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CHEMISTRY
TARGET IIT JEE

SOLID STATE

THEORY AND EXERCISE BOOKLET

CONTENTS

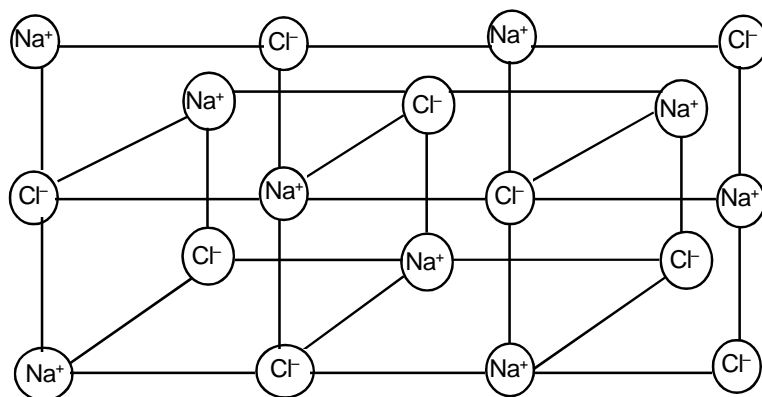## JEE SYLLABUS :

SOLID STATE

Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c, a, b, g), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects.
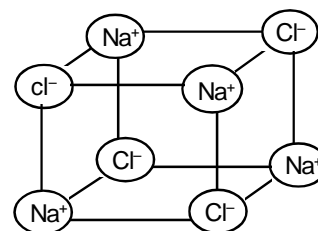
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Solid State

THEORY

Crystal Lattice

Unit Cell

⇒ The smallest part of a crystal which when repeated in all directions results in formation of crystal latlice is called a unit cell
⇒ The points in the crystal where atoms or ions are placed is called latlice point.
⇒ There are eight corners in a unit cell.
⇒ In a cube (unit cell) there are twelve edges.
⇒ There are six faces in a unit cell.
⇒ An edge is common to four cubes (unit cells)
⇒ A corner is common to eight cubes (unit cells)
⇒ A face is common to two cubes (unit cells)
⇒ Based on one corner six edges can be drawn.
⇒ Based on one edge four faces can be drawn.
⇒ A corner is common to twelve faces.
⇒ One cube (unit cell) is surrounded by six cubes (unit cells)

Corner = 8
Edge = 12
Face = 6

⇒ An atom placed at corner contributes $1/8^{th}$ to the unit cell.
⇒ An atom placed at edge centre contributes $1/4^{th}$ to the unit cell.
⇒ An atom placed at face centre contributes half to the unit cell.
⇒ There are in totality 12 face diagonals in a cube.
⇒ When two opposite corners of a cube are joined by a line it is called body diagonal.
⇒ There are in totality four body diagonals in a cube .
⇒ The point where two body diagonals intersect with each other is called body centre .
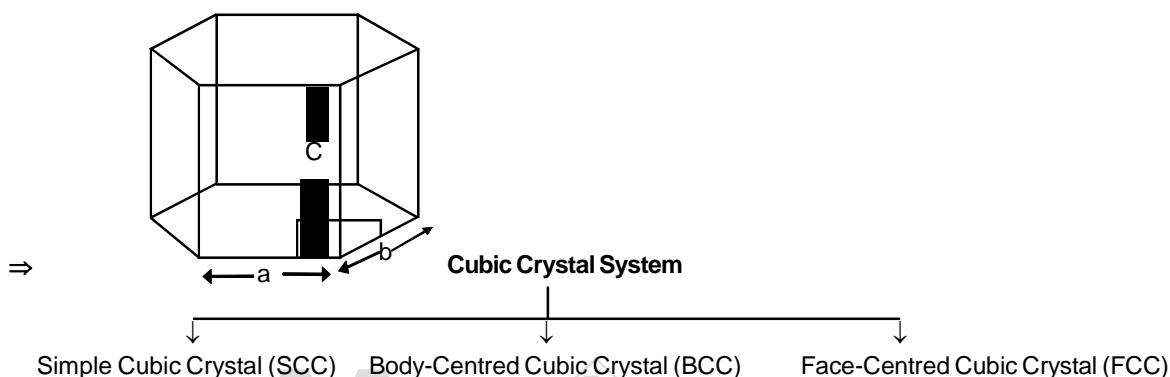⇒ An atom at body centre contributes one to the unit cell.
⇒ **Crystal system :**
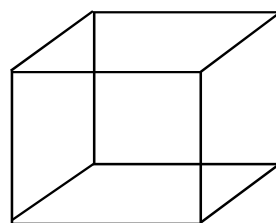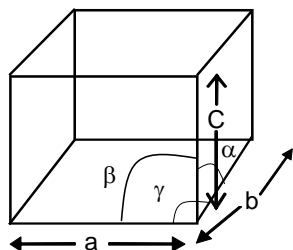
Face diagonal
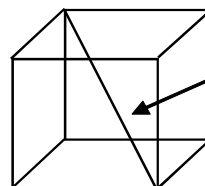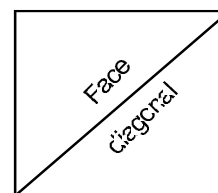
Body diagonal

CTOMTRH

System	Axial lengths	Axial angles	Examples
Cubic (C)	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cu, NaCl, KCl, Alums, Diamond, Zinc blende
Tetragonal (T)	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin(Sn), SnO_2, TiO_2 , $CaSO_4$
Orthorhombic (O) or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3, K_2SO_4, $BaSO_4$, $PbCO_3$, $CaCO_3$, Rhombic sulphur
Monoclinic (M)	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	$Na_2SO_4.10 H_2O$, $PbCrO_4$, Monoclinic sulphur
Triclinic (T)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3
Rhombohedral (R) or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3$, ICl, As, Sb, Bi, Calcite $(CaCO_3)$,
Hexagonal (H)	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	ICl, Graphite , Mg, Zn, Cd, ZnO, PbI_2

$\Rightarrow$ **Cubic Crystal System**

Simple Cubic Crystal (SCC)   Body-Centred Cubic Crystal (BCC)   Face-Centred Cubic Crystal (FCC)

$\Rightarrow$ **Simple Cubic Crystal (SCC) :**
$\Rightarrow$ **Definition : (i)** Eight atoms at corners
                    (ii) Each corner atom touches the nearest. corner atom

$\Rightarrow$ $Z = \dfrac{1}{8} \times 8$ $\Rightarrow$ 1 atom per unit cell
$\Rightarrow$ $2r = a$ $\Rightarrow$ $r = a/2$
$\Rightarrow$ Coordination Number = Number of nearest neighbours
$\Rightarrow$ Coordination Number (C.N.) of corner atom = 6
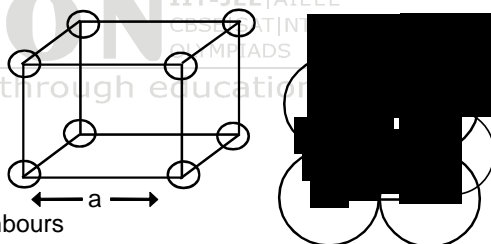
$\Rightarrow$ $\eta = \dfrac{\text{Total volume occupied}}{\text{Total available volume}}$ $= \dfrac{1 \times 4/3 \, \pi \, r^3}{a^3}$ $= \dfrac{1 \times 4/3 \times \pi \left(\dfrac{a}{2} \times a/2 \times a/2 \right)}{a^3} = \dfrac{\pi}{6} = 0.52$

