and an additional point is present at the centre of the unit cell.

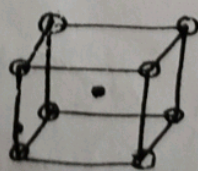
(d) End face centred ∴ points are present at the corners and at the centre of the two ends.



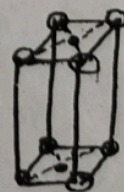
(a)



(b)



(c)



(d)

Space lattice

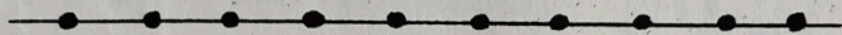
(14)

(1)

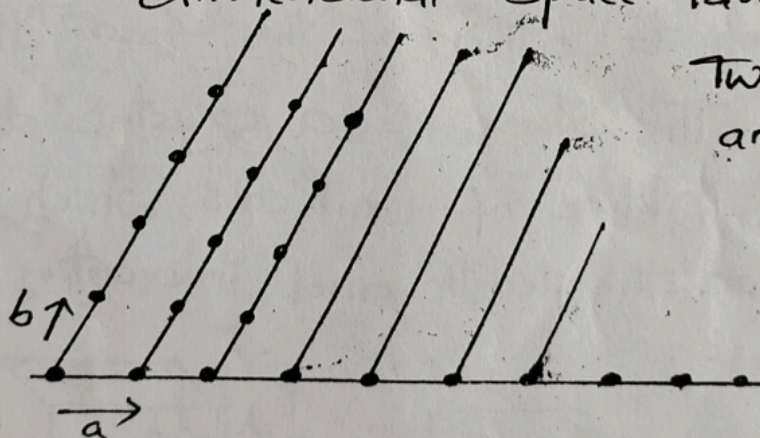
The regular arrangement of an infinite set of points (atoms, ions/molecules) in space is called a space lattice.

* The space lattice may be one dimensional, two dimensional and three dimensional depending upon the number of parameters required to define it.

(a) One dimensional space lattice
only one repeat distance (a)

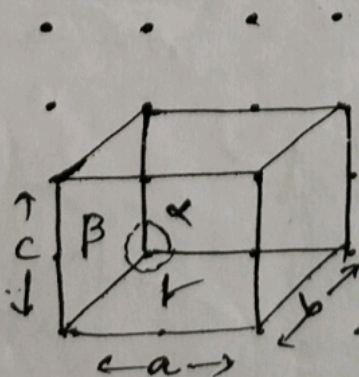


(b) Two dimensional space lattice



Two repeat distances
and an interfacial
angle (γ)

(c) Three dimensional space lattice



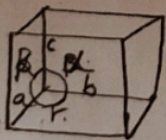
Three repeat distances
and three interfacial
angles.

15

* Space lattice with reference to crystal can be defined as an array of points showing the arrangement of constituents in the three dimensional space. = space lattice construction

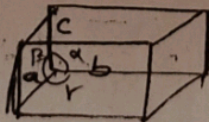
Bravais lattices and Types of Crystal systems

Bravais showed that the unit cells can be arranged in a regular three dimensional order in the seven types of crystal systems in 14 different ways. These arrangements are called Bravais lattices. The 14 Bravais lattices may belong to either of the four types of unit cells. The shape of a crystal depends upon the nature of unit cells, which inturn depends on the length and intercepting edges & angles.



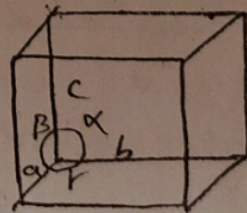
$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$



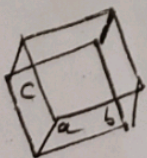
$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$



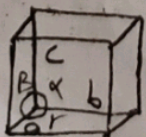
$$a \neq b \neq c$$

$$\alpha \neq \beta = \gamma = 90^\circ$$



$$a \neq b \neq c$$

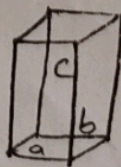
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



