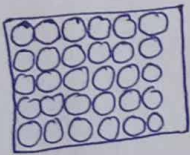# UNIT – III
CRYSTAL STRUCTURE

The universe is made up of radiation and matter. Matter exists in mainly three states – solids, liquids and gases. All these states are composed of atoms, molecules and ions.

Crystal Physics or Crystallography – branch of Physics deals with the study of all possible types of crystals and their physical properties.
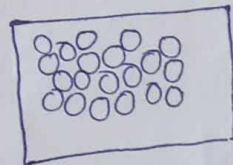
The solids are classified into two categories. { Crystallin / Amorphou

Crystalline	Amorphous
• Atoms are arranged in regular periodic pattern.	• Atoms are not arranged in regular, periodic manner.
• Long order in arrangement of particle (upto 10^7 atoms or more)	• Short order in arrangement of particles
• They are anisotropic substances	• They are Isotropic substances (Thermal conductivity, electrical conductivity, refractive index ete all are sem in all directions)

- Crystal has a sharp M.P.

- They possess regular shape.

- Ex. Cu, Silver, Carbon. Can sugar etc.

- They have no. sharp M
  (The bonds b/w atoms are not equally strong. so when heated weakest bonds are ruptured first at low tempr and stronger ones at high tempr.

- They do not possess regular shapes

- Ex. Glass, rubber, plastic etc.

Solids :- basic Concept → Definite shape
→ Definite volume
→ strong Intermolecular force.

→ If a solid possesses regular arrangement of atoms but not periodicity then it cannot be a crystal.

Lattice :— The periodic arrangement of atoms in a crystal is called a lattice - that looks a net - like structure.

Two dimensional array of points is shown in figure, and is called plane lattice. O is as origin and two axes OA & OB then we can see the points along OA are separated by interval 'a' while those along OB by an interval 'b'. If we extend the array of points to form a 3-D crystal structure, then the array of atoms points is called **Space lattice or crystal lattice**.
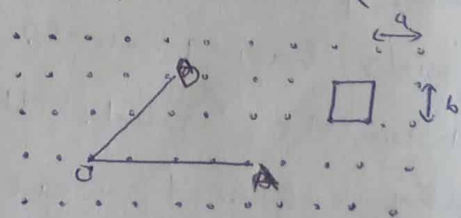
Translation Vectors:— The position vector of any other lattice points is defined as

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

where n_1 & n_2 are integers representing the no. of lattice points along OA and OB and $\vec{a}$ & $\vec{b}$ are the integrals

along OA & OB and are called **primitives vectors or unit** ②

vectors.

for 3-D arrangements

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

<u>Unit Cell</u> :— and a primitive cell from fig. it is clear
that if we consider a parallelopiped
in a 3-D lattice with its sides
represented by the vector $\vec{a}, \vec{b}$ & $\vec{c}$.
This parallelopiped is called a
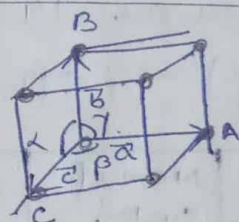unit cell. Thus <u>unit cell is that</u>
<u>smallest geometrical shape by the</u>
<u>repetition of which complete crystal structure can be represented</u>

The volume of a unit cell is represented
by $(\vec{a} \times \vec{b}) \cdot \vec{c}$. { A primitive cell is a type of unit-
at the corners only cell which contains lattice points
and is a minimum volume unit-
cell. A unit cell
is also primitive cell

<u>Crystal Structure</u> & <u>Basis</u> :—

A <u>lattice</u> represents the geometrical arrangement of points in
space. But in crystal, there is geometrical arrangement of atoms
or molecules. Hence to represent the crystal structure with the
help of lattice, each point is assumed to be associated with
an atom or molecule. The atom or the molecule associated
with a lattice point is called the basis. Each basis is identical
in composition, arrangement and orientation. In a crystal
of element (aluminium, barium), an atom of that element is
situated at each point of the lattice. But in a crystal of
compound (Nacl, Gcl) a molecule or the atoms of component
elements of compound is situated at each point of the
lattice. Crystal structure is represented by the regular
and periodic arrangement of basis of atoms in all directions

Thus   lattice + basis   =   crystal structure

Lattice   +   (Basis =   Crystal structure.
                containing two
                ions)

Types of Crystals :-   All crystals are classified into
seven systems on the basis of the shape of the unit
cells. These are described in terms of the lengths of unit
cells and the angle include between them.

Bravais Space Lattice:-   Bravais in 1948 explained that
there are 14 different types of lattices under 7 crystal
systems. These are frequently called Bravais 'lattices'.

S. No.	Name of System	Primitive	angles	No. of Possible lattice	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	3 (P, I, F)	NaCl.
2.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$	2 (P, C)	Na_2SO_4 or $FeSO_4$
3.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	1 (P)	$CuSO_4$
4.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	2 (P, I)	$NiSO_4$, SnO_2
5.	Orthorhom -bic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	4 (P, C, I, F)	KNO_3, $BaSO_4$
6.	Rhombohe -dral (or Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	1 (P)	$CaSO_4$
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	1 (P)	Quartz SiO_2, Zn. or Cd etc.