$\Rightarrow$ $\eta \% = \eta \times 100 = 52\%$ (occupied) $\Rightarrow$ 48 % empty

$\Rightarrow$ **Density , $\rho = \dfrac{\text{Mass}}{\text{Volume}}$**   12 g $\longrightarrow$ 1 mole atom. C

M gm $\longrightarrow$ 6.023×10^{23} atoms. (NA)

$\Rightarrow$ $\rho = \boxed{\dfrac{1M/NA}{a^3} = \dfrac{M}{N_A \cdot a^3}}$ $\dfrac{M}{N_A} \longrightarrow$ 1 atom $\Rightarrow$ Mass of one atom $= \dfrac{M}{N_A}$

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$\Rightarrow$ **Body-Centred Cubic Crystal (BCC) :**

$\Rightarrow$ **Definition : (i)** 8 atoms at corners
(ii) One atom at body centre
(iii) Corner atom don't touch each other.
(iv) Body centred atom is touched by all corner atom

Body diagonal ($\sqrt{3}$ a)

Face diagonal ($\sqrt{2}$ a)
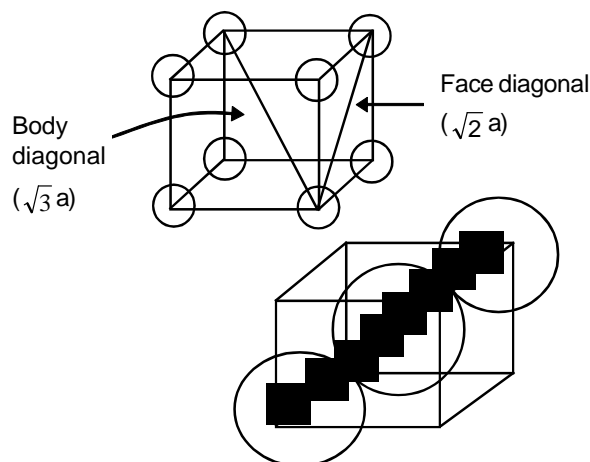
$\Rightarrow$ $Z = \dfrac{1}{8} \times 8 + 1 = 2$ atoms per unit cell

$\Rightarrow$ $4r = \sqrt{3} \ a \Rightarrow r = \dfrac{\sqrt{3}}{4} a$

$\Rightarrow$ Coordination Number of central atom = 8

$\Rightarrow$ Coordination Number of corner atom = 8

$\Rightarrow$ $\eta = \dfrac{2 \times 4/3 \, \pi \, r^3}{a^3} = \dfrac{2 \times \dfrac{4}{3} \pi \times \left(\sqrt{3} \ a/4\right)^3}{a^3} = \dfrac{\sqrt{3} \, \pi}{8} \Rightarrow \boxed{\eta = 0.68}$

$\Rightarrow$ $\eta \% = \eta \times 100 = 68\%$ (occupied)
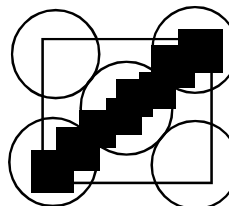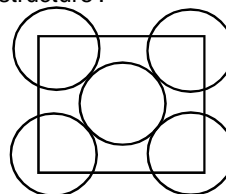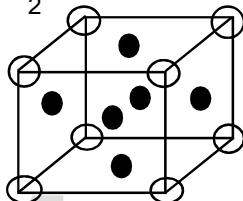
$\Rightarrow$ **Density** , $\rho = \dfrac{\text{Mass}}{a^3} = \dfrac{2 \times M/N_A}{a^3} \Rightarrow \boxed{\rho = \dfrac{2 \times M/N_A}{a^3} = \dfrac{2 \times M}{N_A \times a^3}}$

Example : (i) Alkali metals, and **(ii)** Alkaline earth metals Crystallise in bcc structure .

$\Rightarrow$ **Face – Centred Cubic Crystal (FCC) :**

$\Rightarrow$ **Definition : (i)** Eight atoms at eight corners
 (ii) One atom at each face centre
 (iii) Corner atoms do not touch each other
 (iv) Face centre atom is touched by four atoms at corners
   of the respective face.

$\Rightarrow$ $Z = \dfrac{1}{8} \times 8 + \dfrac{1}{2} \times 6 = 1+3 = 4$

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

$\Rightarrow$ Coordination Number of Face centred atom = 12
Coordination Number of Corner atom = 12

$\Rightarrow$ $\eta = \dfrac{4 \times 4/3 \, \pi \, r^3}{a^3} = \dfrac{4 \times 4/3 \times \pi \times \left(\dfrac{a}{2\sqrt{2}}\right)^3}{a^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74$
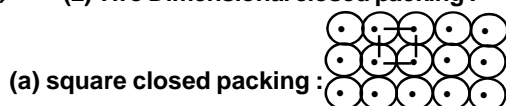
$\Rightarrow$ $\eta \% = \eta \times 100 = 74 \%$ (occupied)

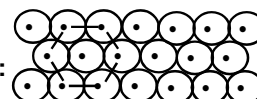$\Rightarrow$ $\rho = \dfrac{4 \times M/N_A}{a^3} \Rightarrow \boxed{\rho = \dfrac{4M}{N_A \times a^3}}$

$\Rightarrow$ **Example :** Transition metals crystallise in fcc structure.

$\Rightarrow$ **CLOSED PACKING IN CRYSTALS :**

$\Rightarrow$ **(1) One Dimensional closed packing**

$\Rightarrow$ **(2) Two Dimensional closed packing :**

(a) square closed packing : **(b) Hexagonal closed packing :**

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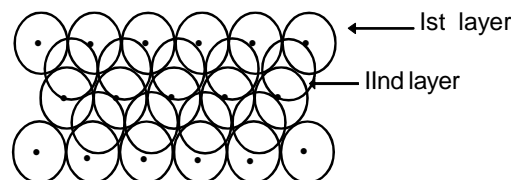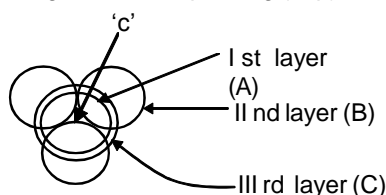**MOTION** IIT-JEE|AIEEE CBSE|SAT|NTSE OLYMPIADS
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⇒ **(3) Three Dimensional closed packing :**
 (a) If third layer on 'c' void :
 ABABAB - - - - - - - type crystal or
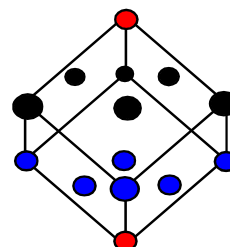 hexagonal closed packing (hcp)

← Ist layer
← IInd layer

'c'

I st layer
(A)
II nd layer (B)
III rd layer (C)

(b) If third layer on 'b' or 'd ' void:
ABCABCABC - - - - - - -type crystal
or cubic closed packing (ccp) or fcc.