$$a \neq b \neq c$$

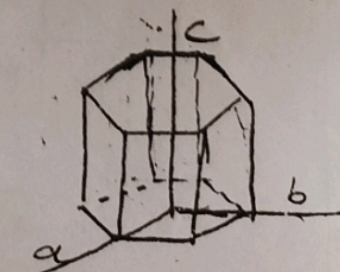
$$\alpha = \gamma = 90^\circ$$

$$\beta \neq 90^\circ$$



$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



$$a = b \neq c$$

$$\alpha = \beta = 120^\circ$$

$$\gamma = 90^\circ$$

Crystal System	Maximum Symmetry	axes length	Angles	Space lattices	Examples
1. Cubic	9 planes 13 axes 1 centre	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Simple Body centred Face centred	NaCl , KCl , ZnS , Cu_2O
2. Tetragonal	5 planes 5 axes	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Simple Body centred	SnO_2 , ZnO , TiO_2
3. ortho rhombic	3 planes 3 axes	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Simple Body centred Face & end face	KNO_3 , K_2SO_4 , BaSO_4 Rhombic sulphur
4. Trigonal (or) Rhombohedral	7 planes 7 axes	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Simple	NaN_3 , CaSO_4 , Quartz
5. Hexagonal	7 planes 7 axes	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	End face centred	ZnO , HgS , CdS
6. Monoclinic	1 plane 1 axes	$a \neq b \neq c$	$\alpha = \beta = \gamma \neq 90^\circ$ $\beta = 120^\circ$	Simple End face centred	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Monoclinic sulphur}$
7. Triclinic	No plane No axes	$a_1 = b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3

Defects in crystals

(17)

An ideal crystal of a crystalline solid is one which has same unit cell containing the same lattice points throughout the entire crystal.

- * At absolute zero, most of the ionic crystal consists of charged particles arranged in a regular fashion and so there will be no defect.
- * As the temperature rises there is a chance of displacement of ions and some of the lattice sites may remain unoccupied by the ions. i.e. vacant place is created in the crystal may leads to deviation (or) imperfections are called defects.

* The defects in crystals are of following types.

- * Stoichiometric defects

- * Non stoichiometric defects.

* Stoichiometric defects : Stoichiometric

Compounds are those in which the number of positive and negative ions are exactly in the same ratio indicated by their chemical formula

$$\frac{n^+}{n^-} \cong 1$$

* In stoichiometric compounds two types of defects are observed.

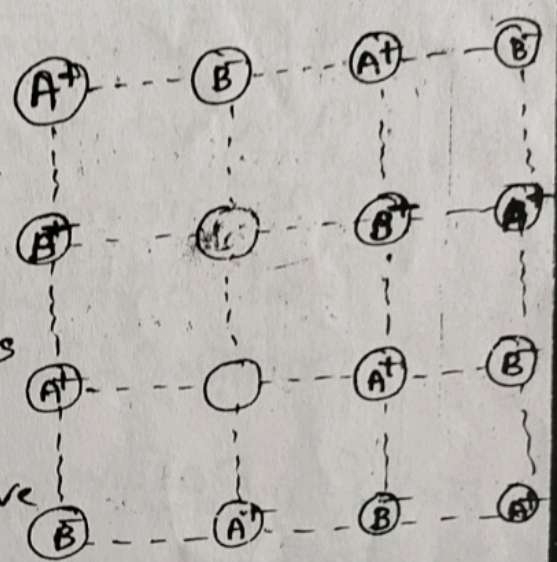
- (i) Schottky defect

- (ii) Frenkel defect

(i) Schottky defect: This type of defect arises due to a vacancy at a cation site which of course is accompanied by a vacancy at an anionic site to maintain the electrical neutrality of the system.

* This type of defect occurs in ionic compounds with

- (a) High coordination numbers and
- (b) where the positive & negative ions are of similar size.

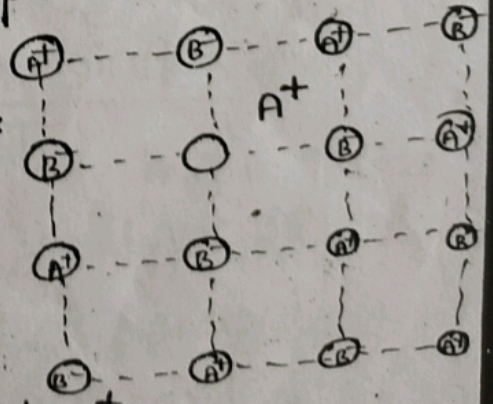


Ex: Alkali halides (NaCl and CsCl)

* The number of ions in lattice is lesser and so the density of the solid decreases.

(ii) Frenkel defect: This type of defect arises due to a vacancy at a cation site. Actually the cation moves to an interstitial position between lattice points.