Total: 14

P = Primitive   I = Body centred
C = Base Centred   f = face centred

On this basis (Bravais lattice), following four types of ③ lattices are possible:

(I) **Simple or primitive lattice:**- The lattice in which centres are only at the corners of unit cell. (P)

(II) **Base centered lattice:**- The lattice in which in addition to the centres at the corners of unit cell, there is one centre at its base. (C)

(III) **Body Centered lattice:**- The lattice in which in addition to the corners of unit cell, there is one centre at the centre of the unit cell also. (I)

(IV) **face centered lattice:**- The lattice in which in addition to the centres at the corners of unit cell, there is one centre at the centre of each of the face of the unit cell. (F)
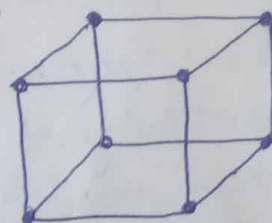
Cubic lattics:- $a = b = c$ & $\alpha = \beta = \gamma = 90°$

$$\therefore \text{Volume} = a^3.$$

following three types of lattices are possible.

1. **Simple or Primitive:**- One lattice point- on each corner of unit cell, also called simple cubic cell (SCC). Ex. - CsCl (cesium chloride)
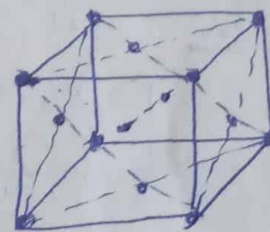
 (S.C.C)

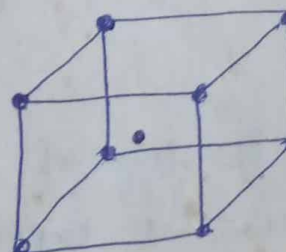2. **face Centered:**- One lattice at each corners of cell and one centre (or lattice point) at the centre of each (six) faces of unit cell.
(f.c.c)   Ex. - NaCl.

 (f.c.c)

3. **Body Centered:**- One centre at each corners and one centre at the centre of unit cell. (B.C.C). Ex. - α-iron.

 (B.C.C)

Number of Lattice Points or Atoms Per unit cell in

Cubic Lattice :—

(i) Simple Cubic lattice :- In case of simple cubic lattice each corner atom is shared by 8 unit cell. Thus a corner atom share $1/8^{th}$ of an atom. As there are 8 corners atoms in all, each cube has

$$8 \times \frac{1}{8} = 1 \text{ atom}$$

(II) Body centered Cubic lattice :- There are 8 corner atoms and one centre atom. So, no of atoms which belong to this cube are —

(1) One centre atom

(ii) $8 \times \frac{1}{8} = 1$ corner atoms

$$\therefore = 1+1 = 2 \text{ atoms}$$

(III) face centered Cubic lattice :- The are 8 corner atoms (shared by two joining cubes) and 6 face centered atoms, so no of atoms which belong to this cube are —
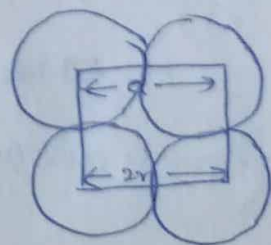
$$6 \times \frac{1}{2} = 3$$

$$8 \times \frac{1}{8} = 1$$

$$1 + 3 = 4 \text{ atoms}$$

Atomic Radius :- The distance between the centers of two neighbouring atoms is called nearest neighbour distance. for a closely packed crystal, this distance would be $2r$ for an atom of radius r. This distance r is called atomic radius which can be represented in terms of edge of cube a for certain unit cell structures.

(1) Simple Cube :- $a = 2r$

$$\Rightarrow \boxed{r = \frac{a}{2}}$$

(II) **Body Centered**

$$PQ = r + 2r + r = 4r.$$

$$PR = RS = a$$

$$\Rightarrow PS = a\sqrt{2}$$

$$\therefore PQ = \sqrt{(PS)^2 + (SQ)^2}$$
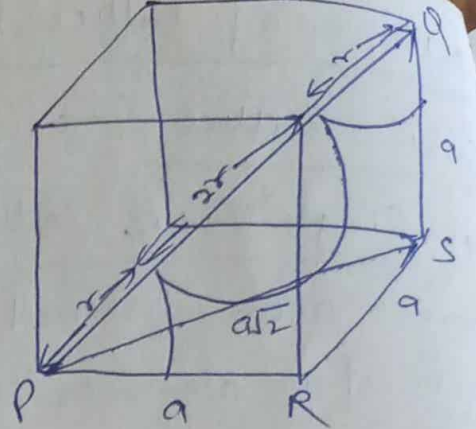
$$(4r)^2 = \sqrt{(\sqrt{2}a)^2 + a^2}$$

$$(4r)^2 = 2a^2 + a^2 \qquad \Rightarrow 16r^2 = 3a^2$$

$$(4r)^2 = 3a^2 \qquad \qquad r = \frac{\sqrt{3}a}{4}$$

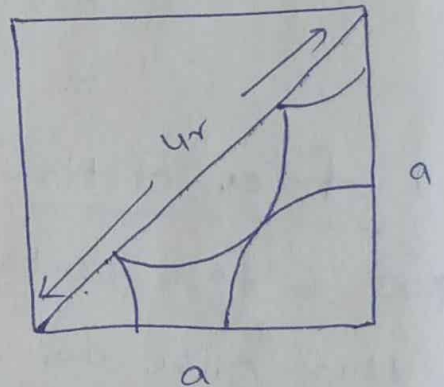$$\Rightarrow \boxed{r = \frac{a\sqrt{3}}{4}}$$

