5 mark chapter

CH-1- SOLID STATE

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Introduction

- The smallest particle of solids are atoms, ions or molecules.

Types of solids

① Crystalline solid
② Amorphous solid

① Crystalline solid ⇒

- There is a regularity and periodicity in the arrangement of constituent particles in crystalline solid.
- The ordered arrangement of particles extends over a long range.
- Crystalline solids have sharp melting points, i.e. they melt at a definite temperature.
- All crystalline substances except those having cubic structure are anisotropic.

  In other words their properties like refractive index, thermal & electrical conductivity, etc. are different in different directions.

② Amorphous solid ⇒

- The constituent particles in amorphous solid are randomly arranged.
- particles do not have long range ordered structure but they do have a short range order.
- Amorphous solid do not have sharp melting points. They melt gradually over a temperature interval.
- These solids are isotropic.

crystalline solids	amorphous solids.
- Regular arrangement of particles.	- Irregular arrangement of particle.
- long order in arrangement of particles.	- short ~~arang~~ order in arrangement of particles.
- True solid.	- Pseudo solid. / supercooled liq.
- sharp melting point.	- Ranged melting point.
- anisotropic in nature.	- Isotropic in nature

Diamond → naturally formed single crystal.

* Isomorphism ⇒

- Two or more substances having the same crystals structure are said to be **isomorphous**.
- In these substances the chemical composition has the same atomic ratio.

Ex 1) NaF and MgO
atomic ratio → 1:1

2) $NaNO_3$ and $CaCO_3$
atomic ratio → 1:1:3

* Polymorphism ⇒

- A single substance that exists in two or more forms or crystalline structures is said to be **polymorphous**.
- Polymorphs of a substance are formed under different conditions.

Ex 1) Calcite & aragonite are two forms of calcium carbonate.
2) α-quartz, β-quartz & cristobalite are three of the several forms of silica. (SiO_2)

- When polymorphism occuring in elements is called **allotropy**.
  Ex: three polymorphic forms of carbon are diamond, graphite & fullerene.
  → hardest known natural material.

Classification of Crystalline solids

1. Ionic crystal
2. Covalent network crystals
3. molecular crystal → weak dipole-dipole interactions / very weak dispersion or London forces / Intermolecular Hydrogen bonds.
4. Metallic crystal

① Ionic Crystal ⇒

- Constituent particles of ionic crystals are **charged ions**. The **cation** and **anion** may differ in size.
- The particles of ionic crystals are held by **electrostatic force of attraction** bet^n oppositely charged ions.
- Ionic crystals are **hard** and **brittle**.
- They have **high melting points**.
- These are **nonconductors** of electricity in solid state. However, they are good conductors when melted or dissolved in water.

Ex NaCl, K_2SO_4, CaF_2, KCl are ionic crystals.
LiF

② Covalent network crystals ⇒

- The constituent particles in covalent network solids are atoms.
- The atoms in these crystals are linked by a continuous system of covalent bond.
- Covalent network crystals are very hard. In fact they are the hardest and most incompressible of all the materials.
- These crystals have high melting and boiling points.
- covalent solids are poor conductors of heat and electricity.

Ex diamond, quartz (SiO_2), boron nitride, carborandum. etc.

③ Molecular crystals ⇒

- The constituent particles of molecular solids are molecules of the same substance.
- The molecules are held together by various intermolecular forces of attraction.

a] weak dipole-dipole interactions in polar molecules such as solid HCl, H_2O, SO_2, which posses permanent dipole moment.

b] Very weak dispersion or London forces in non-polar molecules such as solid CH_4, H_2.
These forces are also involved in monoatomic solids like Ar, Ne.

- Because of weak intermolecular attractive forces, molecular solids are usually soft substances with low melting points.
- These solids are poor electrical conductors and are good insulators.

④ Metallic crystals ⇒

- Metals are malleable, i.e. they can be hammered into thin sheets.
- Metals are ductile i.e. they can be drawn into wires.
- metals have good electrical and thermal conductivity.

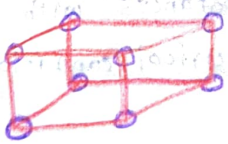
Ex Metals such as Na, k, Ca, Li, Fe (Z=26), Au, Ag, Co, etc.

c] Intermolecular hydrogen bonds in solids such as H_2O (ice), NH_3, HF and so forth.

Type / property	Ionic solids	covalent network solids	molecular solids	metallic solids
1. particles of unit cell	cations and anions	covalentely bonded atoms	monoatomic or polyatomic molecules	metallic ions in a sea of electrons
2. Interparticle forces	Electrostatic	covalent bonds	London, dipole–dipole force and hydrogen bond	metallic bonds
3. Hardness	Hard & brittle	very hard	Soft	variable From very soft to hard.
4. melting points	High 600°C to 3000°C	High 1200°C to 4000°C	Low -272°C to 400°C	wide range -39°C to 3400°C
5. Thermal & electrical conductivity.	poor electrical cond^{n} insolid state. good conductors when melted.	poor conductors	poor conductors of heat and electricity	good conductor of heat and electricity.
6. Ex	NaCl, CaF_2	diamond, silica	ice, benzoic acid	Na, Mg, Cu, Au

Crystal Structure

unit cell ⇒ The smallest repeating structural unit of a crystalline solid is called unit cell.



