SOLID STATE

By - S. Alam

→ The state of matter which possess rigidity i.e. the consituent particles do not change their position is called as "solid state".

⇒ characteristics of SOLIDS —
* They have definite shape and volume.
* They possess rigidity i.e. Particles donot move from their fixed position.
* Intermolecular force is very high.
* The space between the particles is very low.
* They possess high density and very low of compressibility.

→ TYPES OF SOLIDS
* Amorphous solids   * Crystalline solids.
* The solids in which particles are not arranged in regular older are called as Amorphous solids. eg. Rubber, glass, coal etc.
CHARACTERISTICS
* They donot have any definite pattern of arrangment of constituting particles.
* They donot have sharp cleavage i.e, they produce irregular or rough surface on cleavage.
* They are isotropic i.e. arrangement of binding constituents is random and disordered. Hens all the directions are equal and therefore all the properties are same in all the direction.
* They have short range older i.e. regular and repeating arrangement is observed over a shorter distance only.
* They melt over a range of temperature so, they donot have sharp melting point.

* The solids in which particles are arranged in a regular and definite older are called as "Crystalline solids" h.o
CHARACTERISTICS
* They have a definite pattern of arrangement of constituting particles.
* They have sharp cleavage
* They are anisotropic. ie arrangement of binding constituents

is regular. And they show magnitude of the some of the physical properties such as refractive index, electrical and thermal conductivities, coefficients of thermal expansion different in different directions.
* They have long range order which means regular and repeating arrangement is observed throught the crystal.
* They have sharp melting point i.e. whole crystal melt in a very short span of time.

* The solids in which the arrangement of building constituents is not regular but haphazards are known as Amorphous solids. eg. Silicon, quartz etc.

CHARACTERISTICS OF AMORPHOUS SOLIDS
* They donot have regular arrangement of constituents
* They are Isotriopic i.e. the magnitude of some physical properties is same in all directions.
* When cut with a sharp edged tool they cut into two pieces with irregular surfaces.
* They donot have sharp melting point i.e. they melt gradually over a range of temperature.
* They have only short range order i.e. a regular arrangement is found within a short region.

⇒ Space lattice or Crystal lattice — A regular three dimen-sional arrangement of points atoms in space is called a space or crystal lattice.
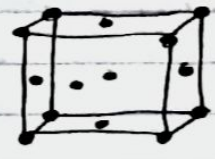
⇒ A three dimentional group of lattice points which when respected in space generates a crystal is called a Unit Cell

⇒ Types of unit cells.
* Simple or primitive cubic cell → Particles are present on the corners only.
* Face centered unit cell - The unit cell in which particles.
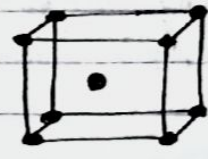
are present at the corners of the unit cell as well as on each face of that cell is called as f.c.c.
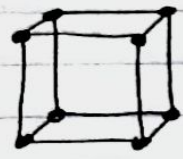
SCC   FCC   BCC   ECC

Primitive   Non - Primitive.

*Body Centered cubic Cell (bcc) - In this unit cell one lattice pt is present at the centere of the unit cell in addition to the corness.

*End Centred Cubic cell - In this unit cell the e two lattice pts are present at alternative faces in addition to the corners.
* No of particles present in a unit cell.

* In SCC :- Space scc has 8 p lattice pts at corness
Contribution of one atom in a unit cell $= \frac{1}{8}$

No of particles $= \frac{1}{8} \times 8$
$= 1.$

* In BCC :- If bcc contain 9 lattice pts out of which the particles which are present at corners give $\frac{1}{8}$ part to a unit cell and which present at the centere of the unit cell give one.
No of particles at corness $= \frac{1}{8} \times 8$
$= 1$
No of particles at center $= 1$
Total particles in BCC $= 1 + 1$
$= 2$

* In fcc the particles which are present at corners contribute $\frac{1}{8}$ and which are present at each face contribute $\frac{1}{2}$. to a unit cell.
No. of particles at corness $= \frac{1}{8} \times 6 = 1$
No. of particles at faces $= \frac{1}{2} \times 6 = 3$
Total particles in fcc $= 1 + 3 = 4$.

*__Bravais lattice__ Basis of various combination of lattice spacing along three axis i.e. length of the intersecting edges (a, b, c) and three angles between edges (α, β, γ) we can define seven crystal systems-

System	Axial distances	Axial angles	Examples
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Copper, Zinc blende, KCl, NaCl
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
3. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma - 90, \beta \neq 90°$	Monoclinic sulphur, $PbCrO_2$
5. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Graphite, ZnO, CdS, PbI_2
6. Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite, Cinnabar
7. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Potassium dichromate, $CuSO_4 \cdot 5H_2O$, H_3BO_3

* __Close packing in crystals__ — Packing of spheres takes place in such a way that they occupy the maximum available space, hence crystal has maximum density. This type of packing is called as close packing.