(III) **face Centered :-**

$$(4r)^2 = a^2 + a^2$$

$$4r^2 = 2a^2$$

$$\boxed{r = \frac{\sqrt{2}\,a}{4}} \quad or \quad \frac{a}{2\sqrt{2}}$$

Calculation of Lattice Constant :- Let 'a' be the side

of unit cell of a cubical lattice. (ie a is the lattice const)

$$\therefore \text{volume of unit cell } V = a^3$$

If ρ be the density of material of crystal, then

mass of unit cell $= a^3 \rho$ ——(1)

Let 'n' be the no. of lattice points per unit cell, M
be the molecular weight of the crystal and N be the
Avogadro's number, then mass of each molecule $m = \frac{M}{N}$.

Mass of each unit cell $= n \times m = n \frac{M}{N}$ ——(11)

from (1) & (11) $\qquad a^3 \rho = \frac{nM}{N}$

$$a^3 = \frac{nM}{\rho N}$$

$$a = \left\{ \frac{nM}{N\rho} \right\}^{1/3}$$

⑤

for S.C.C, $\quad n=1 \qquad a = \left\{ \frac{M}{N\rho} \right\}^{1/3}$

for f.C.C. $\quad n=4. \qquad a = \left\{ \frac{4M}{N\rho} \right\}^{1/3}$

for b.C.C. $\quad n=2 \qquad a = \left\{ \frac{2M}{N\rho} \right\}^{1/3}.$

Packing fraction of Relative Density of Packing :— (f)

The ratio of total volume of atoms (or molecules) in a unit cell of a crystal to the volume of unit cell is called its packing fraction ie

$$\text{packing density} = \frac{\text{Total volume of atoms in a unit cell}}{\text{Volume of one unit cell}}$$

1. Simple Cubic Lattice :- The no. of atom in unit cell = 1 = n

atomic radius → $r = a/2$

volume of atom occupying the unit cell $= 1 \times \frac{4}{3} \pi r^3$

$$= \frac{4}{3} \pi \left(\frac{a}{2} \right)^3$$

volume of unit cell $= a^3$

$$\therefore \quad f = \frac{\frac{4}{3} \pi \left(\frac{a}{2} \right)^3}{a^3} = \frac{\pi}{6} = 0.52$$

$$\boxed{f = 52\%}$$

2. Body centered Cubic Lattice :- $n = 2$

atomic radius $= \frac{a\sqrt{3}}{4}$

volume of unit cell $V = a$

Volume of atoms occupying the unit cell $= 2 \times \frac{4}{3} \pi r^3$

$$= 2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a \right)^3$$

Volume of unit cell $= a^3$

∴ atomic packing fraction

$$f = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a \right)^3}{a^3}$$

$$= \frac{\sqrt{3}}{8} \pi = 0.68 = 68\%$$

(III) <u>face centered cubic crystals</u> :–

The no. of atoms per unit cell $= 4$

atomic radius $= \frac{\sqrt{2}}{4} a$.

Volume of atoms occupying the unit cell $= 4 \times \frac{4}{3} \pi r^3$

$$= 4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}}{4} a \right)^3$$
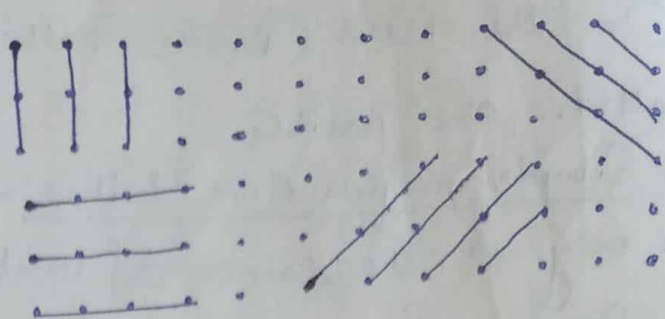
volume of unit cell $= a^3$

∴ packing fraction $= \dfrac{4 \times \frac{4}{3} \pi \times \frac{2\sqrt{2}}{4 \times 4 \times 4} a^3}{a^3}$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

$$= 74\%.$$

Lattice Planes:-

A crystal lattice is made
of a large number of
parallel equidistant planes.
Known as lattice planes
and can be chosen in a number of ways, as shown in
figure.

Miller Indices:-

In a crystal, to express the incli

-nation of lattice plane w.r.t three directions, Miller
gave a method according to which a crystal plane is
represented by the three numbers h, k, l. These numbers
are called Miller Indices. Miller indices are the
smallest integers whose ratio is equal to the reciprocal
of the intercepts on the X, Y, Z axes by the plane.