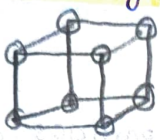
Types of Unit cell

1. Primitive or simple unit cell
2. Body-centred unit cell
3. Face-centred unit cell
4. Base-centred unit cell

Lattice :- geometrical arrangement of points in a 3-Dimensional periodic array.

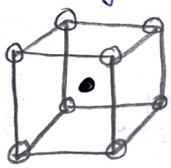
① **Primitive or simple unit cell** ⇒

In primitive unit cell, the constituents particle are present at its corner only.



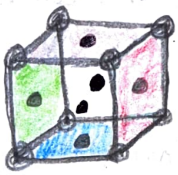
② **Body centred unit cell** ⇒

In this type of unit cell, one constituent particle is~~are~~ present at centre of the body in addition to corner particle.



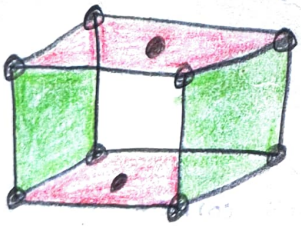
③ **Face centred unit cell** ⇒

The unit cell consists of a particle at the centre of each of the Faces in addition with corner particles.



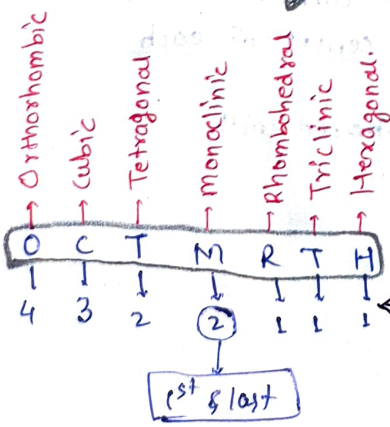
④ **Base centred unit cell** ⇒

This unit cell consist of particles at the centre of any two of its opposite Faces in addition to corner particles.



* **Crystal Structure**

- 14 lattices, which describe the crystal structure, are called Bravais lattices.
- Seven crystal systems are associated with 14 Bravais lattices also called 14 unit cells.
- The seven crystal systems are named as cubic, tetragonal, orthorhombic, rhombohedral, monoclinic, triclinic & Hexagonal system.



Cubic System

1] Simple cubic unit cell (scc) has a particle at each of the eight corners of cube.

11] Body-centred cubic unit cell (bcc) has particles at its eight corners and an additional particle in the centre of the cube.

111] Face-centred cubic unit cell (Fcc) has particle at the centre of each of six faces in addition to the particles at eight corners of the cube.

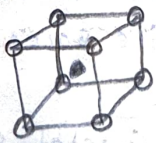
number of particles in cubic unit cell

1] Primitive or simple cubic unit cell :-

- A simple cubic unit cell contains eight particles at its corner.
- When these unit cells are stacked together then the particle at each corner is shared by eight other particles.
- No. of particles in simple cubic unit cell is $\frac{1}{8} \times 8$ = 1 particle.

2] Body-centred cubic unit cell :-

- In this unit cell, eight particles are present at its corner in addition with one particle in centre of the unit cell.
- No. of particles in body-centred unit cell = $\frac{1}{8} \times 8 + 1$ = 2 particles

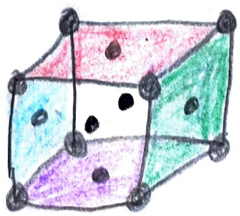


3] Face-centred cubic unit cell :-

- Fcc unit cell contains eight particles at it's corner in addition with one particle present in the centre of each face.
- Each particles of the centre of face is shared with neighbouring cube.
- No. of particles in Fcc is

$$= \frac{1}{8} \times 8 + 6 \times \frac{1}{2}$$

$$= 4 \text{ particles}$$



4] Base-Centred unit cell :- no. of particles = 2 Particles.

Relationship between molar mass, density of the substance and unit cell edge length

3m

Numerical :-

i] If the edge length of unit cell is 'a' and Volume of unit cell is 'a^3'

ii] Consider the mass of one particle is 'm' and no. of particles is 'n'.

$\therefore$ Mass of unit cell = $m \times n$ ——— (1)

iii] The density of unit cell is given by,

$$\rho = \frac{\text{mass of unit cell}}{\text{Volume of unit cell}}$$

$$\rho = \frac{m \times n}{a^3} \quad \text{——— (2)}$$

iv] Molar mass of a substance is given by,

M = mass of one particle × No. of particles per mole

$M = m \times N_A$

$m = \frac{M}{N_A}$ ——— (3) where, N_A = Avogadro number

v] Substitute equation (3) in equation (2)

$$\rho = \frac{M \times n}{N_A \times a^3}$$

$$\boxed{\rho = \frac{n\,M}{N_A \cdot a^3}} \quad \text{——— (4)}$$

Trick
↳ density = $\frac{n\,a\,M}{N_A \cdot V \cdot a^3}$ → Volume.