I st layer (A)
II nd layer (B)
'b' , 'd '
III rd layer (C)
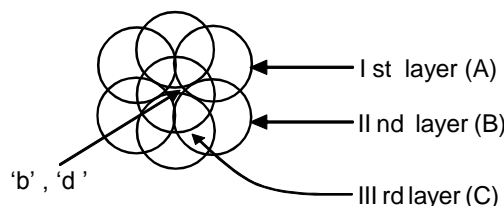
⇒ **Summary :**

Type	CN	η
SCC	6	52%
BCC	8	68%
FCC or CCP	12	74%
HCP	12	74%

⇒ **Crystals**

Atomic crystals (only atoms)
(Found at corner edges face
and body centres)

Ionic crystals

NaCl
type

CsCl
type

ZnS
type

Antifluorite
type(A_2B)

Cor...
typ...

Fluorite
type (CaF_2)

C   T   O   M   T   R   H
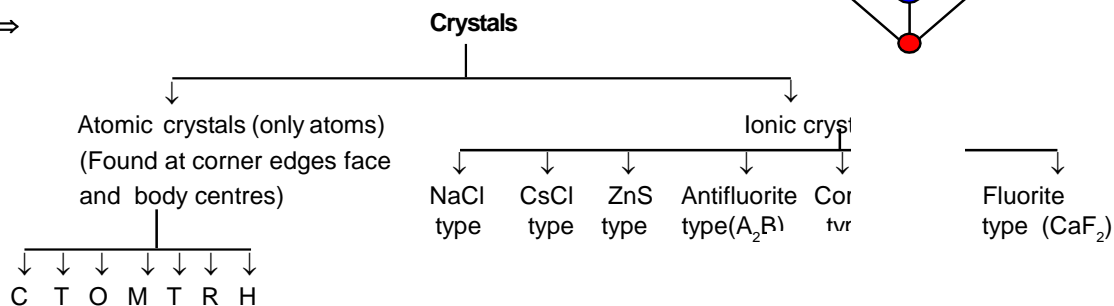
⇒ **Cations** ⊕   ⇒ **Anions** ⊖
⇒ very small in size   ⇒ Larger in size (corners, edges and body centres)
⇒ Are generally found in voids

VOIDS

Tetrahedral void (T.V.)   ...al void (O.V.)

Tetrahedron   Octahedron
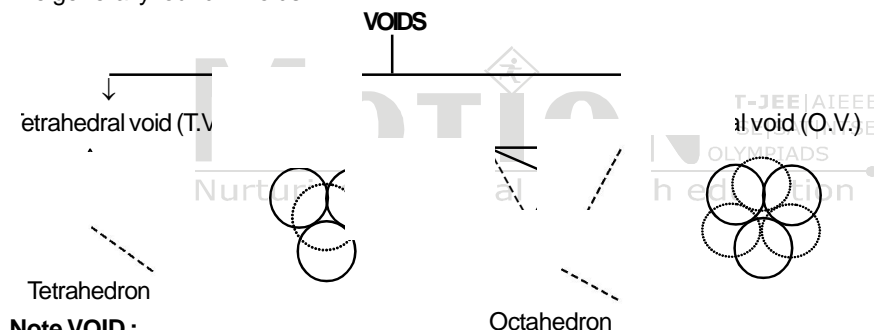
⇒ **Note VOID :**
 (i) FCC or CCP (very common)   **(ii)** HCP   **(iii)** BCC (rare)
⇒ **Tetrahedral Void (T.V.)**   **Octahedral Void (O.V.)**
⇒ Are located at body centre of mini cube   ⇒ One octahedral void is situated at body centre.
⇒ Two T.V.s are located at each body   ⇒ One O.V. is situated at each edge centre.
 diagonal

⇒ There are eight T.V.s in a unit cell   ⇒ No. of O.V.s = 1/4 × 12 + 1 = 4

⇒ The distance of a T.V. from a corner is $\sqrt{3}\,a/4$ ⇒ The O.V. at edge centre contributes 1/4th to the
                                                                          unit cell.

⇒ The Coordination number of anything   ⇒ The distance of body centre O.V from the corner is

which is kept in T.V. is 4

$\sqrt{3} \, a/2$

$\Rightarrow$ The O.V which is situated at edge centre is at a distance of $a/2$ from the corner.

$\Rightarrow$ The Coordination number of anything which is kept in a O.V. is 6.

$\Rightarrow$ **IN FCC or CCP and HCP :**

No. of tetrahedral voids = 2 × No. of atoms

No. of octahedral voids = No. of atoms

Example:

In FCC, 4 atoms are there

Hence T.V. = 2 × 4 = 8 and O.V. = 4

$\Rightarrow$ **IONIC CRYSTALS :**

(1) Rock salt type or NaCl type :

$\Rightarrow$ **Note :** While judging the coordination number of cations, nearest anions are counted, and while juding the coordination number of anions, nearest cations are counted.

$\Rightarrow$ **Definition :** **(i)** Anion – FCC **(ii)** Cations – O.V.

$\Rightarrow$ C.N. (Na^+) = 6, C.N. (Cl^-) = 6 $\Rightarrow$ There fore it is also called 6 : 6 Coordination.

$\Rightarrow$ 4 Na^+ + 4 Cl^- = 4 NaCl

$\Rightarrow$ Z = 4

$\Rightarrow$ Simplest formula = NaCl

$\Rightarrow$ $\rho = \dfrac{4 \times 58.5/N_A}{a^3 \times 10^{-30}}$

$\Rightarrow$ $2r^+ + 2r^- = a \Rightarrow r^+ + r^- = a/2$

Example : Generally all alkali metals and alkaline earth metals halides.

(2) CsCl type :

$\Rightarrow$ **Definition :** **(i)** Anions (Cl^-) $\rightarrow$ corners **(ii)** Cations (Cs^+) $\rightarrow$ Body centre

$\Rightarrow$ C.N. (Cs^+) = 8, C.N. (Cl^-) = 8 $\Rightarrow$ There fore it is also called 8 : 8 coordination .

$\Rightarrow$ 1 Cs^+ + 1 Cl^- = 1 CsCl

$\Rightarrow$ Z = 1

$\Rightarrow$ Simplest formula = CsCl

$\Rightarrow$ $\rho = \dfrac{1 \times M/N_A}{a^3 \times 10^{-30}}$

$\Rightarrow$ $2r^+ + 2r^- = \sqrt{3} \, a \Rightarrow r^+ + r^- = \sqrt{3} \, a/2$

$\Rightarrow$ **Example :** NH_4Cl, NH_4Br, NH_4I

(3) Zincblende type or ZnS type :

$\Rightarrow$ **Definition :** Cations $\rightarrow$ at alternate T.V.s

Anions $\rightarrow$ at FCC

$\Rightarrow$ C.N. (Zn^{2+}) = 4, C.N. (S^{2-}) = 4 $\Rightarrow$ There fore it is also called 4 : 4 coordination.