→ first find the lengths of intercepts on the crystal axes
X, Y, Z, let- $l_1 = pa$, $l_2 = qb$, $l_3 = rc$

→ find reciprocal $\left(ie \frac{1}{p}, \frac{1}{q}, \frac{1}{r}\right)$

→ Take L.C.M of denominator of these reciprocals and
multiply it with each reciprocal to make it a full integer.
These no. h, k, l are called miller indices.

$$h : k : l = p^{-1} : q^{-1} : r^{-1}$$

Ex. Let intercepts are $3a, 4b$ & $5c$ on x, y & z axis

$p = 3, q = 4, r = 5$

$\frac{1}{3}, \frac{1}{4}, \frac{1}{5}$

$\therefore L.C.M = 60$

$h : k : l = p^{-1}, q^{-1} : r^{-1} = \frac{60}{3} : \frac{60}{4} : \frac{60}{5}$

$= (20 : 15 : 12)$ Ans.

If length of intercept by a plane on a crystal axis is -ve.
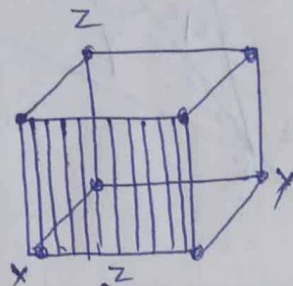then it expressed by putting a bar (−) on that number.
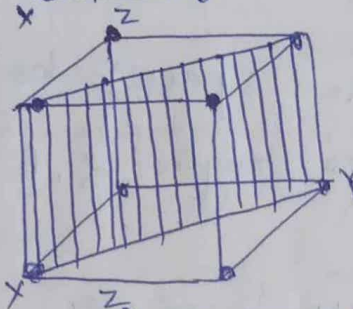
Properties of Cubic Lattices

Property	s.c.c.	f.c.c.	b.c.c.
1. No. of atoms per unit cell	1	4	2
2. Coordination number	6	12	8
3. Volume of unit cell	a^3	a^3	a^3
4. Atomic radii (r)	$a/2$	$a/a\sqrt{2}$	$a\sqrt{3}/4$
5. Packing density	$\pi/6$ 52%	$\pi/3\sqrt{2}$ 68%	$\pi\sqrt{3}/8$ 74%
6. Lattice constant	$(M/NP)^{1/3}$	$(4M/NP)^{1/3}$	$(2M/NP)^{1/3}$

Miller Indices :-

1. $(1,0,0)$

2. (110)

$d_{,\infty,\infty}$
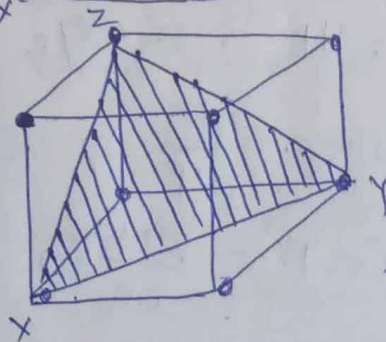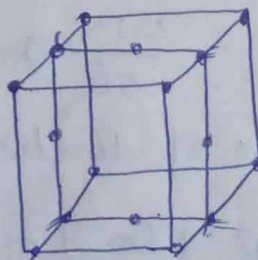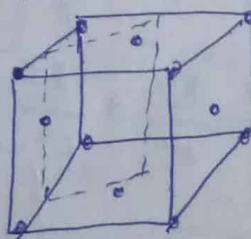
Principal crystal planes of s.c.c.

3. (111)

4. (200)

crystal planes of fcc crystal.

5. (220)

Interplaner Spacing :- or Lattice Interval

Let us consider a set planes (h, k, l) in a unit cell. This plane PQR makes intercepts a/h, b/k, c/l on the three cortesian - coordinate axes P, Q and R respectively.

Consider O as the original - a lattice point passing through the origin. Draw a perpendicular ON from O (origin) to the plane.

$ON = d$, is the distance between adjacent planes or interplanar spacing between parallel planes.

Normal ON makes angles α, β & γ with x, y & z axes respectively.

$$OP = a/h, \quad OQ = b/k, \quad OR = c/l$$

$\therefore \triangle ONP, \quad Cos\,\alpha = \dfrac{ON}{OP} \Rightarrow Cos\,\alpha = \dfrac{dh}{a} \quad (III)$

$\triangle ONQ, \quad Cos\,\beta = \dfrac{ON}{OQ} \Rightarrow Cos\,\beta = \dfrac{d}{b/k} = \dfrac{dk}{b}$

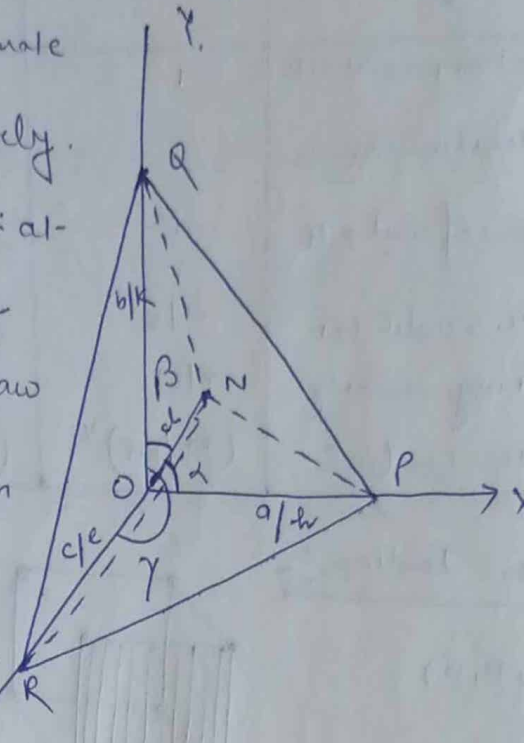$\triangle ONR, \quad Cos\,\gamma = \dfrac{ON}{OR} \Rightarrow Cos\,\gamma = \dfrac{d}{c/l} = \dfrac{dl}{c}$

according to the law of direction cosines.