* One dimensional close paking — When the spheres are combined touching each other.

OOOOOOOOOO

* Two dimensional packing :— When the rows are combined touching each other

* __Square close packing__
- Central sphere is is contact with four other spheres.
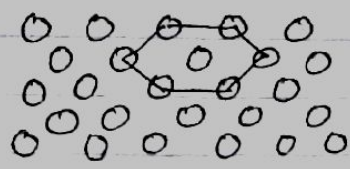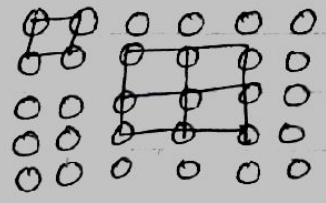⇒ less efficient

⇒ Horizontal as well as vertical alignments occur

* __Hexagonal close packing.__
⇒ Central sphere is in contact with six other spheres.
⇒ More efficient as more space is occupied by spheres.
⇒ Third row vertically aligned with the first row.

* **Three dimensional close packing** – It can takes place in two ways

i. hcp   ii. ccp

(i) **Hexagonal close packing :-** When spheres in every third layer are directly above the first and fourth above the second layer it is known as hcp or hexagonal close packing. It follows AB AB AB... pattern. When the third layer is placed over second layer it covers the tetrahedral voids.
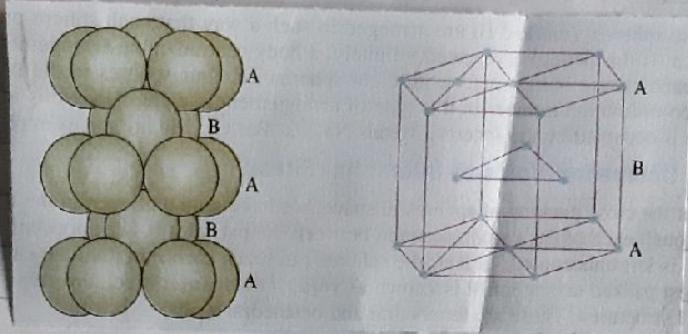
(ii) **Cubic close packing :-** When a third layer is placed over the second layer in such a way that octahedral voids are covered. It follows ABCABCABC.... pattern. eg. Ni, Cu, Au, etc.
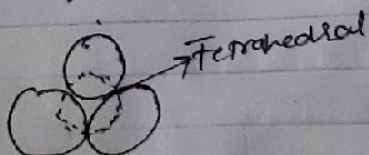
* In both the cases 74% space is occupied and co-ordination number is 12.
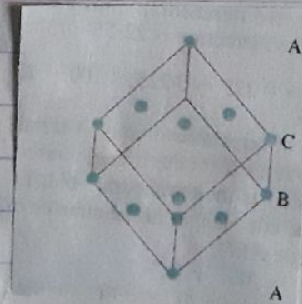
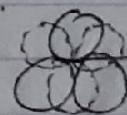* **Voids :-** The empty space in a crystal is called void or hole. They are of two types.
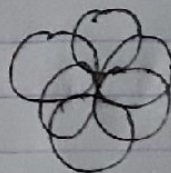
* Tetrahedral   * Octahedral
A simple triangular void surrounded   A double triangular void
by the four spheres.   surrounded by the six spheres.
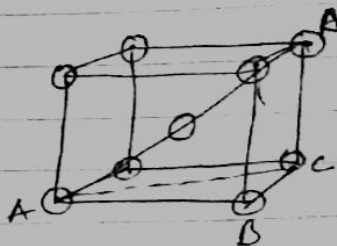

→ Tetrahedral

→ Octahedral void

* __Radius__ of __tetrahedral voids__:

Let the radius of the sphere $= R$
& radius of the void $= r$

AC $= 2R$

In $\triangle ABC$

$$AC^2 = AB^2 + BC^2$$
$$= a^2 + a^2$$
$$AC = \sqrt{2a^2}$$
$$= a \cdot \sqrt{2}$$
$$\therefore \quad 2R = a\sqrt{2}$$

$$R = \frac{a\sqrt{2}}{2}$$

$$\boxed{R = \frac{a}{\sqrt{2}}} \quad — \quad i$$

In $\triangle AED$

$$AD^2 = AC^2 + CD^2$$
$$= 2a^2 + a^2$$
$$AD = \sqrt{3} \cdot a$$

$$\therefore \quad AD = 2R + 2r$$

$$2R + 2r = \sqrt{3} \cdot a$$

$$\boxed{R + r = \frac{\sqrt{3} \cdot a}{2}} \quad — \quad ii$$

By dividing eq. es ii by (i)

$$\frac{R+r}{R} = \frac{\sqrt{3} \cdot a}{2} \times \frac{\sqrt{2}}{a}$$
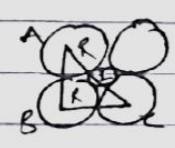
$$1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1$$

$$\boxed{\frac{r}{R} = \frac{1.73}{1.414} - 1} \qquad \boxed{\frac{r}{R} = 0.225}$$

* Radius of the octahedral voids.

Let the R is the radius of sphere and
r is the radius of octahedral void.

In $\triangle ABC$

$$AC^2 = AB^2 + BC^2$$
$$(2r + 2R)^2 = (2R)^2 + (2R)^2$$
$$(2R + 2r)^2 = 8R^2$$

$$2R + 2r = \sqrt{8}R$$

$$4(R+r)^2 = 8R^2$$

$$(R+r)^2 = \frac{8R^2}{4}$$

$$R+r = \sqrt{2R^2}$$

$$r = 1.414R - R$$

$$\boxed{r = 0.414R}$$

Tetrahedral voids	Octahedral voids.
* Radius of the void is 22.5% as compared to that of the spheres	* Radius of the void is 41.4% as compared to that of the sphere.
* Each void is surrounded by 4 spheres.	* Each void is surrounded by 6 spheres.
* There are two tetrahedral voids per sphere	* There is one octahedral void per sphere.

* Packing efficiency: The percentage or fraction of total space filled by the particles in a unit cell

$$Packing\ efficiency = \frac{Volume\ of\ the\ spheres}{Volume\ of\ unit\ cell} \times 100$$

* Packing efficiency of scc.

Volume of the sphere $= Z \times \frac{4}{3}\pi r^3$

$= 1 \times \frac{4}{3}\pi r^3$

$$\boxed{a = 2r}$$
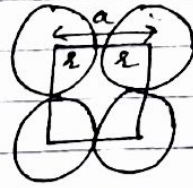
$= \frac{4}{3}\pi r^3$

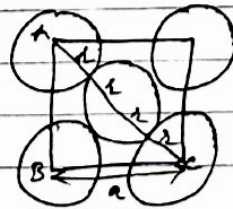Volume of the unit cell $= a^3$ $\therefore a = 2r$

$= (2r)^3$

$= 8 r^3$

Packing efficiency $= \dfrac{\frac{4}{3}\pi r^3}{8 r^3} \times 100$

$= \dfrac{\pi}{6} \times 100$

$= \dfrac{314}{6} = 52.4\%$

* Packing efficiency of e fcc:

In $\triangle$ ABC

$AC^2 = AB^2 + BC^2$

$= a^2 + a^2$

$AB = \sqrt{2} \cdot a$ $AC = 4r$

$4r = \sqrt{2} \, a$

$r = \dfrac{\sqrt{2} \cdot a}{4}$

$r = \dfrac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2} \cdot r$

Volume of sphere $= 4 \times \frac{4}{3}\pi r^3$

$= \dfrac{16}{3}\pi r^3$

Volume of the unit cell = a^3

$$= (2\sqrt{2} \cdot r)^3$$
$$= 16\sqrt{2}\, r^3$$

Packing efficiency $= \dfrac{\text{Volume of the spheres}}{\text{Volume of the unit cell}} \times 100$

$$= \dfrac{\frac{16}{3}\pi r^3}{16\sqrt{2}\, r^3} \times 100$$

$$= \dfrac{\pi}{3\sqrt{2}} \times 100$$

$$= \dfrac{314}{3\sqrt{2}} = \underline{\underline{74\,\%}}$$
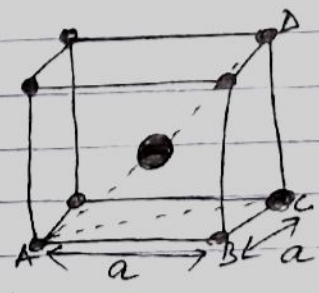
★ Packing efficiency of BCC.