Close packed structures

- Close packing in one dimension
- Close packing in two dimension
  - Square close packing
  - Hexagonal close packing
- Close packing in three dimension
  - staking of square close packed layers.
  - staking of two hexagonal close packed layers
  - Placing third hexagonal closed packed layer

Packing of particles in crystal lattice

- The number of neighbouring spheres that touch any given sphere is its **coordination number.**

* Close packed structure :-

a] Close packing in one dimension ⇒

- A close packed **one dimensional structure** results by arranging the spheres to touch each other in a row.

Imp b] Close packing in two dimensions ⇒

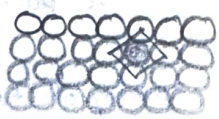
- A close packed two dimensional (planar) structure results by stacking the rows together such that they are in contact with each other.

two ways to obtain close packing in two dimensions.

- Square close packing
- Hexagonal close packing

i) Square close packing ⇒

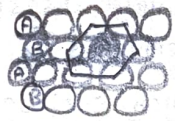
- One dimensional rows of close packed spheres are stacked over each other such that the spheres align vertically and horizontally.
- If the first row is labelled as 'A' type, and 2nd row is also labelled as 'A' type. Hence the arrangement is called A, A, A, ... type two dimensional arrangement.
- **Co-ordination number = 4.**



square planner.

ii) Hexagonal close packing ⇒

- Close packed one dimensional row shows that there are depressions between the neighbouring spheres.
- If the second row is arranged in such a way that its spheres fit in the depressions of the first row, a staggered arrangement results.
- If the first row is called 'A' type row and second row is called 'B' type row.
- Placing the 3rd row in staggered manner in contact with second row gives rise to an arrangement in which the spheres in the third row are aligned with the spheres in the first row.
- The resulting two dimensional arrangement is 'ABAB....' type.
- Co-ordination number = 6



c] Close packing in three dimensions ⇒

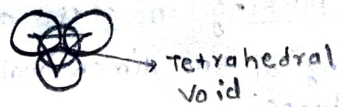
- Stacking of two dimensional layers gives rise to three dimensional crystal structures.

i) Stacking of square close packed layers ⇒

- Stacking of square close packed layers generates a three dimensional simple cubic structure.
- Here, the second layer is placed over the first layer so as to have its spheres exactly above those of the first layer.
- Subsequent square close packed layers are placed one above the other in the same manner.
- All the layers are labelled as 'A' layers.
- This arrangement of layers is described as 'AAAA....' type.
- Co-ordination number = 6

ii) Stacking of two hexagonal close packed layers ⇒

- To generate a close packed three dimensional structure, hexagonal close packed layers are arranged in a particular manner.
- Spheres of the second layer are placed in the dipression of the first layer.
- If the first layer is labelled as 'A' layer, second layer labelled as 'B' layer because the two layers are aligned differently.
- All triangular voids of the first layers are not covered by the spheres of the second layer.
- The triangular voids that are covered by spheres of the second layer generate tetrahedral void.
- A tetrahedral void is surrounded by 4 spheres.
- On joining the centres of these four spheres a tetrahedron is formed which encloses the tetrahedral voids.



iii) Placing third hexagonal close packed layer ⇒

- One way of doing this is to align the spheres of the third layer with the spheres of the first layer.
- The resulting pattern of the layers will be 'ABAB....'.
- This arrangement results in hexagonal close packed (hcp) structure.

MHT-CET

- Metals such as Mg, Zn have hcp crystal structure.

- The second way of placing the third hexagonal close packed layer on the second is to cover the octahedral voids by spheres of the third layer.
- The spheres of the third layer do not align with the 2nd sphere and ~~3rd~~ first sphere.
- The third layer is called 'C' layer.
- The spheres of the 4th layer get aligned with the spheres of the first layer. Hence, the 4th layer is called 'A' layer.
- This pattern of stacking hexagonal close packed layers is called 'ABCABC....'.
- This arrangement results in cubic close packed (CPP) structure.

* Coordination number in close packed structure :-

(a) In the simple cubic (sc) crystal structure, that results from stacking of square close packed layers, each sphere is surrounded by 6 neighbouring spheres, 4 in its own layer, 1 above and 1 below.

Hence - Co-ordination number of any sphere in sc is 6.

(b) In both hcp and ccp/fcc structures that results from stacking of hexagonal close packed layers in two different ways, each spheres is surrounded by 12 neighbouring spheres, 6 in its own layer, 3 above and 3 below.

Hence the co-ordination number of any sphere in hcp or ccp/fcc structure is 12.

Imp 2|3m

Packing efficiency

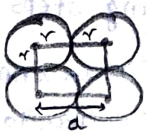
If A is the particles then
① tetrahedral void is 2A
② octahedral void is A

- Packing efficiency is the Fraction or a percentage of the total space occupied by the spheres (particles).

$$\text{Packing efficiency} = \frac{\text{Volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

* Packing efficiency of metal crystal in simple cubic lattice :-

- Packing efficiency of metal crystal in simple cubic lattice is obtained by following steps.