$\Rightarrow$ 4 Zn^{2+} + 4 S^{2-} = 4 ZnS

$\Rightarrow$ Z = 4

$\Rightarrow$ Simplest formula = ZnS

$\Rightarrow$ $\rho = \dfrac{4 \times M/N_A}{a^3 \times 10^{-30}}$

$\Rightarrow$ $r^+ + r^- = \sqrt{3} \, a/4$

$\Rightarrow$ **Example :** CuI, CuBr, CuCl

(4) Antifluorite type or A_2B type :

$\Rightarrow$ **Definition :** Cations $\rightarrow$ all T.V.s

Anions $\rightarrow$ FCC

$\Rightarrow$ C.N. of cations = 4 , C.N. of Anions = 8

$\Rightarrow$ 8 cations + 4 anions $\Rightarrow A_8B_4$ $\Rightarrow$ 4 A_2B

$\Rightarrow$ Z = 4

$\Rightarrow$ Simplest formula = A_2B

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$\Rightarrow$ $\rho = \dfrac{4 \times M/N_A}{a^3 \times 10^{-30}}$

$\Rightarrow$ $r^+ + r^- = \sqrt{3}\, a/4$

$\Rightarrow$ **Example :** Na_2O , K_2O, Li_2O etc.

(5) Fluorite type or CaF_2 type :

$\Rightarrow$ **Definition :** Cations $(Ca^{2+}) \to$ FCC , Anions $(F^-) \to$ Tetrahedral voids

$\Rightarrow$ C.N. of cations (Ca^{2+}) = 8 , C.N. of anions (F^-) = 4

$\Rightarrow$ $4\, Ca^{2+} + 8F^- = 4\, CaF_2$

$\Rightarrow$ Z = 4

$\Rightarrow$ Simplest formula = CaF_2

$\Rightarrow$ $\rho = \dfrac{4 \times M/N_A}{a^3 \times 10^{-30}}$

$\Rightarrow$ $r^+ + r^- = \sqrt{3}\, a/4$

$\Rightarrow$ **Example :** BaF_2 , $BaCl_2$, SrF_2 , $SrCl_2$, CdF_2 , PbF_2

$\Rightarrow$ **Radius ratio :** For calculation of radius ratio following facts should be kept in mind :

(1) Anion $\to$ Anion should not touch each other

Cation $\to$ Anion should always touch each other

$\Rightarrow$ **NaCl type structure :** Cation $\to$ O.V. , Anion $\to$ fcc

$\Rightarrow$ $r^+ + r^- = a/2$ and in limiting case $r^- = \dfrac{a}{2\sqrt{2}}$

$\Rightarrow$ $r^+/r^- = \sqrt{2} - 1 = 0.414$ where $\dfrac{a/2}{a/2\sqrt{2}} = \sqrt{2} = 1.414$

$\Rightarrow$ $0.732 > r^+/r^- > 0.414$ as $\dfrac{r^+ \uparrow}{r^- \downarrow} \Rightarrow \left[r^+/r^- \right] \uparrow$

$\Rightarrow$ **CsCl type structure :** Cation $\to$ Body centre , Anion $\to$ All corner

Here , $r^+ + r^- = \sqrt{3}\, a/2$ ——(I)

For limiting case , $2r^- = a \Rightarrow r^- = a/2$ ——(II)

Dividing (I) by (II)

$r^+/r^- + 1 = \sqrt{3} \Rightarrow r^+/r^- = 0.732$

$\uparrow \left[\dfrac{r^+ \uparrow}{r^- \downarrow} \right] = 0.732 \uparrow \Rightarrow r^+/r^- > 0.732$

$\Rightarrow$ **ZnS type structure :** **Cation** $\to$ Alternate tetrahedral voids

Anion $\to$ FCC

$r^+ + r^- = \sqrt{3}\, a/4$

and in limiting case , $r^- = a/2\sqrt{2}$

$1 + r^+/r^- = \sqrt{6}/2 \Rightarrow r^+/r^- = \sqrt{6}/2 - 1$

$0.414 > r^+/r^- > 0.225$

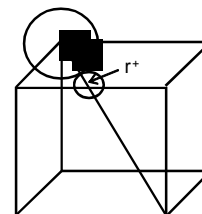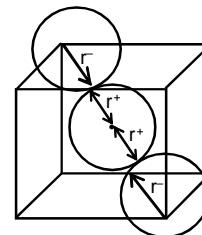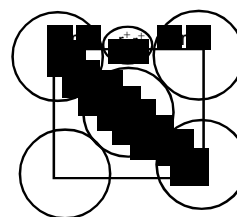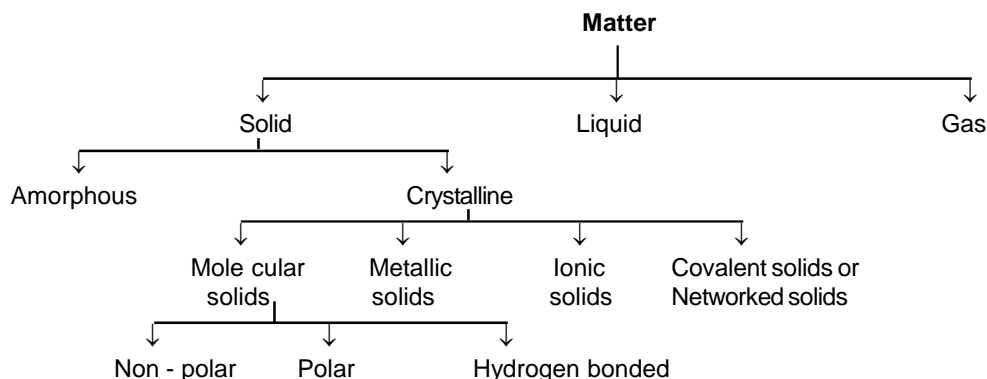$\Rightarrow$ **Summary :**

ZnS: $0.225 < r^+/r^- < 0.414$

NaCl : $0.414 < r^+/r^- < 0.732$

CsCl : $0.732 < r^+/r^-$

$\Rightarrow$ Antifluorite type (A_2B type) has the same radius ratio as that of ZnS type structure .

Matter

- Solid
- Liquid
- Gas

Solid branches into:
- Amorphous
- Crystalline

Crystalline branches into:
- Molecular solids
- Metallic solids
- Ionic solids
- Covalent solids or Networked solids

Molecular solids branch into:
- Non - polar
- Polar
- Hydrogen bonded

	Solid	Liquid	Gas
(1)	Have definite volume	Have definite volume	Have indefinite volume
(2)	Their shape is fixed	Their shape is indefinite volume	Their shape is indefinite
(3)	They have strongest intermolecular attraction. Hence their shape as well as volume is fixed	Their force of attraction is intermediate between solids and gases . So shape is variable but volume is fixed.	They have very weak force of attraction . Hence molecules are very - very loosely connected with each other and hence have neither shape nor volume fixed.