$$Cos^2\alpha + Cos^2\beta + Cos^2\gamma = 1$$

$$d^2\left[\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}\right] = 1$$

$$d = \dfrac{1}{\left[\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}\right]^{1/2}}$$

for cubic crystal $a = b = c$

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

for tetragonal crystal $a = b \neq c$

$$d = \left[\frac{h^2 + K^2}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$$

$$d_{100} = a \quad, \quad d_{110} = \frac{a}{\sqrt{2}} \quad, \quad d_{111} = \frac{a}{\sqrt{3}}$$

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

Crystal Structure & analysis:-

BRAGG's Law:-

We know that the x-rays can penetrate solids. Since the wavelength of the x-rays ($\sim 1 A^\circ$) is of the order of interplaner spacing, these rays get strongly diffracted from different crystal planes. By analysis the different x-rays, we can gather information about the internal atomic arrangement of a crystal

Let us consider a set of parallel lattice planes of a crystal having spacing between them is equal to d. Let a narrow beam of x-rays of wavelength λ be incident on the planes at glancing angle θ. The reflected beam
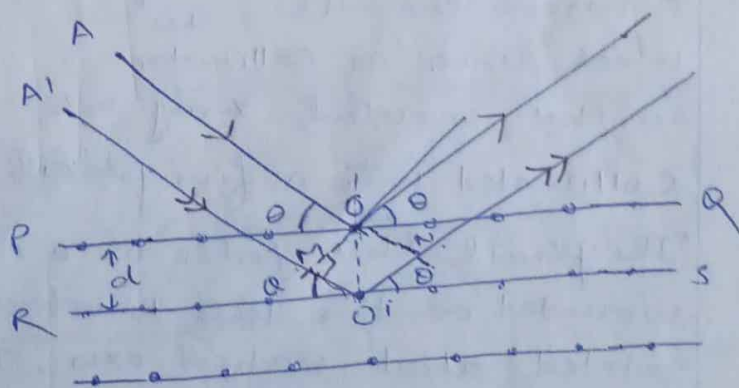
will leave at an angle θ to the plane. Consider the rays reflected at two consecutive planes PQ and RS. Thus the rays AO & A'O' are reflected at O & O' respectively.

If OM & ON are perpendiculars drawn from O on O'A' and O'B', then path difference between the beam reflected at two consecutive planes will be

$$MO' + O'N = d \sin\theta + d \sin\theta = 2d \sin\theta$$

If this path difference is an integral multiple of the wavelength λ, the reflected beams will interfere constructively giving maximum intensity. Thus strong reflection will be observed in the direction which corresponds to a path difference $\lambda, 2\lambda, 3\lambda \ldots$ between the rays reflected at consecutive planes.

i.e

$$\boxed{2d \sin\theta = m\lambda}$$

where 'm' is an integer. This result is the Bragg's equation. It is useful in calculating the distance d between crystal lattice planes once we know the wavelength λ and measure the angle of diffraction θ.

Bragg's Spectrometer :—

The Schematic arrangement of Bragg's spectrometer is shown in figure. X-ray beam from an X-ray tube is made to pass through o narrow channels S, which serves as Collimator so that incident x-ray are collimated into a fine pencil.

The pencil then falls on a crystal C (Nacl) mounted on turn table T which can be rotated about vertical axis. The position of turn table can be read on a scale (figure - 1) V_1. The reflected x-rays after passing

$\lceil$ points w.r.t on consor ...

X-Ray from
X-ray
tube.

S₁

V_1

c

T

V_2

S₂

G

I
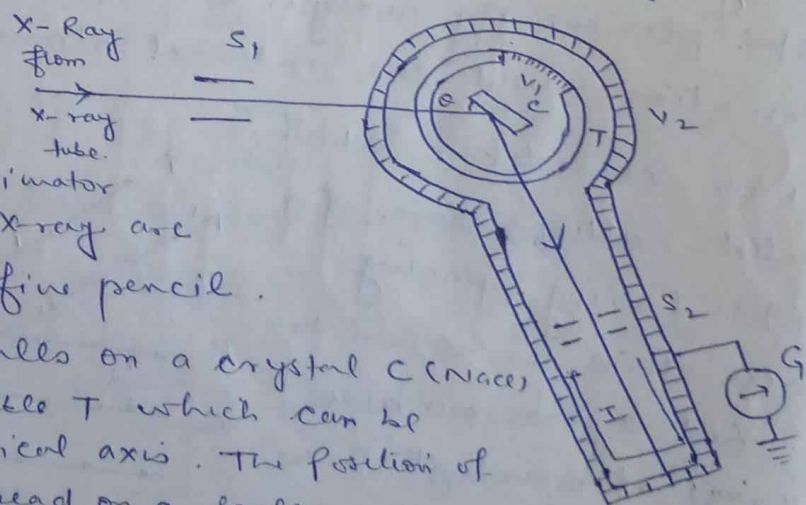
through the slit S_2 enters the ionisation chamber I. (It is simply a container for a gas or vapour with two electrodes) which is mounted on a special movable arm about the same axis of the crystal. The position of ionisation chamber can be read by a second vernier V_2. The X-rays entering the chamber ionise the gas causing a current to flow between the two electrodes which can measured by galvanometer G.