Step:1 : Radius of sphere

From Figure,

$a = 2r$

$\therefore r = \frac{a}{2}$

Step:2 : volume of sphere

Volume of sphere is given by,

$\frac{4}{3}\pi r^3$

Since, $r = \frac{a}{2}$

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

$= \frac{4}{3} \times \frac{\pi \times a^3}{8_2}$

$= \frac{\pi a^3}{6}$

Volume of sphere $= \frac{\pi a^3}{6}$

Step:3: Total volume of particles

In simple cubic unit cell,
the no. of particles present is only one.

$\therefore$ Total volume of particles $= 1 \times \frac{\pi a^3}{6}$

$\therefore$ Total volume of particles $= \frac{\pi a^3}{6}$

Step:4: Packing efficiency

$$\text{Packing efficiency} = \frac{\text{Total volume occupied by particle in unit cell}}{\text{Total volume of unit cell}} \times 100$$

Since, Total volume of unit cell $= a^3$

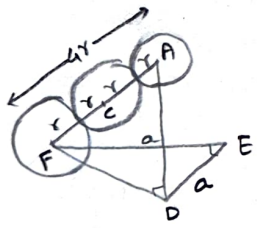
$$\text{Packing efficiency} = \frac{\pi a^3}{6 \times a^3} \times 100$$

Packing efficiency $= 52.33\%$

The unoccupied space in unit cell is $= 100 - 52.33$
$= 47.67\%$

* **Packing efficiency of metal crystal in body-centred cubic lattice :-**

- Packing efficiency of metal crystal in body-centred cubic lattice is obtained by following steps:



Step:1: Radius of sphere

In $\triangle FED$, $\angle E = 90^\circ$

Acc. to pythagoras theo,

$FD^2 = ED^2 + EF^2$

Since, $ED = EF = a$

$FD^2 = a^2 + a^2$

$FD^2 = 2a^2$ ——— (1)

In $\triangle ADF$, $\angle D = 90^\circ$

Acc. to pythagoras theo,

$AF^2 = AD^2 + FD^2$

$AF^2 = a^2 + 2a^2$

$AF^2 = 3a^2$ ——— (2)

From Fig,

$AF = 4r$

Substitute in eqn (2)

$(4r)^2 = 3a^2$

taking square root on both side

$4r = \sqrt{3}a$

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

Step:2: Volume of sphere

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

Since, $r = \frac{\sqrt{3}a}{4}$

Volume of sphere $= \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3 = \frac{4}{3} \times \pi \times \frac{3\sqrt{3}a^3}{4\times4\times4}$

Volume of sphere $= \frac{\sqrt{3}\pi a^3}{16}$

Step:3: Total volume of particles

- In body centred cubic cell, there are two particles present.

Total volume of particles $= 2 \times \frac{\sqrt{3}\pi a^3}{16} = \frac{\sqrt{3}\pi a^3}{8}$

Step:4: Packing efficiency

$$\text{Packing efficiency} = \frac{\text{Total volume of particles in unit cell}}{\text{Total volume of unit cell}} \times 100$$

$$= \frac{\sqrt{3}\pi a^3}{8 \times a^3} \times 100 = \frac{\sqrt{3}\pi}{8} \times 100$$

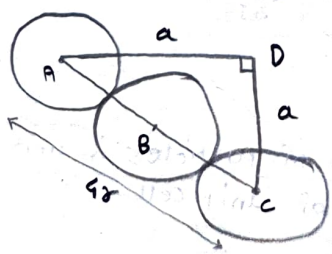
Packing efficiency = 68%

The unoccupied space in unit cell is $= 100 - 68$

$= 32\%$

* **Packing efficiency of metal crystal in Face centred cubic lattice (or ccp or hcp lattice)**

- The packing efficiency of metal crystal in Face centred cubic lattice involves Following steps.



Step : 1 - Radius of sphere

In $\triangle ADC$, $\angle ADC = 90^\circ$

Acc. to pythagoras theo.

$AC^2 = AD^2 + DC^2$

$AC^2 = a^2 + a^2$ ——[From fig]

$AC^2 = 2a^2$

$AC = \sqrt{2}\, a$

Since,

$AC = 4r$

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

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

$r = \frac{\sqrt{2} \times \sqrt{2}\, a}{2 \times 2 \times \sqrt{2}}$ ——[multiply numerator & Denominator by $\sqrt{2}$]

$r = \frac{2 \times a}{2 \times 2\sqrt{2}}$

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

Step : 2 - Volume of sphere

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

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

$= \frac{4\pi a^3}{3 \times 8 \times 2\sqrt{2}}$

$\boxed{\text{Volume of sphere} = \frac{\pi a^3}{12\sqrt{2}}}$

Step : 3 - Total volume of particles

- In FCC, there are 4 particles.