⇒	Amorphous		Crystalline
(1)	Particles are arranged in regular fashion but only for small distance.	(1)	Have a long range order of a regular arrangement of particles
(2)	Amorphous substances melt over a range of temperature	(2)	Crystalline substances have sharp melting points.
(3)	The two surfaces, here are irregular	(3)	When a crystalline substance is cut into two pieces, the two surfaces generated are plane and smooth.
(4)	Amorphous substances are isotropic	(4)	Crystalline substances have different value of all physical properties in different directions . This phenomenon is called anisotropy and crystalline substances are anisotropic .
(5)	Amorphous substances are pseudosolids or super - cooled liquids	(5)	They are true solids .

⇒ **Molecular solids :** Those solids which consists of small molecules are called molecular solids.

⇒ **They are of three types :**

(1) **Non - polar molecular solids :**

(electronegativity sequence ($F > O > N \approx Cl > Br > S > C \approx H$)

(I) The solids which have zero dipole moment are called non-polar molecular solids.

(II) The molecules are held together by weak Vander waal's forces . Hence they are either gas or liquids at room temperature.

(III) They are poor conductor of electricity due to their non-polar nature.

(2) **Polar molecular solids :**

(I) Those solids which have non-zero dipole moments are called polar molecular solids.

(II) Polar molecular solids have dipole - dipole interaction, which is slightly stronger than vander waal's force and hence they have larger melting and boiling points than the non - polar molecular solids .

(III) **Example :** Solid CO_2 , Solid NH_3

(IV) They are generally liquids or gases at room temperature.

(3) **Hydrogen bonded molecular solids :**

(I) Those molecular solids which are bonded with each other by hydrogen bonds are called hydrogen bonded molecular solids .

(II) **Example :** Ice

(III) They are non-conductor of electricity

(IV) Generally they are liquid at room temperature or soft solids .
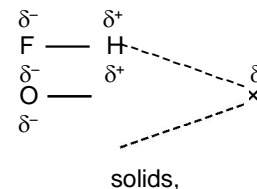
⇒ **IONIC SOLIDS :** All those solids whose constituent particles are ions   solids,

Example : NaCl, CsBr, AgBr, CsCl
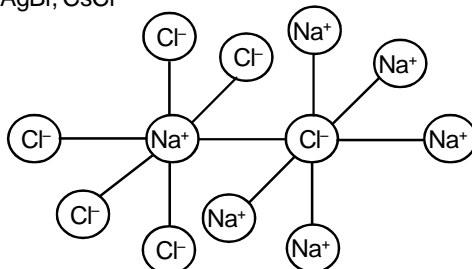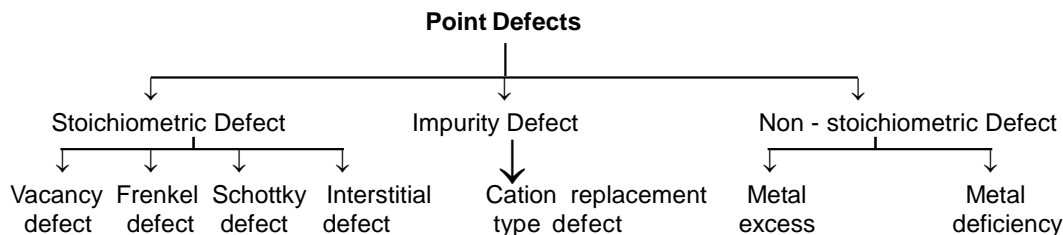
⇒ **METALLIC SOLIDS :**
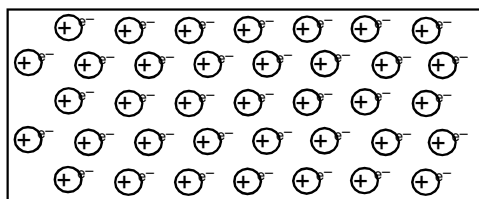
Electron sea model

⇒ All those solids which are bonded by metallic bonds are called metallic solids.

⇒ Inner core electrons are immobile

⇒ Metallic solids show a great electrical conductivity due to availability of large number of free electrons whose movements constitute electric current.

⇒ Metallic solids are malleable and ductile.

⇒ Metallic solids have lustre.

⇒ Metallic solids have good thermal conductivity.

⇒ **COVALENT SOLIDS OR NETWORKED SOLIDS :**

154 pm
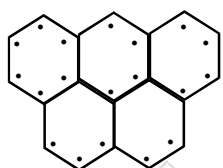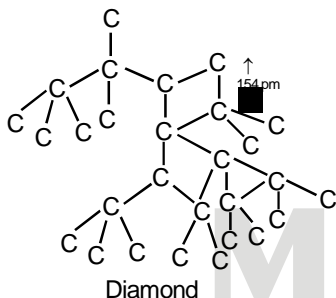
Graphite (in top view)

Diamond

(I) Whenever electric field is applied, electrons move between the layers.

(II) Graphite is a good conductor of electricity due to availability of free electrons.

(III) Networked solids are hard and brittle.

(IV) Carbon - carbon bond has got partial double bond character in graphite.

(V) Two layers in graphite are attached with each other by weak vander waal force.

**(VI)** Graphite can be used as a lubricant at high temperatures .

⇒ **Point Defects**

```
                              Point Defects
        ┌─────────────────────────┼─────────────────────────┐
Stoichiometric Defect        Impurity Defect        Non - stoichiometric Defect
  ┌──────┬──────┬──────┐           │                   ┌──────────┐
Vacancy Frenkel Schottky Interstitial  Cation replacement  Metal        Metal
defect  defect  defect   defect        type defect         excess       deficiency
```

⇒ **Point Defects :** All those defects in which atoms are found missing from their lattice points are called point defects.

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⇒ **Stoichiometric Defects :** All those defects which do not affect the formula or stoichiometry of the compound are called stoichiometric defects. It is of four types :

(I) **Vacancy Defect :** When atoms are found missing from the atomic crystals, such defects are called vacancy defects.
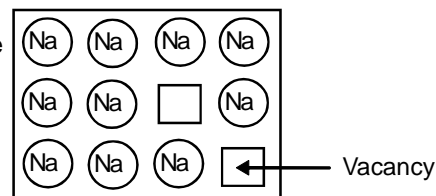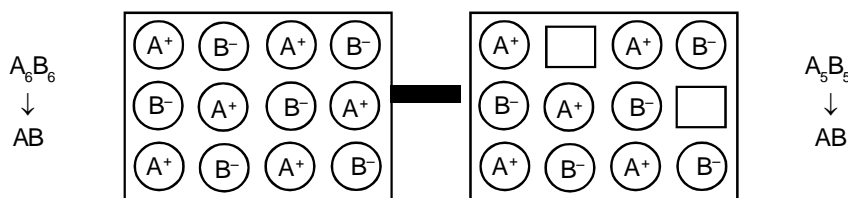
(II) **Interstitial Defect (a) :** When constituent particles of ionic or atomic crystal occupy interstitial position, such type of defect is called interstitial defect.