In $\triangle ABC$
$$AC^2 = 2a^2$$

In $\triangle ACD$

$AD^2 = AC^2 + CD^2$

$\qquad = 2a^2 + a^2$

$AD = \sqrt{3}\cdot a$

or $\sqrt{3}a = 4r$

$$\boxed{a = \dfrac{4}{\sqrt{3}} \cdot r}$$

Volume of spheres $= 2 \times \frac{4}{3}\pi r^3$

$$= \dfrac{8}{3}\pi r^3$$

Volume of the unit cell $= a^3$

$$= \left(\dfrac{4}{\sqrt{3}} \times r\right)^3$$

$$= \dfrac{64}{3\sqrt{3}} r^3$$

$AD = 4r$

Packing efficiency $= \dfrac{\text{Vol. of spheres}}{\text{Vol. of unit cell}} \times 100$

$$= \dfrac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}} \times r^3}$$

$$= \dfrac{\pi\sqrt{3}}{8} \times 100$$

$$= \dfrac{3.14 \times 1.73 \times 100}{8}$$

$$= \underline{\underline{68\,\%}}$$

Problem:— Iron crystallizes in a bcc structure. Calculate the radius of the atom if the edge length of the unit cell is 286 pm.

* Calculation of density of a unit cell

density . Mass of the unit cell = No of atoms in a unit cell × mass of one atom

mass of one atom = $\dfrac{\text{Molar mass } (M)}{N_A}$

mass of the unit cell = $Z \times \dfrac{M}{N_A}$

Volume of the unit cell = a^3 pm³
= $a^3 \times 10^{-30}$ cm.

density of the unit cell = $\dfrac{\text{mass of the unit cell}}{\text{volume of the unit cell}}$

$$\boxed{\rho = \dfrac{Z \times M}{a^3 \times 10^{-30} \times N_A}}$$

where, Z = No. of atoms in a unit cell
M = Molar mass
a = Edge of the unit cell
N_A = Avogadro No. = 6.022×10^{23}.

* Crystal structure of some salt (A B type)
  * Rock salt (NaCl)
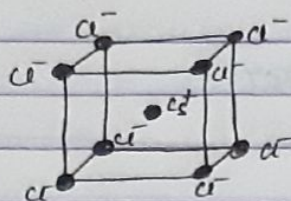 * Caesium chloride (CsCl)
  * Zinc blend (ZnS)

* Rock salt
  • It has fcc arrangement (ccp)
  • co-ordination number is 6:6
  • A unit cell of NaCl consist of four NaCl units ie. 4Na⁺ & 4Cl⁻.

CAESIUM CHLORIDE TYPE [CsCl]

* It has bcc arrangement.
* Co-ordination number 8:8.
* A unit cell of CsCl consist of only one unit of CsCl i.e one Cs and one Cl^- ion.

ZINC BLEND (ZnS)

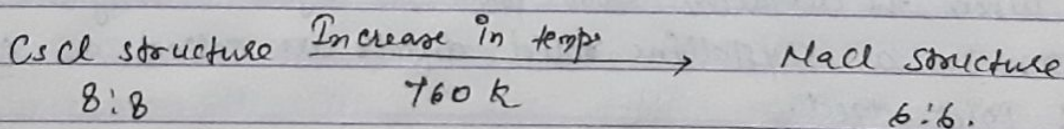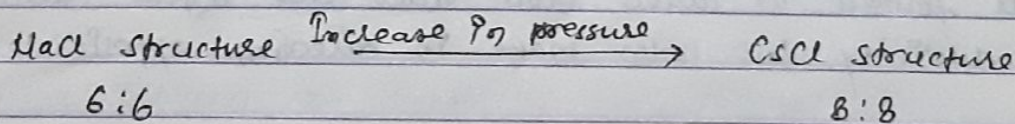* It has ccp arrangement.
* It has 4 ZnS formula per unit cell.
*

RADIUS RATIO RULE -

Ratio of radius of cation to the radius of anion is called as radius ratio.

$$Radius\ ratio = \frac{Radius\ of\ cation\ (r^+)}{Radius\ of\ anion\ (r^-)}$$

Limiting Radius	Structural Arrangement	Structure type	CN	example
0.155 - 0.225	Planner triagular		3	B_2O_3
0.225 - 0.414	Tetrahedral	ZnS	4	CuCl
0.414 - 0.732	octehedral	NaCl	6	NaBr
0.732 - 1.000	Body Centered	CsCl	8	CsBr, NH_4Br

*Effect of Temperature and pressure on a crystal type:

NaCl structure $\xrightarrow{\text{Increase in pressure}}$ CsCl structure
   6:6   8:8