$\therefore$ Total volume of particles $= 4 \times$ volume of sphere

$= 4 \times \frac{\pi a^3}{12\sqrt{2}}$

$\boxed{\text{Total volume of particles} = \frac{\pi a^3}{3\sqrt{2}}}$

Step : 4 - Packing efficiency

$\text{packing efficiency} = \frac{\text{Total volume of particles in unit cell}}{\text{volume of unit cell}} \times 100$

$= \frac{\pi a^3}{3\sqrt{2} \times a^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\,\%$

$\boxed{\text{Packing efficiency} = 74\,\%}$

The unoccupied space in unit cell is $100 - 74 = \boxed{26\,\%}$

unit cell	Relation betn a and r	volume of 1 particle	Total volume occupied by particles in unit cell	packing efficiency	unoccupied space.
Sc 6 → Coordination no.	$r = \frac{a}{2}$ $r = 0.5a$	$= \frac{\pi a^3}{6}$	$= \frac{\pi a^3}{6}$ $= 0.5237\ a^3$	52.4 % $= 0.5237\ a^3$	47.67 %.
bcc 8 → Coordination no.	$r = \frac{\sqrt{3}}{4}a$ $r = 0.433a$	$= \frac{\sqrt{3}\pi a^3}{16}$	$= \frac{\sqrt{3}}{8}\pi a^3$ $= 0.34a^3$	68 %	32 %
Fcc / ccp / hcp 12 → Coordination no.	$r = \frac{\sqrt{2}}{4}a$ or $r = \frac{a}{2\sqrt{2}}$ $r = 0.3535a$	$= \frac{\sqrt{2}\pi a^3}{12\sqrt{2}}$	$= \frac{\pi a^3}{3\sqrt{2}}$ $= 0.185a^3$	74 %	26 %

* Number of particles and unit cells in x g of metallic crystal :

- The no. of particles and the no. of unit cells in given mass of a metal can be calculated from the known parameters of unit cell,

no. of particles 'n' per unit cell and volume 'a^3' of unit cell.

Density (ρ) and molar mass (M) of a metal.

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{\text{no. of particles in unit cell}}{\text{volume of unit cell}} \times \frac{M}{N_A}$$

we know that,

$$\therefore \rho = \frac{n}{a^3} \times \frac{M}{N_A}$$

$$\therefore M = \frac{\rho a^3 N_A}{n}$$

- No. of particles in 'x' g metal :

∵ molar mass, M, contains N_A particles

∴ x g of metal contains $\frac{x N_A}{M}$ particles.

$$\Rightarrow \text{No. of particles in 'x' g} = \frac{x N_A \times n}{\rho a^3 N_A} = \frac{xn}{\rho a^3}$$

- No. of unit cells in 'x' g metal :

∵ 'n' particles correspond to 1 unit cell

∴ $\frac{xn}{\rho a^3}$ particles correspond to $\frac{xn}{\rho a^3} \times \frac{1}{n}$ unit cells.

∴ no. of unit cells in 'x' g metal $= \frac{x}{\rho a^3}$

- no. of unit cell in volume 'V' of metal $= \frac{V}{a^3}$.

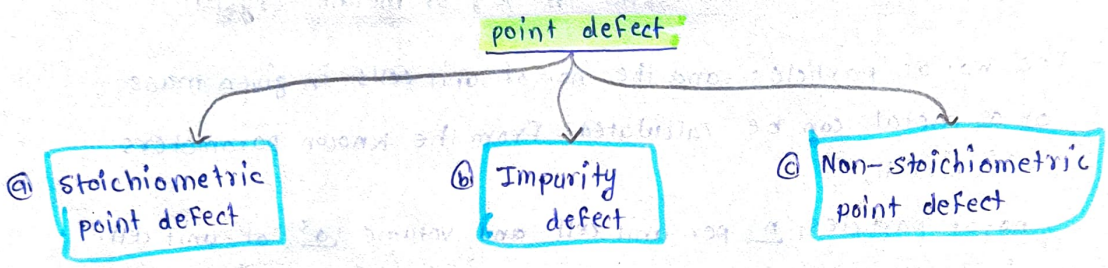
1. Sure

Crystal defect or imperfections

- The real, naturally occuring crystaline ~~structure~~ substances do not have perfect crystal structure
- They have some disorders or irregularity in the stacking of atoms.
- Such irregularity in the arrangement of constituent particles of a solid crystal are called defects or imperfections.

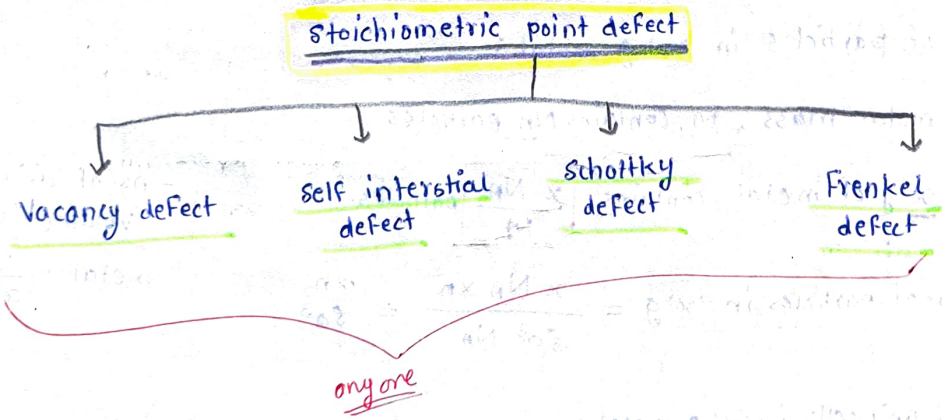
* **Point defect** ⇒

- These defects are irregularities produced in the arrangement of basis at lattice points in crystalline solids.