* This defect occurs in compounds having low coordination number because in such compounds the attractive forces being less & are easy to move into the interstitial site.



(b) * ions are of different sizes.

(c) Compounds having highly polarising cation & easily polarisable anion.

Ex: AgBr, ZnS

19

* The number of these defects in crystal generally increases with the rise of temperature hence they are called Thermodynamic defects.

* Non-stoichiometric defects:

→ Non stoichiometric compounds are those in which the number of positive and negative ions are not in the ratio indicated by their ideal chemical formulae. e.g. in FeO ratio of positive and negative ions $0.94:1$. The balance of positive and negative charge is maintained either by having extra electrons (or) extra positive charges, which make the structure regular.

⇒ These are of two types.

1. Metal excess defects

2. Metal deficiency defects.

1. Metal excess defects: This type of defect may arise in two ways.

(a) Anion Vacancies:

This type of defect involves the removal of anion thereby causing an increase in the cation concentration. The electrons which originally associated with anions are trapped in the lattice and thus the system remains electrically neutral. The

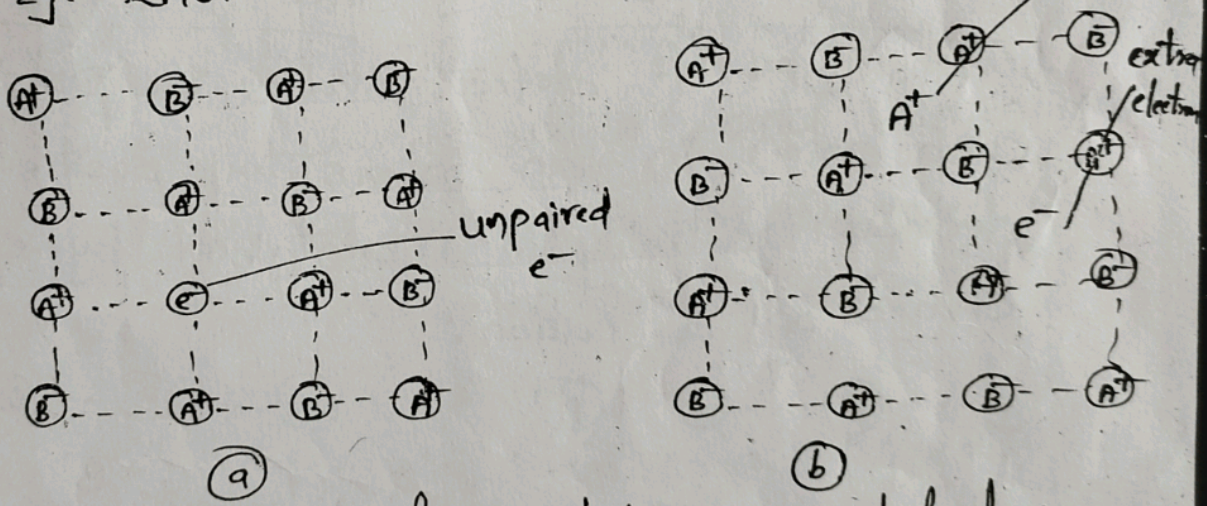
anion may leave the ⁽²⁰⁾ surface in the form of gas.

* This defect is found in crystals which are found to have Schottky defects. ex: NaCl

(b) extra cation occupying the interstitial sites.

This type of defect involves the presence of an extra positive ion in an interstitial position. electrical neutrality is maintained by an electron which is also present in an interstitial position.

→ This type of defect is like Frenkel defect
Eg. ZnO.



Consequences of Metal excess defects:

(i) Crystals having either of the metal excess defects have free electrons and if these migrate they conduct an electric current. amount of current is very small and hence these materials are called semiconductors.