CsCl structure $\xrightarrow[\text{760 K}]{\text{Increase in temp}}$ NaCl structure
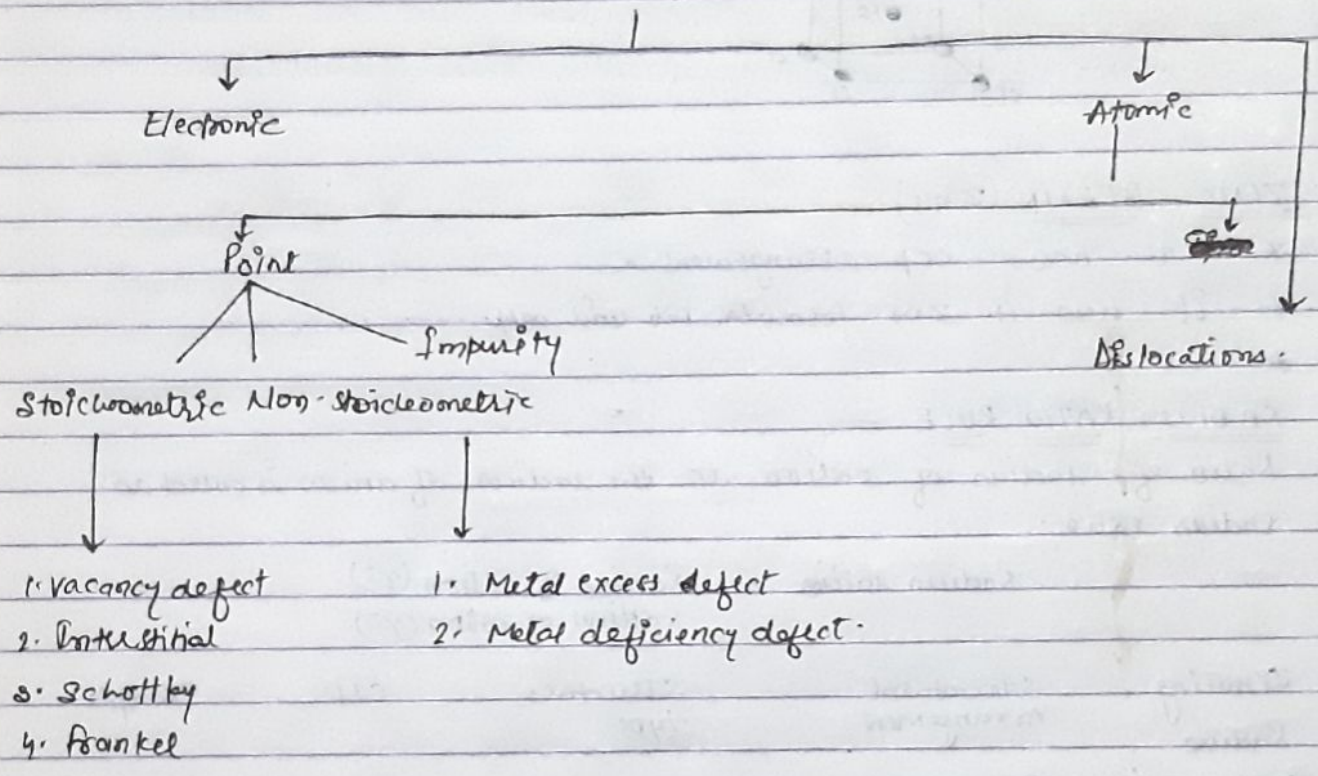   8:8   6:6.

* **IMPERFECTION IN SOLIDS**
Any departure from perfectly ordered arrangement of atoms in a crystal is called as **Crystal defect**.

NB ⇒ Perfect order of arrangement of atoms in a crystal is possible only at 0 k. Rise the temp above 0 k produces disorder.

CRYSTAL DEFECT

Electronic   Atomic

Point   Dislocations:

Stoichometric   Non-stoicleometric
      Impurity

1. Vacancy defect   1. Metal excess defect
2. Interstitial   2. Metal deficiency defect.
3. Schottky
4. frankel

* **Electronic defects** — The defects which arise due to the irregularity in the arrangement of e⁻ are known as electronic defects. The electrons above 0 k occupy higher energy state depending upon the Temperature.
When an electron is thermally removed the electron deficient site formed is called hole. Holes also impart electrical conductivity but holes move in direction opposite to that of e⁻.

* When the deviation exist from the regular arrangement around an atom in a crystalline solid defects are called as **Atomic defect** or **point defect**.
* If some lattice sites are missing from their position this is **vacancy defect**.

* The defects in the crystal in which ratio of cation and anion do not change is called as stoichiometric defect.

* If equal no. of cation and anions are missing from their lattice sites. This imperfection is called as <u>schottky</u> <u>defect</u>. The persence of a schottky defect in a crystal decrease its density. It is found in those crystals which have high co-ordination number and same size of ions. eg. NaCl, KCl, CsCl.