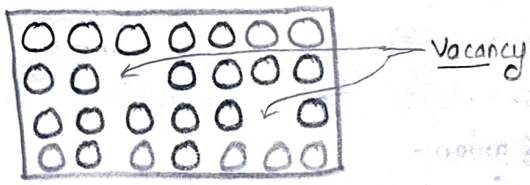
(a) Stoichiometric point defect :-

- chemical Formula of a compound shows Fixed ratio of atoms or no. of cations and anions.
  This Fixed ratio is the stoichiometry of the compound.
- In stoichiometric defect, the stiochiometry remains unchanged.



i] Vacancy defect :

- During crystallization of a solid, a particle is missing from its regular site in the crystal lattice.
- The missing particle creates a vacancy in the lattice structure.
- Thus, some of the lattice sites are vacant because of missing particles.
- The crystal is, then, said to have a vacancy defect.
- The vacancy defect can also be developed when the substance is heated.



*Consequences:
Due to absence of particles,
- mass of the substance decreases
- volume remains unchanged
- density decreases.

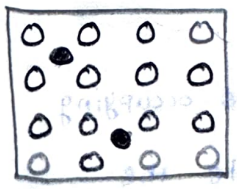
ii] Self interstial defect in elemental solid :

- Interstial sites in a crystal are the space or voids in betn the particles at lattice points.
- when some particles of a crystalline elemental solid occupy interstial sites in the crystal structure, it is called self interstial defect.

Two ways

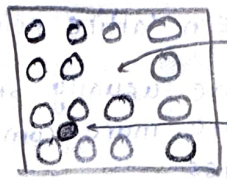
Firstly, an extra particle occupies an empty interstial space in the crystal structure.

- This extra particle is same as those already present at the lattice points.



Consequences:
- The extra particles increase the total mass of a substance without increasing volume. Hence its density ↑.

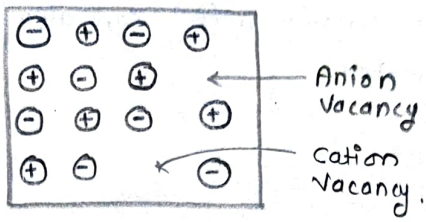
Secondly, in an elemental solid a particle gets shifted from its original lattice point and occupies an interstial space in the crystal structure.



Consequences:
- This defect preserves the density of the substance because there is neither loss nor gain in mass of substance.

iii] Schottky defect : Jm

- In an ionic solid, equal no. of cations and anions are missing from their regular positions in the crystal lattice creating vacancies.
- It means that a vacancy created by a loss of cation is always accompanied by a vacancy formed by a loss of anion.



* **Cond^n for the formation of schottky defects.**

Schottky defect is found in ionic compounds with the following characte...

- ✔ High degree of ionic character.
- ✔ High co-ordination no. of anions.
- ✔ Small diff. bet^n size of cation & anion.

The ratio $\frac{r_{cation}}{r_{anion}}$ is not far below unity.

* **Consequences of schottky defect**

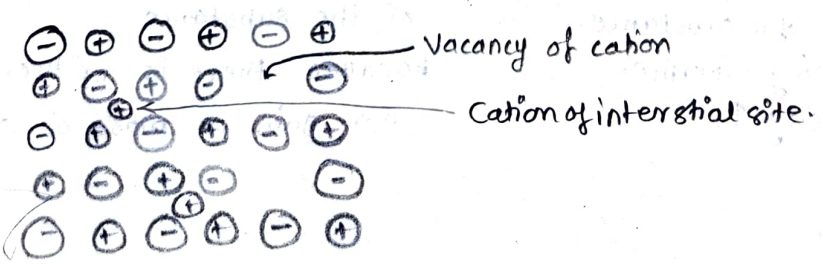
- As the no. of ions ↓, mass ↓. However, volume remains unchanged. Hence, the density of a substance decreases.
- The no. of missing cations and anions is equal, the electrical neutrility of the compound is preserved.

*** This defect is found in ionic crystals such as NaCl, AgBr & KCl.

CET

iv] Frenkel defect :

- Frenkel defect arises when an ion of an ionic compound is missing from its regular lattice site and occupies interstial position between lattice points.
- The cations are usually smaller than anions.
- It is, therefore more common to find the cations occupying interstial sites.
- It is easier for the smaller cations to accomodate the interstial spaces.



* Conditions For the Formation of ~~Ex~~ Frenkel defect :-

- Frenkel defect occurs in ionic compounds with large difference between sizes of cation and anion.
- The ions of ionic compounds must be having low co-ordination no.

* Consequences of Frenkel defect :

- As no ions are missing From the crystal lattice as a whole, the density of solid and its chemical properties remain unchanged.
- The crystal as a whole remains electrically neutral because the equal numbers of cations and anions are present.

* This defect is found in ionic crystal like ZnS, AgCl, AgBr, AgI, CaF_2.