2. Metal deficiency defects :

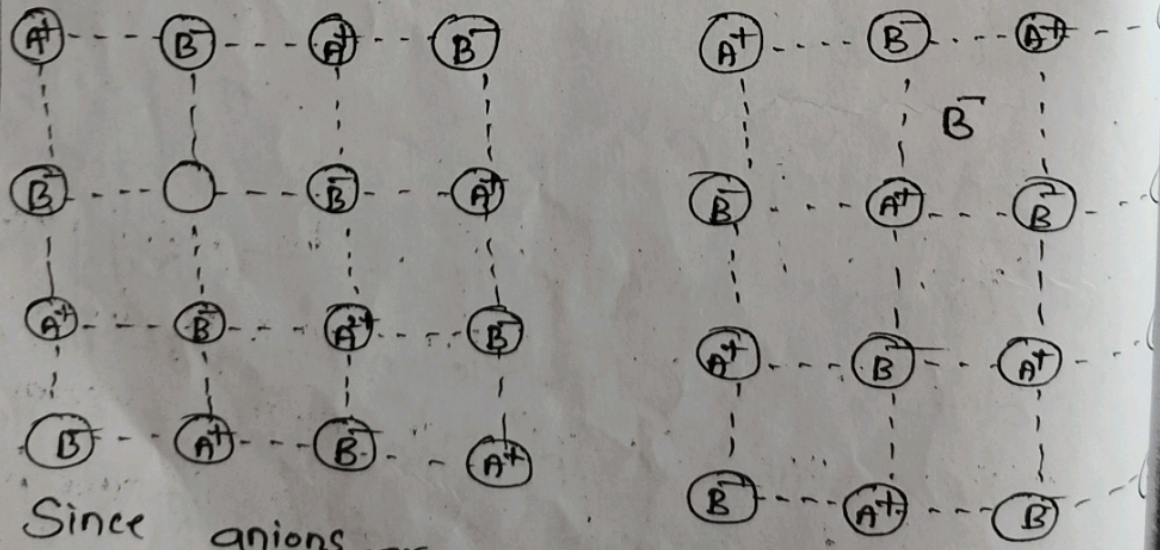
These defects also arise in two ways.

(a) Cation Vacancies : In this type, a positive ion is missing from its lattice sites and the charge is balanced by the oxidation of some cations to higher valency state and not by gain of positive ions. Thus the lattice remains deficient of metal atoms.

Ex: FeO, FeS, NiO - - - -

(b) Extra anions occupying the interstitial sites

This type of defect involves the presence of extra anion in an interstitial position. The electrical neutrality is maintained by extra charge on a cation.



⇒ Since anions are usually large in size, it is impossible to fit into the interstitial sites. Hence no example of crystals possessing this defect known at present

X-ray diffraction⁽²²⁾ and crystal structure⁽¹⁾

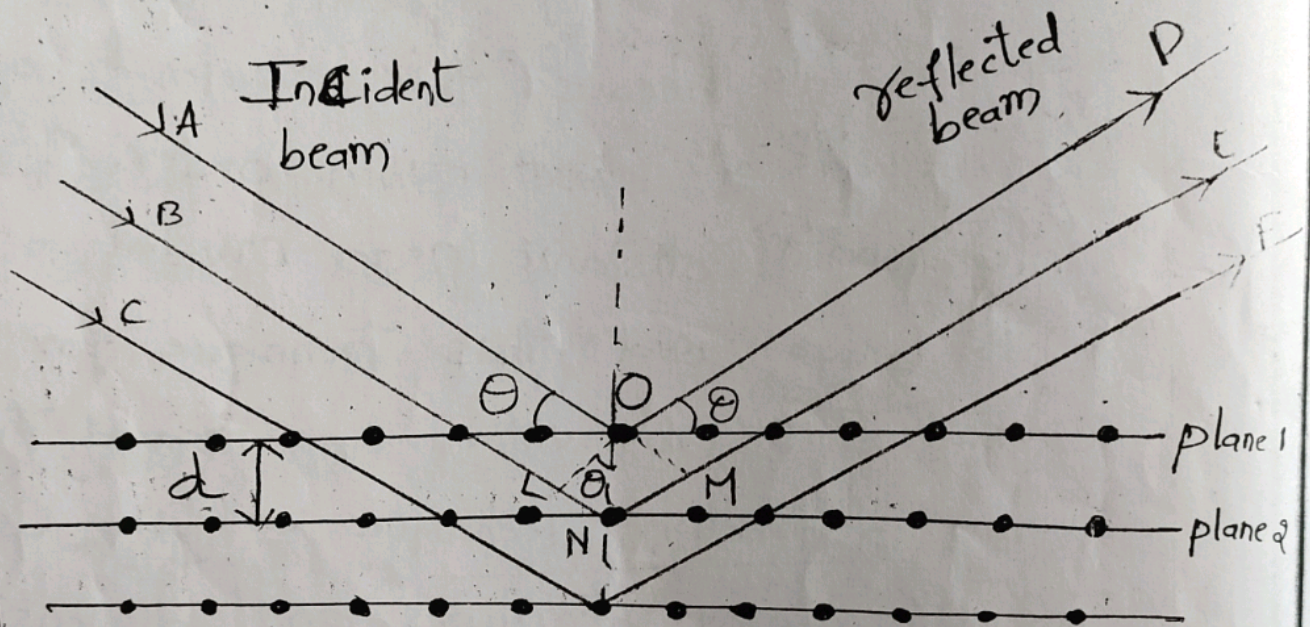
Bragg's law

X-ray Diffraction :