for each small rotation of the crystal the ionisation chamber is rotated twice the rate of. of the crystal to receive the reflected beam.

It is observed that as the glancing angle θ is varied, the ionisation in chamber is also varies. The curve between glancing angle θ and ionisation current is plotted.
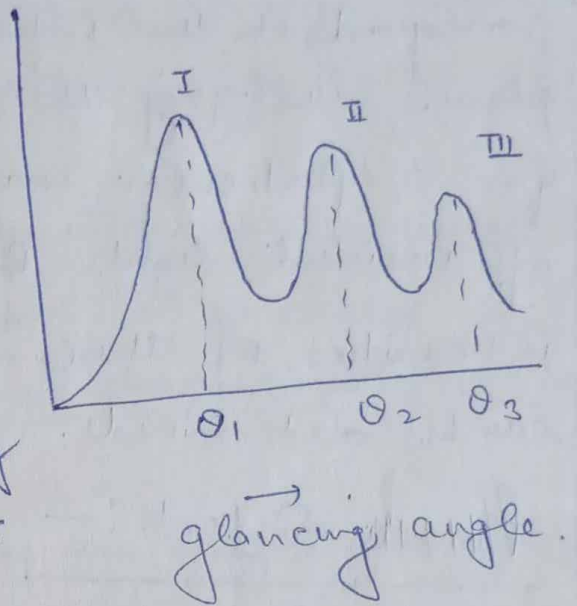
By observing the values of θ at varies orders n, θ λ/d can be determined using formula

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

d - spacing of the crystal planes, d, is known the wavelength of x-rays can be calculated.

Laue Method :-

This method is used for determination of crystal structure and the details of electron charge distribution within the solid.
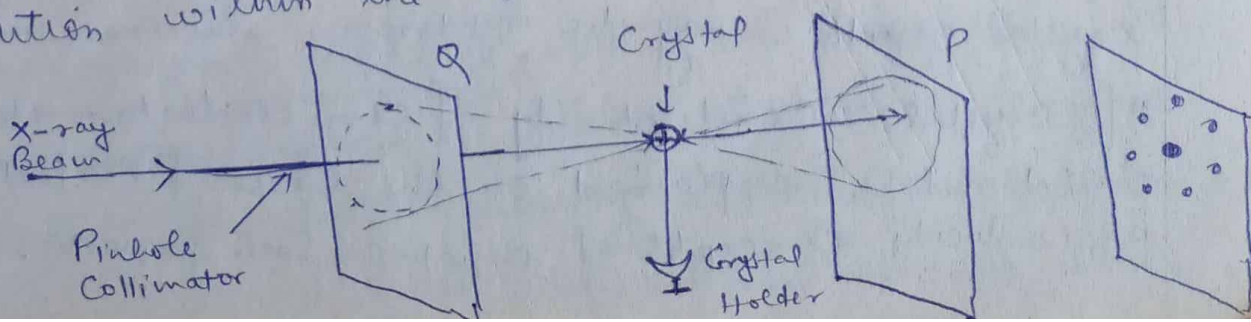
When a continuous X-ray beam through a pinhole is allowed to fall on the crystal, then this beam is diffracted by the crystal, the transmitted - diffracted and the reflected - diffracted beams are received by the films P and Q, respectively as shown in figure.

The transmitted - diffracted beams form a series of spots which is the characteristic of crystal structure and is called Laue Pattern. Each spot in the Laue pattern corresponds to the interference maxima for a set-of crystal planes satisfying the Bragg's condition $(2d \sin\theta = n\lambda)$ for a particular wavelength selected from the beam of incident light. By studying the position and intensities of these Laue spots, the crystal structure can be determined.

Ideal Crystal :- In which atoms are arranged in perfectly regular manner without flaws in all directions of crystal.

Defects :-

The deviations of crystals from their perfect periodicity (or regularity) are called defects. OR Imperfections in crystal.

Point defect   **Lattice defect**

- If the deviation from a periodic arrangement is localized to the vicinity of only several atoms, called point defect.

- If the deviation extends through microscopic regions in the crystal, it is called a lattice defect.
  (Because it produces discontinuity in the lattice).

Point defect

| Vacancies	Substitutional	Interstitial
(I) Vacancy	(II) Substitutional.	(III) Interstitial.

I) • A missing atom or vacant atomic site in a crystal. This may be arise due to imperfect packing during the original crystallisation or thermal vibrations of atom at high temperatures

II) • A foreign atom replaces a parent atom in the crystal. Penta or tri valent impurity atom doped in pure s/c (Si or Ge).