CET

Frenkel defect is not found in pure alkali metal halides because cations of alkali metal due to large size cannot occupy interstitial space.

[b] Impurity defect :-

- Impurity defect arises when Forigin atoms, that is, atoms different From the host atoms, are present in the crystal lattice.

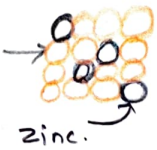
Impurity defect
- Substitutional impurity defect
- interstial impurity defect.

i] Substitutional impurity defect :

- In this defect, the Foreign atoms are Found at the lattice sites in place of host atoms.
- The regular atoms are displaced From their lattice sites by impurity atoms.

For ex :-

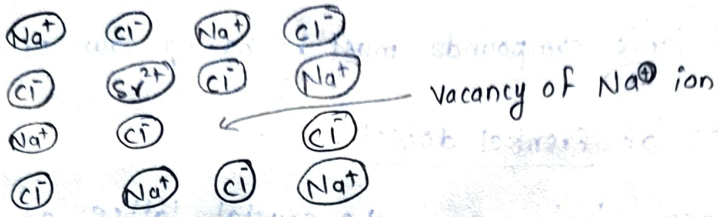
* Solid solutions of metals (alloy) :



- Brass is an alloy of Cu and Zn.
- In brass, host Cu atoms are replaced by impurity of Zn atoms.
- The Zn atoms occupy regular sites of Cu atoms.

- **Vacancy through aliovalent impurity :**

- Vacancies are created by the addition of impurities of aliovalent ions different to an ionic solid.

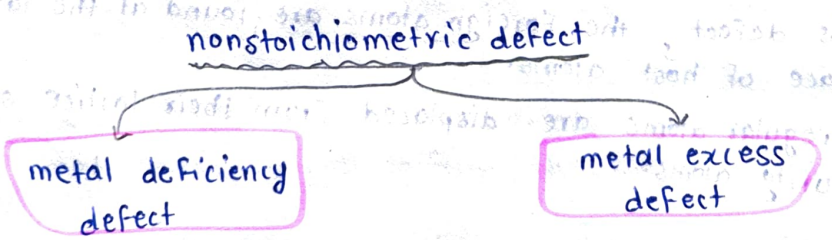


ii] Interstitial impurity defect :-

- In this defect, the impurity atoms occupy interstial spaces of lattice structure.
- For ex: in steel, Fe atoms occupy normal lattice sites. the carbon atoms are present at interstial spaces.

[c] Nonstoichiometric defects :-

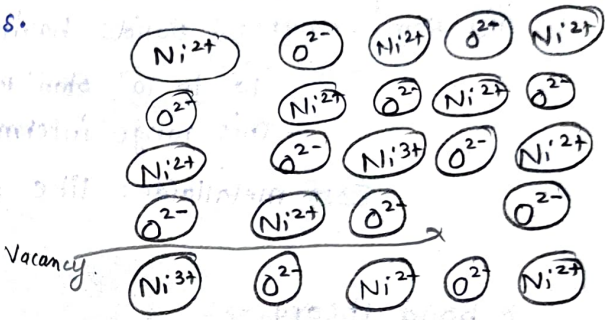
- Nonstoichiometric defect arises when the ratio of number of atoms of one kind to that of other kind or the ratio of number of cations to anions becomes different from that indicated by its chemical formula.
- In short, stoichiometry of the compound is changed.



i] Metal deficiency defect :

- This defect is possible only in compounds of metals that show variable oxidation states.
- In some crystals, positive metal ions are missing from their original lattice sites.
- The extra negative charge is balanced by the presence of cation of the same metal with higher oxidation state than that of missing cation.

For ex → in the compound NiO one Ni^{2+} ion is missing creating a vacency at its lattice site. The difficiency of two positive charges is made up by the presence of two Ni^{3+} ions at the othe lattice sites of Ni^{2+} ions.

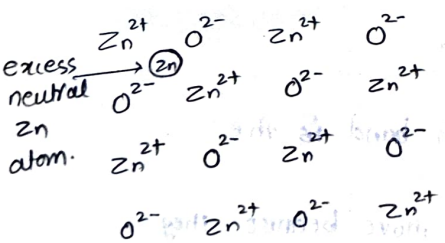


ii] Metal excess defect :

Two types.

- A neutral ator or an extra positive ion occupies interstial position :

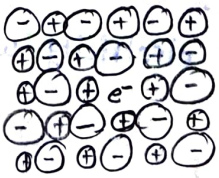
- ZnO presents two ways of metal excess defect.
- In the first case in ZnO lattice one neutral Zn atom is present in the interstial space.



- By anion Vacancies (colour or F-centres) :

- This type of defect imparts colour to the colourless crystal.

For ex. when Nacl crystal is heated in the atmosphere of sodium vapour, sodium atoms are deposited on the crystal surface.



CET CET * Nacl shows yellow colour due to the formation of F-centres.

- The stoichiometric Formula of Nacl is the $Na_{1+x}Cl_{1.0}$.

Electrical properties of solid

i] **Conductors** : Solids having electrical conductivities in the range 10^4 to 10^7 $ohm^{-1}m^{-1}$ are called conductors.