*

Anion vacancy

→ cation vacancy.
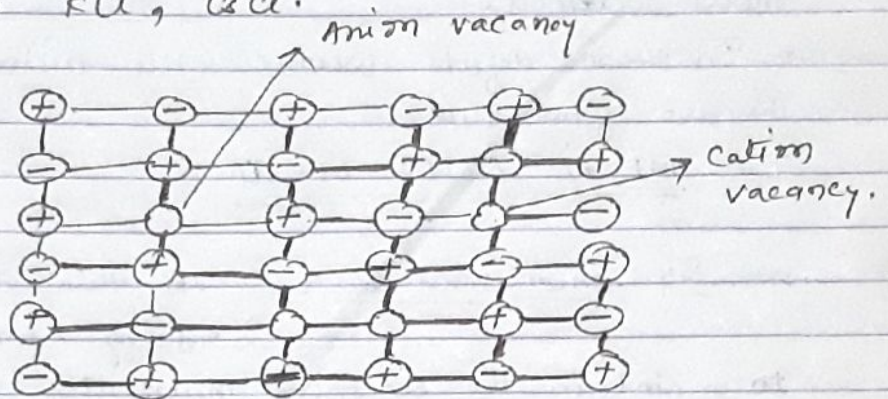
<u>Schottky defect</u>

* <u>Frankel Defects.</u>
* The defect which arise when an ion is missing from its lattice site and occupy an interstitial position. The crystal as a whole remain electrically neutral because no. of cation and anion remain the same. eg AgCl, ZnS. etc. It is shown by the solids which have low co-ordination number & large differences in the size of cation & anion.
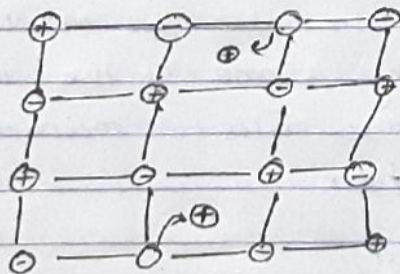
* Differences between the schottky and Frankel Defects.

Schottky	Frankel.
• Same no. of ions are missing from their normal site	• Ions do not leave the lattice and occupy position else where.
• It lowers the density of a crystal.	• The density of the solid remain unaffected.

- There is no change in the dia electric constant value
- It is noticed in the solids which have high co-ordination no. of ions.

- Increases.
- It is notices in the solids with low co-ordination no. of ions.

* The imperfection in the solids which disturb the stoichiometric ratio of the ions are known as non-stoichiometric defects.

* In these defects whether the anion or cation increases. They are of two types.
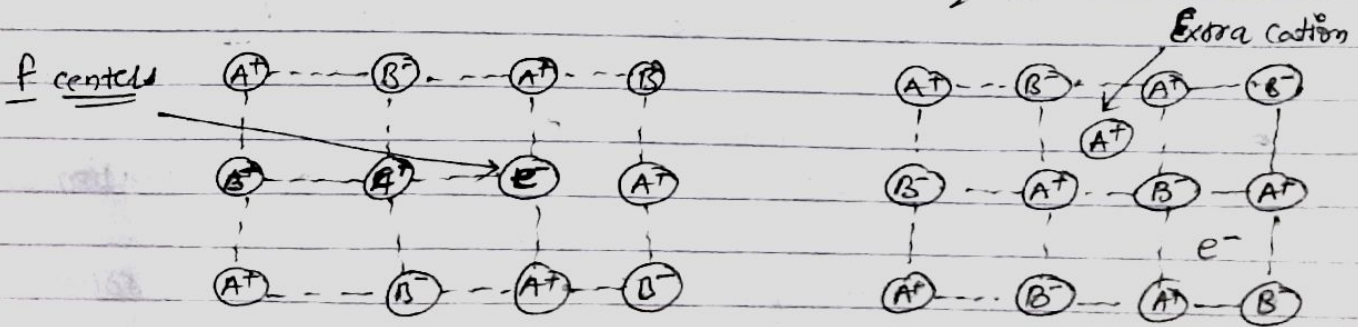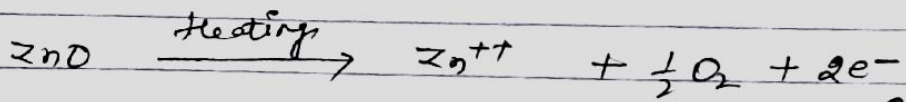
I - **METAL EXCESS DEFECT**

* **By anion vacancies :-** In this case one or more anion is missing from their lattice site and to maintain the electrical neutrality of the crystal, Positions are occupied by the electrons.