III) • In crystal in which packing fraction is low, an extra small sized atom can enter the interstitial space in the parent crystal without disturbing the regularity positional atom.

Note. Vacancy & interstitial impurity are the inverse phenomena.

SCHOTTKY DEFECT :-

In ionic crystal if there is a vacancy in +ve ion site then charge neutrality of crystal may be achieved by creating a vacancy in the neighbouring -ve ion site. Such a pair vacant site is called "Schottky defect."
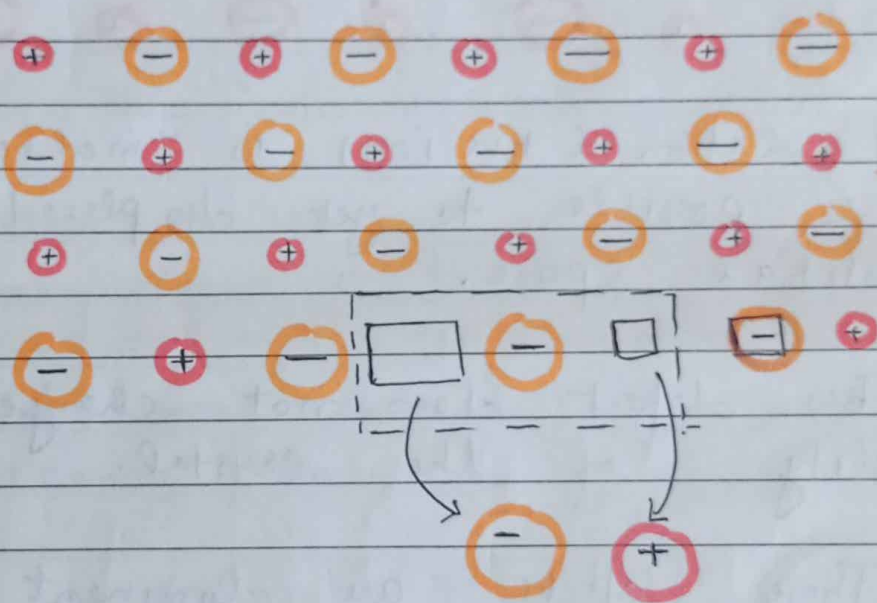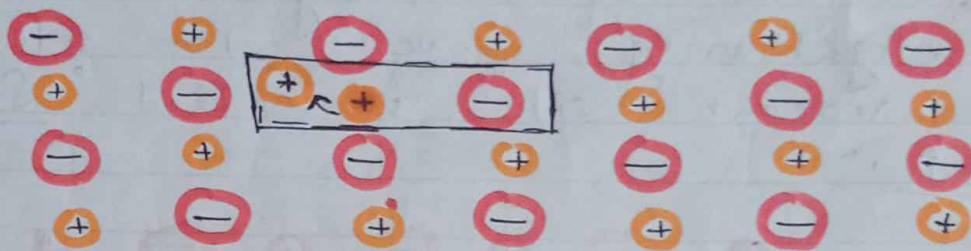

Ex. NaCl

- Equal no. of cations and anions are missing from the lattice

- Cation and anion are shifted to surface i.e volume increase and hence density decrease

$$\left(d = \frac{m}{v}\right)$$

FRENKEL DEFECT :-

In non-metallic crystals if an ion is displaced from its regular site to an interstitial site, the defect is called FRENKEL defect.

- As cation (+ve ion) is smaller in size, it is possible to get displaced into interstitial space.

- This defect does not change the electrical neutrality of the crystal.

- These defects are dominent in open structure like silver halids

- density remain same.

Note:- both the kinds of defects must be present in all solids at all tempr.

Concentration of Schottky defect in a Crystal at tempr T :-

Consider a pure crystal made up of equal no. of opposite charged ions.

Let $n \rightarrow$ No. of Schottky defects

$N \rightarrow$ Total no. of ions in the crystal.

$E_p \rightarrow$ Energy required to create a pair of vacancy sites.

$\therefore$ Increase in energy associated with vacant sites $=$ $n E_p$. $= U$

Total no. of ways in which an anion or cation vacancy may be created

$$= \frac{N!}{(N-n)! \, n!}$$

Total of ways in which n pairs of cation anion vacancies may be created

$$W = \left[\frac{N!}{(N-n)! \, n!} \right] \left[\frac{N!}{(N-n)! \, n!} \right]$$

$$W = \left[\frac{N!}{(N-n)! \, n!} \right]^2 \qquad\qquad (1)$$

∴ Entropy increase (ie disorder).

which is given by

$$S = K_B \log W \qquad \text{(II)}$$

Where K_B = Boltzmann's Constant.