- ⇒ The German physicist "Laue" in 1913 suggested the possibility of diffraction of α -rays by crystals. because the wavelength of α -ray was of about same order as the interatomic distance in a crystal.
- ⇒ W.H. Bragg used this technique for NaCl crystal. This observation has proved that α -ray diffraction technique is highly useful in determining structures and dimensions of crystals as well as in the study of a no. of properties of α -ray themselves.
- ⇒ The Bragg equation :
 - ⇒ According to Bragg a crystal could be employed not only as a transmission grating but also as a reflection grating.
 - ⇒ X rays are incident on a crystal face these penetrate into the crystal & strike the atoms in successive planes. From each of these planes the α -rays are reflected like the reflection of a beam of light from a bundle of glass plates of equal thickness.

(25)

⇒ Based on this model, Bragg derived a simple relation between wave length of x-ray, the interplanar distance b/w the planes and the angle of reflection is known as Bragg's equation (or) Bragg's law.



- Consider figure the reflection of monochromatic x-rays striking the parallel equidistant planes.
- The distance b/w parallel plane in the crystal structure = d
- Suppose a beam of x-rays falls on the crystal at grating angle θ and reflected from the upper plane at the same angle θ . While others will be absorbed and get reflected from the successive layers.

⇒ The waves ⁽²⁴⁾ reflected by different layers planes will be in phase with one another only when the difference in path length is an integral number of wavelength.

$$\text{path difference} = n\lambda$$

Where $n = 1, 2, 3, 4, \dots$

→ To determine the path difference of x-ray AOD and BNE. draw perpendiculars OL and OM to the incident and reflected beams.

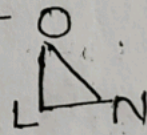
→ The path difference is equal to

$$\text{path difference} = LN + NM$$

$$\therefore n\lambda = LN + NM$$

In $\triangle OLN$

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



In $\triangle OMN$

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

Since $ON = d$

then $\sin\theta = \frac{LN}{d}$ (or) $d \sin\theta = LN$ and $\sin\theta = \frac{NM}{d}$

$$\text{(or)} \quad d \sin\theta = NM$$

therefore path difference $LN + NM = 2d \sin\theta$

$$\text{(or)} \quad n\lambda = 2d \sin\theta \quad \therefore \text{path difference} = n\lambda$$

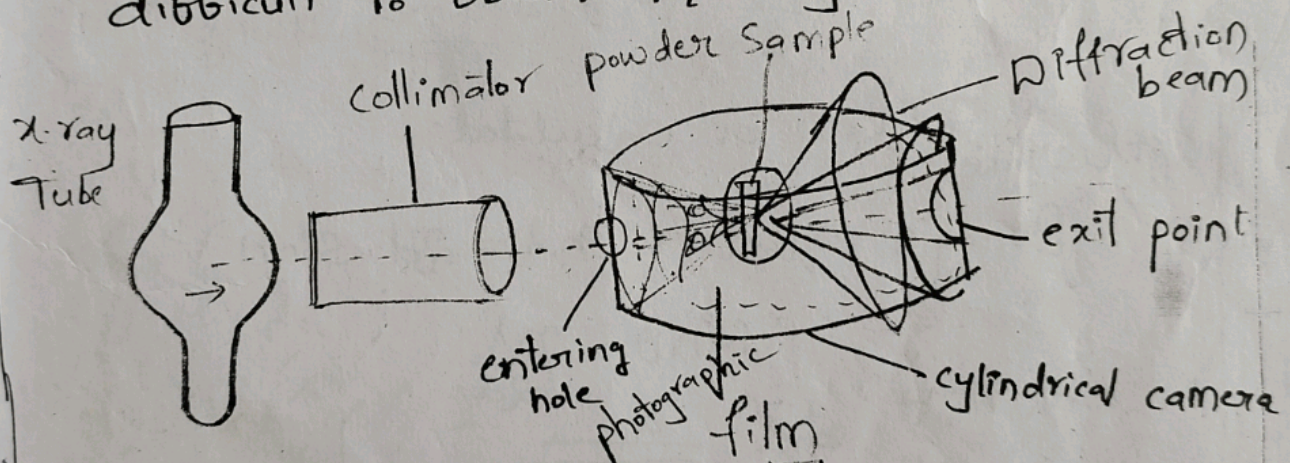
This is called Bragg equation. Knowing θ, n and λ, d can be calculated.