(b) Interstitial defect results in increase density of the crystal.

$$A_6B_6 \quad \xrightarrow[\text{defect}]{\text{after}} \quad A_7B_7$$
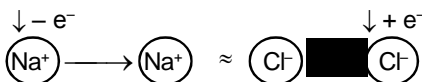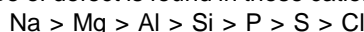$$\downarrow \qquad\qquad\qquad \downarrow$$
$$AB \qquad\qquad\qquad AB$$
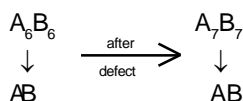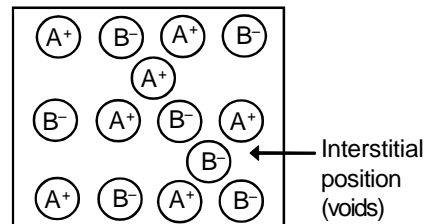
(III) **Schottky Defect : (a)** Whenever equal number of cation and anions are found missing from their lattice points, the defect is called . Schottky defect.
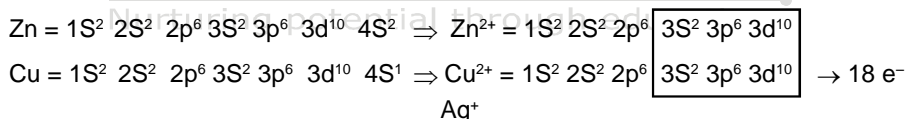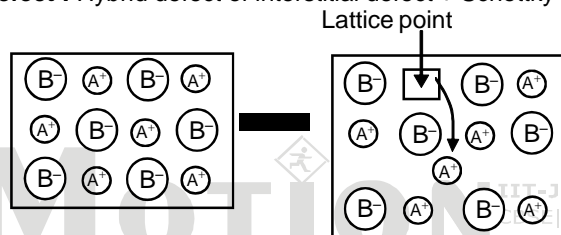
$$A_6B_6 \qquad\qquad\qquad\qquad\qquad\qquad\qquad A_5B_5$$
$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$
$$AB \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad AB$$

(b) This type of defects decrease the density of the crystal.

(c) This type of defect is found in those cations and anions which have comparable size .

$$Na > Mg > Al > Si > P > S > Cl$$

$$\downarrow -e^- \qquad\qquad\qquad\qquad\qquad \downarrow +e^-$$

$$(Na^+) \longrightarrow (Na^+) \approx (Cl^-) \blacksquare (Cl^-)$$

Example : $NaCl, CsCl, CsBr, AlCl_3$

(IV) **Frenkel Defect :** Hybrid defect of interstitial defect + Schottky Defect

Lattice point

$$Zn = 1S^2\ 2S^2\ 2p^6\ 3S^2\ 3p^6\ 3d^{10}\ 4S^2 \Rightarrow Zn^{2+} = 1S^2\ 2S^2\ 2p^6\ \boxed{3S^2\ 3p^6\ 3d^{10}}$$

$$Cu = 1S^2\ 2S^2\ 2p^6\ 3S^2\ 3p^6\ 3d^{10}\ 4S^1 \Rightarrow Cu^{2+} = 1S^2\ 2S^2\ 2p^6\ \boxed{3S^2\ 3p^6\ 3d^{10}} \to 18\ e^-$$
$$Ag^+$$
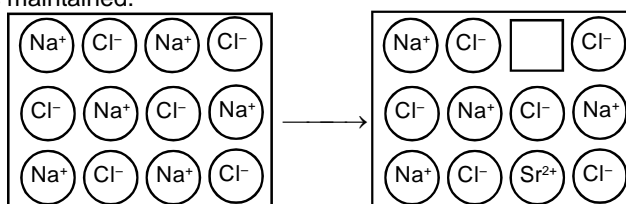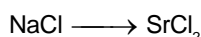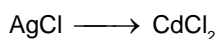
Pseudo inert gas configuration → size is very small →
Large difference in anion and cation size → Cation can be accomodated in interstitial space
Example : $ZnCl_2$, $AgCl$, $CuCl$

⇒ AgBr is an exception which can show both schottky defect and Frenkel defect.

⇒ **Impurity Defect (Cation replacement type defect) :**
Such type of defect in which a new cation or anion from outside replaces the existing ones such that electrical neutrality of the crystal is maintained.
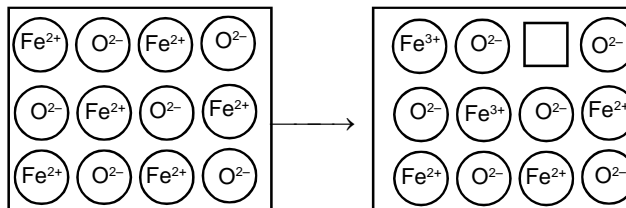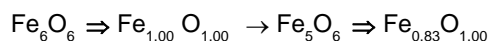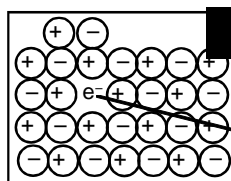
$$AgCl \longrightarrow CdCl_2$$

$$NaCl \longrightarrow SrCl_2$$

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⇒ **Non - stoichiometric defects :** The defects in which the molecular formula of the crystals get altered is called non-stoichiometric defect. It is of two types :

(I) **Metal excess :**

Before Defect → $Na_{14}Cl_{14}$
After Defect → $Na_{15}Cl_{14}$

alkali metal vapour
LiCl → Pink Colour
KCl → Violet Colour

F – centre (German – Farbenzenter for colour centre)

(II) **Metal Deficiency :**

$Fe_6O_6 \Rightarrow Fe_{1.00}\,O_{1.00} \rightarrow Fe_5O_6 \Rightarrow Fe_{0.83}O_{1.00}$

Example : $Fe_xO_1 \rightarrow$ Here x = 0.93 – 0.96
$V_1O_x \rightarrow$ Here x = 0.6 – 1.3 i.e. it shows metal excess and metal deficiency .