These electronic sites are known as 'f' centres. [f = Farb falben means colour   Na = Yellow   Li - Pink.

K = Violet.

Actually these electrons absorb radiation corresponding to a particular colour and impart colour to the crystal.

* **By the Presence of extra cation at the interstitial site :-** Metal excess defects can also be created when there are extra cations occupying some of the interstitial site and the e⁻ at some other sites to maintain the electrical neutrality of the crystal.

$$ZnO \xrightarrow{Heating} Zn^{++} + \frac{1}{2}O_2 + 2e^-$$

Metal excess defect.
due to anion vacancy

II. METAL DEFICIENCY DEFECT

* By cationic vacancies — In some of the crystal certain cation are missing from their lattice sites and their charges are balanced by the persence of extra charges on the neighbouring cation. eg. FeO, NiO.

* By the persence of extra anion at the intersitital site — These defect arise when certain extra anion are present at the interstitial site and their negetive charges are balanced by the neighbouring cation which has higher oxidation state.

⟹ Impurity defect:- A defect in an ionic solid can be introduced by adding foreign ions. If impurity ions have a different oxidation state than that of the host ions vacancies are created

* Cationic vacancies developed due to the introduction of impurity cause higher electrical conductivity of ionic solids.
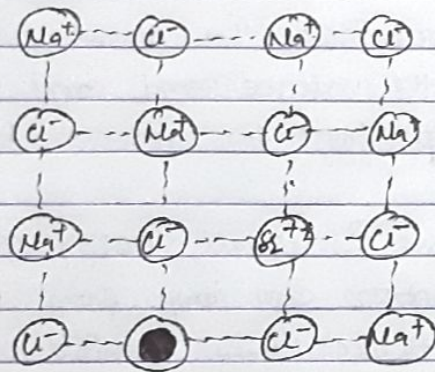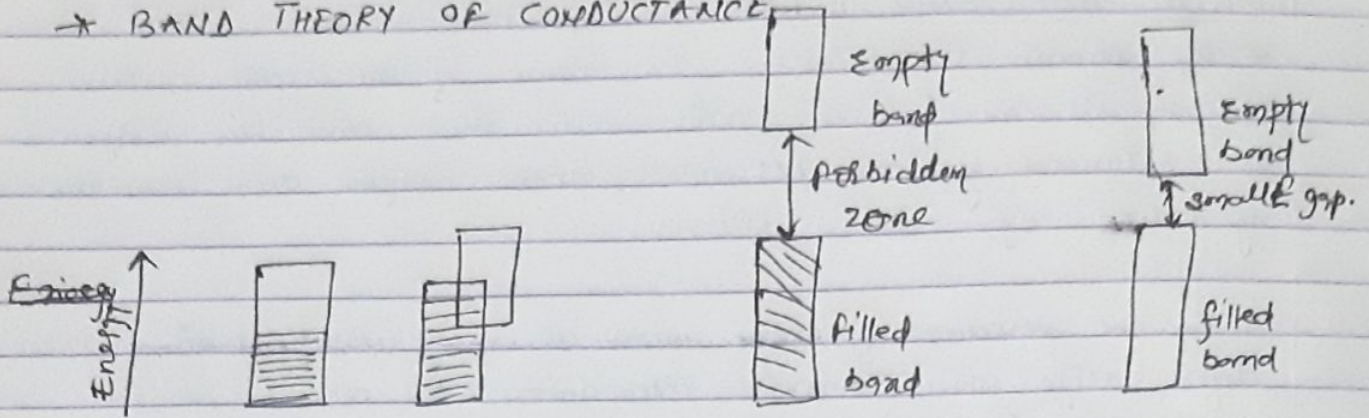

* ELECTRICAL PROPERTIES OF SOLIDS

METALS	—	$10^8\ \Omega^{-1} cm^{-1}$
INSULATORS	—	$10^{-12}\ \Omega^{-1} cm^{-1}$
SEMICONDUCTORS	—	10^{-5} to $10^6\ \Omega^{-1} cm^{-1}$

* On the basis of conductivity the substance which have highest electrical conductivity are known as conductors. This higher value of conductivity may be due to the free e^- or hole (+ve charge).

* BAND THEORY OF CONDUCTANCE

Energy →

| Partially filled band | overlapping band | Insulators (They have large energy gap b/w filledand Empty band) | Semi conductor. |

Metals

* The highest occupied energy band is called as valence band
* While the lowest occupied energy band is conduction band.