Powder crystal Method

(or) Debye - Scherrer method

- * We can determine an unknown crystal's shape and size by measurements of the directions of diffracted beams
- * Diffraction occurs whenever Bragg's law is satisfied.
- * In powder method as little as 1mg of the material is sufficient for the study.
- * The powder method was devised independently by Debye and Scherrer in Germany and Hull in America at about the same time.
- * Very fine powder is placed in a beam of monochromatic X-ray for the investigation of a crystal.
- * Each ~~crystal~~ powder is acting as a crystal
- * Oriented at random direction with the incident beam.
- * Some crystals are oriented in (100) planes
- * Some are oriented in (110) planes
- * The result is that every set of lattice planes capable of reflection.

- * Consider one (hkl) plane ⁽²⁶⁾. One/More crystals by chance, so oriented that their hkl planes make the correct bragg's angle for reflection.
- * Rotation does not occur in powder Method
- * If the ~~presence of~~ powder is used instead of a single crystal.
- * Here a monochromatic x-ray beam is incident on a powder (or) polycrystalline sample.
- * This method is useful for samples that are difficult to obtain in single crystal form.



Diffraction pattern on exit hole film after exposure.

- * It consists of a cylindrical camera
- * powder sample is loaded in a glass tube & placed vertically at the centre.
- * x-ray tube produces a monochromatic x-rays.
- * A photographic film strip placed along cylindrical camera in which will be exposed by the

Scattered radiation.

- * After sufficient time, a film can be developed. This film displays the diffraction pattern.
- * The unscattered radiation leaves the camera through exit hole.

θ = Incident angle. 2θ = Reflected / Diffraction angle

r = Radius of the film. Circumference = $2\pi r$
Corresponds to scattering angle - 360°

$$l = 2\pi r \times \frac{\theta}{360^\circ} \quad l = \text{length of the arc of circle}$$

$$l = 2\pi r \times \frac{2\theta}{360} \quad \text{or } \theta = \frac{360 \times l}{4\pi r} \quad \text{using this}$$

Let us take θ can be calculated.

Bragg's equation $n\lambda = 2d \sin\theta$

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

We know that

$$d = \frac{a}{h^2 + k^2 + l^2}$$

$$\sin\theta = \frac{n\lambda}{2a} (\sqrt{h^2 + k^2 + l^2})$$

Taking Square on both sides

$$\sin^2\theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

$$\frac{n^2 \lambda^2}{4a^2} = \text{constant}$$

$$\sin^2\theta \propto (h^2 + k^2 + l^2)$$

by using $h^2 + k^2 + l^2$ values we can predict the pattern of the plane present inside the cubic crystal.

~~$h^2 + k^2 + l^2 = 1$
 $h^2 + k^2 + l^2 = 2$
 $h^2 + k^2 + l^2 = 3$
 $h^2 + k^2 + l^2 = 4$
 $h^2 + k^2 + l^2 = 5$
 $h^2 + k^2 + l^2 = 6$
 $h^2 + k^2 + l^2 = 7$
 $h^2 + k^2 + l^2 = 8$
 $h^2 + k^2 + l^2 = 9$
 $h^2 + k^2 + l^2 = 10$
 $h^2 + k^2 + l^2 = 11$
 $h^2 + k^2 + l^2 = 12$
 $h^2 + k^2 + l^2 = 13$
 $h^2 + k^2 + l^2 = 14$
 $h^2 + k^2 + l^2 = 15$
 $h^2 + k^2 + l^2 = 16$
 $h^2 + k^2 + l^2 = 17$
 $h^2 + k^2 + l^2 = 18$
 $h^2 + k^2 + l^2 = 19$
 $h^2 + k^2 + l^2 = 20$~~