Matter

Conductors	Insulators	Semi - Conductors
$\sigma = 10^4$ to $10^7\ \Omega^{-1}\ m^{-1}$	$\sigma = 10^{-20}$ to $10^{-10}\ \Omega^{-1}\ m^{-1}$	$\sigma = 10^{-6}$ to $10^4\ \Omega^{-1}\ m^{-1}$
(Amp.)	(nano A)	(mA or μA)

⇒

Vibratory motion on increasing temperature
$\sigma \propto 1/T$ or $T\uparrow \Rightarrow \sigma$ ■

Interstitial position

$\sigma \propto T$ or $T\uparrow \Rightarrow \sigma \uparrow$

Valence bands

Conduction band

Partially filled valence band

Overlapping bands

Empty conduction band

Empty valence band

Filled valence band

Metals (Conductors)
(a)

Empty conduction band

Large energy gap

Filled valence band

Insulator
(b)

Empty conduction band

Small energy gap

Filled valence band
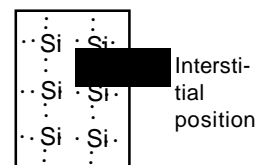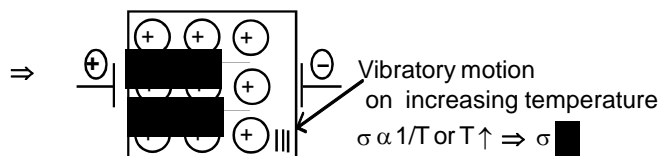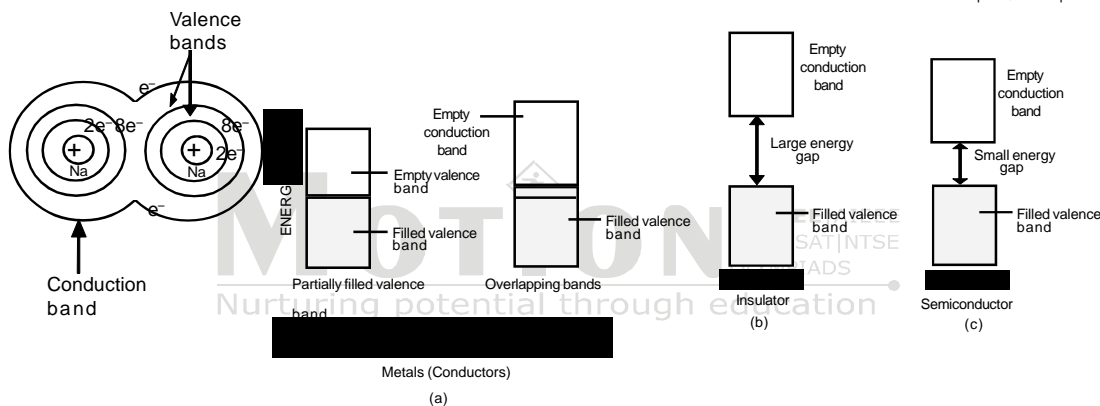
Semiconductor
(c)

Semi conductors

Intrinsic
$Si = 1S^2\,2S^2\,2p^6\,3S^2\,3p^2$
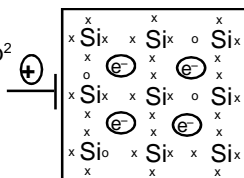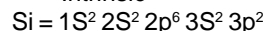
Extrinsic
⇒ Those semiconductors whose conductivity is enhanced by adding some impurity in calculated amount is called as extrinsic semi conductors.
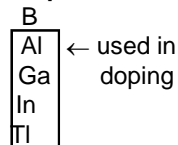
⇒ The pure semi conductors can be called as intrinsic semiconductors because their conductivity is due

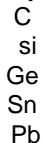⇒ This process of mixing impurity is called doping.

to the electrons which leave the bond and are found in interstitial space .

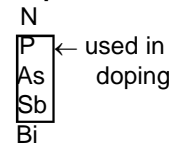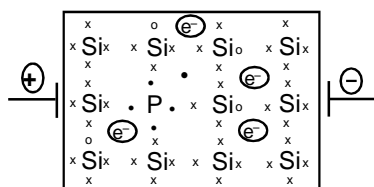$\Rightarrow$ Extrinsic semiconductors also show intrinsic behaviour.

Group –13	**Group –14**	**Group –15**
B	C	N
Al $\leftarrow$ used in	si	P $\leftarrow$ used in
Ga doping	Ge	As doping
In	Sn	Sb
Tl	Pb	Bi

Extrinsic Semi – Conductors

n– type (electron rich semi conductors)
$\Rightarrow$ G – 15 elements are used here for doping

p – type (electron deficient semiconductors)
$\Rightarrow$ G – 13 elements are used here
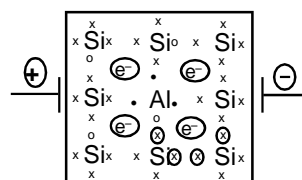

$\Rightarrow$ 1 impurity per 10^{16} atoms

$\Rightarrow$ Here mobile charge carriers are electrons which are negatively charged, Hence n–type.
    Here , $I = I_e$

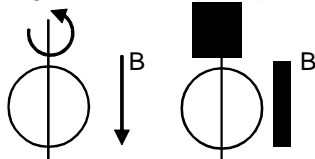$\Rightarrow$ Here mobile charge carrier are positively charged holes hence p – type
    Here , $I = I_e + I_h$

Magnetic properties why ?

Spin Magnetic Moment (SMM)

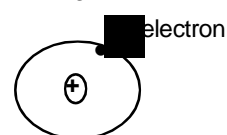

μ_B = 1 B.M (Bohr Magneton)
1 B.M = 9.27×10^{-24} Am^2
μ_B = 9.27×10^{-24} Am^2

Orbital Magnetic Moment (OMM)

$\mu_{OMM} = I \times \mu_B$
where, I = azimuthal quantum number

MAGNETIC PROPERTIES :

The macroscopic magnetic properties of material are consequence of magnetic moments associated with the individual electron. Each electron in an atom has magnetic moment due to two reasons. The first one is due to the orbital motion around the nucleus, and the second is due to the spin of electron around its own axis. A moving electron may be considered to be a small current loop, generating a small magnetic field, and having a magnetic moment along its axis of rotation.

The other type of magnetic moment originates from electron spin which is directed along the spin axis. Each electron in an atom may be thought of as being a small magnet having permanent orbital and spin magnetic moments. The fundamental magnetic moment is Bohr Magneton, μ_s equal to 9.27×10^{-24} Am^2 . For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ (depending upon the two possiblities of the spin). The contribution of the orbital magnetic moment is equal to $\mu_i \mu_B$, where μ_i is the magnetic quantum number of the electron.

Based on the bahaviour in the external magnetic field, the substances are divided different catagories.

(i) **Diamagnetic substances :** Substances which are weakly repelled by the external magnetic field are called diamagnetic substances, e.g. TiO_2, NaCl, Benzene.

(ii) **Paramagnetic substances :** Substances which are attracted by the external magnetic field are called paramagnetic substances, e.g., O_2, Cu^{2+}, Fe^{3+}.

(iii) **Ferromagnetic substances :** Substances which show permanent magnetsim even in the absence of the magnetic field are called ferromagnetic substances e.g., Fe, Ni, Co, CrO_2.

(iv) **Ferrimagnetic Substances :** Substances which are expected to possess large magnetism on the basis of the unpaired electrons but actually have small net magnetic moment are called ferrimagnetic substances, e.g., Fe_3O_4.