* The solids which do not allow the electricity to pass through them are known as insulators. In these solids the energy gap is very high b/w the valence band and conduction band. so electron cannot jump form the valence band to the conduction band.

* In semi conductor these is small energy gap between the two bonds. So, some electrons can jump from § valence band to the conduction band. Hence they exhibit a little conductivity. The conductivity of semiconductors increases with rise in temp. because more electrons are now in the position to jump from valence band to conduction band. Seviem

* Semi conductors are of two types:
  • Intrinsic   • Extrinsic

* Intrinsic semiconductors are the insulators which are capable of conducting the electricity at higher Temp. or irradiated with electro megnetic radiation. eg. Si, Geete.

* Extrinsic semiconductors are formed when impurities of some elements are added to the insulators. This process is known as doping.

* Extrinsic Semiconductors are of two types.
  • n-type   • p-type.

* <u>n-type Semiconductors</u> — are formed when the impurity
                          atoms containing more electrons
than the atoms of the parent insulators are introduced in it
silicon when dopped with Arsenic. The four electrons of arsenic

→ mobile electron.
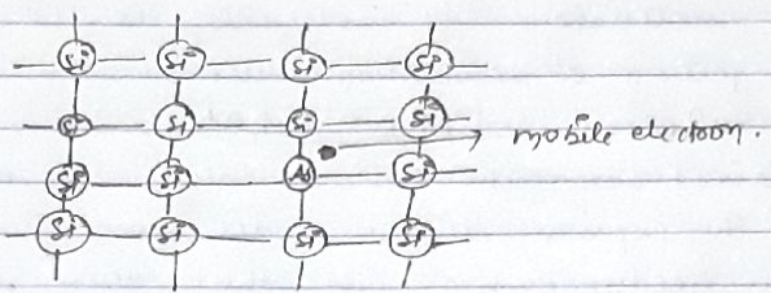
share one electron with each silicon atom while the fifth electron
is extra as well as it is delocalised. These delocalised e⁻
are responsible for the increase in the electrical conductivity.

* <u>P type Semiconductors</u> — they are formed when impurity
atoms containing lesser no. of valence electron are dopped with
atoms which have more no. of valence e⁻.
Silicon when dopped with baron or alumininium the 3 electrons
of boron are shared by the three silicon atoms but the
fourth electron is missing due to which electron hole is created
in the crystal lattice. The electrons of neighbouring atoms can
come to fill this hole. However in doing so another hole will
be created. So, when electric field is applied the electrons
move through these holes.

→ <u>Positive hole</u>
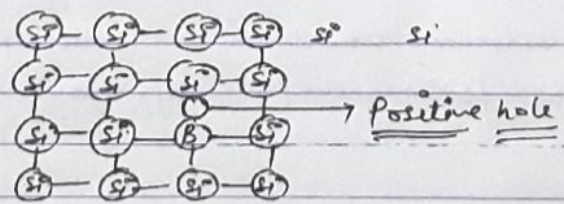
<u>MAGNETIC PROPERTIES OF SOLIDS</u>

* Diagmagnetic — A solid is said to be dia magnetic if
it is repelled by magnetic field. because in diamagnetic

substances all e^- are paired e.g. NaCl, benzene. etc.

* A substance which have some unpaired e^- and attracted by the external electric field is called as <u>paramagnetic</u>. b.Cu^{++} Fe^{2+} etc.

* Certain Paramagnetic substance show permanent magnetism when the magnetic field is removed. These are called <u>ferro-magnetic</u> materials. Only 3 elements Fe, Co, & Ni show ferromagnetism at room temperature. some other examples are - CrO$_2$, EuO etc.   [↑↑↑↑↑↑↑↑]

* Certain Paramagnetic substance align the magnetic moment due to the unpaired electron under the influence of external magnetic field in such a way that they mutually cancel. Such substance are known as Anti-ferromagnetic substance. Ex. MnO, FeO, CaO.

[↑↓ ↑↓ ↑↓ ↑]

* When the magnetic dipoles are oriented in parallel and antiparallel direction in unequal no. so. that there is a net magnetic moment. ferrimagnetism is observed. eg. Fe$_3$O$_4$.

[↑↑↓↓ ↑↑↓↓↑↑]

<u>EFFECT OF TEMP. ON THE MAGNETIC BEHAVIOUR</u>

* ferrimagnetic solids become paramagnetic when heated above 850k.
* Antiferromagnetic solids becomes paramagnetic when heated above 750k.

* The temperature above which a ferromagnetic substance becomes paramagnetic is called curie point or curie temp.

Q- what typ of substance would make better permanent magnet, forromagnetic or ferrimagnetic? Justify your answer.

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