∴ Corresponding change in free energy is given by

$$f = U - TS \qquad \text{(III)}$$

$$= U - T[K_B \log W]$$

$$= nE_p - K_B T \log \left[\frac{N!}{(N-n)! \, n!}\right]^2$$

Using Stirling's formula.

$$\boxed{\log x! = x \log x - x}$$

$$\therefore f = nE_p - 2K_B T \left[\log N! - \log (N-n)! - \log n!\right]$$

$$f = nE_p - 2K_B T \left[N \log N - \cancel{N} - (N-n) \log (N-n) + \cancel{N} - \cancel{n} - n \log n + \cancel{n}\right]$$

$$F = n E_p - 2 k_\beta T \left[N \log N - (N-n) \log(N-n) - n \log n \right]$$

$$F = n E_p - 2 k_\beta T \left[N \log N - N \log(N-n) + n \log(N-n) - n \log n \right]$$

$$\left(\frac{\partial F}{\partial n} \right)_T = E_p - 2 k_\beta T \left[0 - \frac{N}{(N-n)} (-1) \right.$$

$$+ \frac{n}{(N-n)} (-1) + \log(N-n) \times 1$$

$$\left. - n \times \frac{1}{n} - \log n (1) \right]$$

$$\left(\frac{\partial F}{\partial n} \right)_T = E_p - 2 k_\beta T \left[\frac{(N-n)}{(N-n)} + \log(N-n) - 1 - \log n \right]$$

$$= E_p - 2 k_\beta T \left[1 + \log\left(\frac{N-n}{n} \right) - 1 \right]$$

$$= E_p - 2 k_\beta T \left[\log\left(\frac{N-n}{n} \right) \right]$$

At equilibrium free energy is constant.
(change in free energy is minimum).

$$\left(\frac{\partial F}{\partial n} \right)_T = 0$$

$$E_p - 2k_\beta T \left[\log \left(\frac{N-n}{n} \right) \right] = 0$$

$$\frac{E_p}{2k_\beta T} = \log \left(\frac{N-n}{n} \right)$$

$$\frac{N-n}{n} = \exp \left(\frac{E_p}{2k_\beta T} \right)$$

As no. of vacancy pairs is much smaller than the total no. of ions in crystal.

$$N >>> n$$

$$\therefore (N-n) \simeq N.$$

$$\frac{N}{n} = \exp \left[\frac{E_p}{2k_\beta T} \right]$$

$$\boxed{n = N \exp \left[-\frac{E_p}{2k_\beta T} \right]}$$

⇒ This equation gives the Concentration of Schottky defects in a crystal at tempr T.

⇒ The no. of defects increase exponentially with tempr.

$$T \uparrow \qquad , \; n \uparrow$$

Concentration of frenkel Defects

$E_i \rightarrow$ Energy required to displace an atom from its regular lattice site to an interstitial position

$N_i \rightarrow$ Number of interstitial atoms

$N \rightarrow$ " " atoms

$n \rightarrow$ frenkel defects.

The total no. of ways in which frenkel defect

$$W = \left[\frac{N!}{(N-n)! \, n!} \right] \times \left[\frac{N_i!}{(N_i-n)! \, n!} \right]$$

∴ change in free energy.

$$f = U - TS$$

$$= n E_i - T K_B \log \left[\left\{ \frac{N!}{(N-n)! \, n!} \right\} \times \frac{N_i!}{(N_i-n)! \, n!} \right]$$

$$f = n E_i - K_B T \left[\log \left(\frac{N!}{(N-n)! \, n!} \right) + \log \frac{N_i!}{(N_i-n)! \, n!} \right]$$

$$= n E_i - K_B T \left[N \log N - (N-n) \log (N-n) - n \log n \right.$$
$$+ N_i \log N_i - (N_i - n) \log (N_i - n)$$
$$\left. - n \log n \right]$$

$$= n E_i - K_B T \left[N \log N - (N-n) \log (N-n) \right.$$
$$+ N_i \log N_i - (N_i - n) \log (N_i - n)$$
$$\left. - 2n \log n \right]$$

$$\frac{\partial F}{\partial n} = E_i - K_B T \left[0 - \frac{(N-n)}{(N-n)} (-1) - \log (N-n)(-1) \right.$$

$$+ 0 - \frac{(N_i - n)}{(N_i - n)} (-1) - \log (N_i - n) (-1)$$

$$\left. - 2n \times \frac{1}{n} - 2 \log n \right]$$

$$= E_i - K_B T \left[1 + \log (N-n) + 1 + \log (N_i - n) \right.$$
$$\left. - 2 - 2 \log n \right]$$

$$= E_i - K_B T \left[\log (N-n) + \log (N_i - n) - 2 \log n \right]$$

$$= E_i - K_B T \left[\log \frac{(N-n)(N_i-n)}{n^2} \right]$$

As $N \gg n$, $N_i \ggg n$. $\quad \therefore \left(\frac{\partial F}{\partial n} \right)_T$

$$\frac{E_i}{K_B T} = \log \left(\frac{N N_i}{n^2} \right)$$

$$\frac{N N_i'}{n^2} = \exp\left[\frac{E_i'}{K_B T}\right]$$

$$N N_i' = n^2 \exp\left[\frac{E_i'}{K_B T}\right]$$

or $$n^2 = N N_i' \exp\left[\frac{-E_i'}{K_B T}\right]$$

$$\boxed{n = \sqrt{N N_i'} \exp\left[-\frac{E_i'}{2 K_B T}\right]}$$

⟹ No. of defects increases exponentially with tembr.