Ex → metals, electrolytes (ionic solids).

ii] **Insulators** : Solids having low electrical conductivities in the range 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$ are called insulators.

iii] **semiconductor** : Solids having electrical conductivities in the range 10^{-6} to 10^4 $ohm^{-1}m^{-1}$ are semiconductors.

- This range intermediate between conductors & insulators.

Ex → metalloides like Si, Ge, etc.

* **Band theory** →

Define → Electrical conductivities of solid metals, nonmetals and metalloids are explained in terms of band theory.

A band is made of closely spaced electronic energy levels.

i] **Conduction band** :

- The highest energy band containing electrons is the conduction band.
- It is formed by interaction of the outermost energy levels of closely spaced atoms in solids.
- Conduction band may be partially occupied or vacant.
- electrons in conduction band are mobile (→ can move) and delocalized over the entire solid.
- They conduct electricity when electrical partial is applied.

ii] **Valence band** :

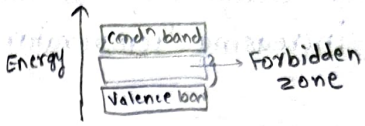
- The band having lower energy than conduction band is the Valence band.
- The electrons in valence band are not Free to move because they are tightly bound to the respective nuclei.

iii] **Band gap :**

- The energy difference between valence band and conduction band is called band gap.

Forbidden zone

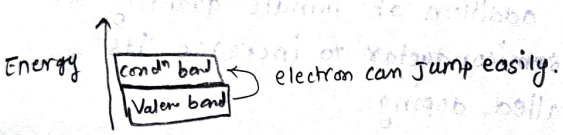
Size of the band gap decides wheather electrons from valence band can be promoted to vacant conduction band or not when band gap is too large to promote electrons from valence band to vacant conduction band by thermal energy, it is called Forbidden zone.



* **Metals ⇒**

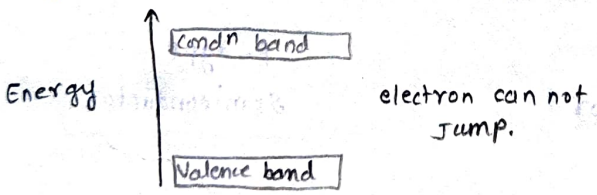
i] **Conductors :**

- There is an almost negligible forbidden energy gap.
- Electrons can easily jump from valence band to conduction band.



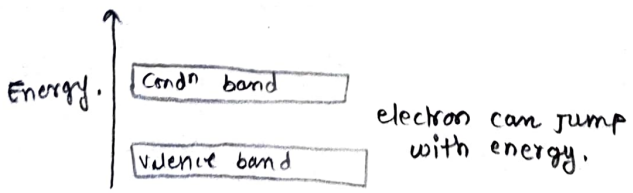
ii] **Insulators :**

- There is a large gap betn valence gap and conduction band.
- Due to large forbidden gap, no electrons can jump from valence band to cond^n band.



iii] **Semiconductor :**

- The forbidden energy gap betn valence band and condn band is smaller than insulator.
- At a temperature above absolute zero a few electrons in the valence band have enough thermal energy to jump through the small band gap and occupy condn band.



Solid	Egap ev.
diamond	5-47
Sodium	0
Silicon.	1.12
Germanium	0.67

semiconductor

a] Intrinsic b] Extrinsic

a] Intrinsic Semiconductor

- The pure semiconductors material which has very low but finite electrical conductivity is called intrinsic semiconductor.
- The conductivity of this semiconductor increases with increasing temperature.

b] Extrinsic semiconductor

- A doped semiconductor having higher conductivity than intrinsic semiconductor is called as extrinsic semiconductor.

Doping → The process of addition of minute quantity of impurities to a semiconductor to increase its conductivity is called doping.

Dopant → The added impurity is called as dopant.

Extrinsic semiconductor

- n-type semiconductor
- p-type semiconductor

→ **n-type semiconductor** : (having more electron).

- n-type semiconductor is obtained when group 15 element is added to intrinsic semiconductor is called n-type semiconductor.
- e^- rich.

Ex: Si(14) : [2,8,4]

→ P-type semiconductor (having more hole)

- P-type semiconductor is obtained by when group 13 element is added to intrinsic semiconductor is called p-type semiconductor.

- Electron deficient.

Ex: Si(14) : (2,8,4)

Magnetic properties of solids

i] Diamagnetic solid :-

- The substance with all electrons paired, are weakly repelled by magnetic Fields. These substances are said to be diamagnetic.

Ex: N_2, F_2, NaCl, H_2O., benzene, etc.

ii] Paramagnetic solid :-

- The substance with unpaired electrons are weakly attracted by magnetic Field. These substances are called paramagnetic substances.

Ex: O, Cu^{2+}, Fe^{3+}, Cr^{3+}, etc.

iii] Ferromagnetism :-

- The substances containing large number of unpaired electrons are attracted strongly by magnetic Field. These substances are said to be Ferromagnetic.

Ex: Fe, Co, Ni, Gd, CrO_2, etc.