(v) **Anti-ferromagnetic substances :** Substances which are expected to posses paramagnetic behaviour, ferromagnetism on the basis of unpaired electron but actually they possess zero not magnetic moment are called anti-ferromagnetic substances, e.g., MnO_2

Note : Ferromagnetic, Anti-ferromagnetic and Ferrimagnetic solids change into paramagnetic at some temperature. It may be further pointed out here that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie Temperature.**

DIELECTRIC PROPERTIES :

Insulators do not conduct electricity because the electrons present in them are hel tightly to the individual atoms or ions and are not free to move. however, when electric field is applied, polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. Thus dipoles are formed. In addition to these dipoles, there may also be permanent dipoles in the crystal. These dipoles may align themselves in an ordered manner so that such crystals have a net dipole moment.

Such polar crystals show the following interersting propeties :

(i) **Piezoelectricity or Pressure - electricity :** When mechanical stress is applied on such crystals so as to deform them, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. A few examples of piezoelectric crystals include Titanates of Barium and Lead, Lead zirconate ($PbZrO_3$), Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and Quarts. These crystals are used as pick-ups in record players where they prodduce electrical signals by application of pressure. They are also used in microphones, ultrasonic generators and sonar detectors.

(ii) **Ferroelectricity :** In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However, on applying, electric field, the direction of polarization changes, this phenomenon is called ferroelectricity due to analogy with ferromagnetism. Some examples of the ferroelectric solids are barium titanate ($BaTiO_3$), Sodium potassium tartarate (Rochelle salt) and Potassium dihydrogen phosphate (KH_2PO_4)

Note : All ferroelectric solids are piezoelectric but the reverse is not true.

(iii) **Anti-ferroelectricity :** In some crystals, the dipoles align themselves in such a way that alternately, they point up and down so that the crystal does not posses any net dipole moment. Such crystals are said to be anti-ferroelectric. A typical example of such crystals is Lead zirconate ($PbZrO_3$)

Superconductivity :

A substance is said to be superconducting when it offers no resistance to the flow of electricity.

Isomorphism :

The property shown by crystals of different chemical substances which exhibit the same crystalline form is known as isomorphism.

Such substances have similar chemical formula, e.g., Na_2HPO_4. $12H_2O$ and Na_3ASO_4. $12H_2O$

• Chemically substances having same type of formulae are not necessarily Isomorphous.

SOLVED EXAMPLES

Ex.1 *A face-centred cubic solid of an element A has a largest sized guest atom B at the body centre octahedral hole if insertion of B doesn't affect the original unit cell dimension; determine the packing fraction of the solid.*

Sol. In the given solid, there is one B and four A per unit cell.
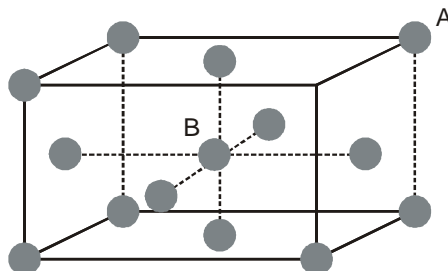
Also, under the condition of largest possible size of B, it will be in contact of A present at the face centres only and the following relatinship will exist :
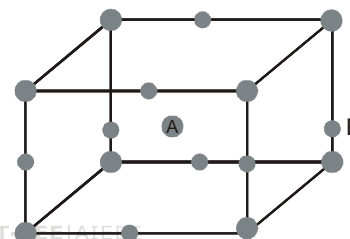
$$4r_A = \sqrt{2} \qquad \text{and} \qquad 2(r_A + r_B) = a$$

solving $\dfrac{r_B}{r_A} = 0.414$

Now, packing fraction

$$(\phi) = \frac{4\pi}{3}(4r_A^3 + r_B^3) \times \frac{1}{a^3} = \frac{4\pi}{3}(4r_A^3 + r_B^3) \times \frac{1}{1\sqrt{2r_A^3}}$$

$$= \frac{\pi}{12\sqrt{2}}\left[4 + \left(\frac{r_B}{r_A}\right)^3\right] = \frac{\pi}{12\sqrt{2}}[4 + (0.414)^3] = 0.7536$$

Ex.2 *An element A has BCC structure and another guest atom B, of largest possible size are present at each edge centres of unit cell of A but without disturbing the original unit cell dimension. Determing the void percentage of this solid.*

Sol. Since B is closer to corner than to face centre, in close contact,
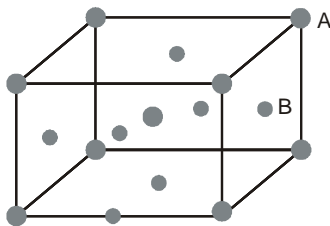
$$2(r_A + r_B) = a$$

$$4r_A = \sqrt{3}\,a \qquad \Rightarrow \frac{r_B}{r_A} = 0.155$$

In a unit cell, there are two A and $12 \times \dfrac{1}{4} = 3B$

$\Rightarrow$ Packing fraction $(\phi) = \dfrac{4\pi}{3}(2r_A^3 + 3r_B^3) \times \dfrac{1}{a^3}$

$$= \frac{\sqrt{3}\,\pi}{16}\left[2 + 3\left(\frac{r_B}{r_A}\right)^3\right] = 0.684 \quad \Rightarrow \text{Void space} = 31.6\%$$

Ex.3 *An element A has a BCC structure and another guest atoms B, of largest possible size, are present at the face centres, but wihtout disturbing the unit cell dimension. Determine the packing fraction of this solid.*

Sol. In the above solid, face centres are closer to body centre, therefore, the relationship.

$$2(r_A + r_B) = 0$$

$$4r_A = \sqrt{3}a \qquad \Rightarrow \quad \frac{r_B}{r_A} = 0.155$$

Now, packing fraction $(\phi) = \frac{4\pi}{3}(2r_A^3 + 3r_B^3) \times \frac{1}{a^3}$

$$= \frac{\sqrt{3}\,\pi}{16}\left[2 + 3\left(\frac{r_B}{r_A}\right)^3\right] = 0.684$$

Ex.4 *Calcium has face-centred cubic lattice and radius of calcium atom is 195.6 picometre. Determine the number of Ca atoms present on surfaces of a mm³ block of calcium metal assuming that atoms in the closest packing calcium metal assuming that atoms are in the closest packing.*

Sol. In FCC, the relation is

$4r = \sqrt{2}a \Rightarrow a = 2\sqrt{2}\,r = 553.24 \times 10^{-9}$ mm.

$\Rightarrow$ Area of a face of unit cell $= a^3 = 3.06 \times 10^{-13}$ mm²
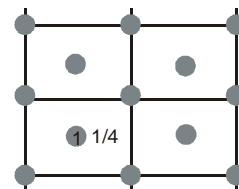
$\Rightarrow$ Surface area of metal block $= 6$ mm²

$\Rightarrow$ Total number of faces of unit cells present on surface

$$= \frac{6}{3.06 \times 10^{-13}} = 1.96 \times 10^{13}$$

Each face contributes two Ca atoms on surface as shown in diagram.

$\Rightarrow$ Total number of Ca atoms present on surface

$$= 2 \times 1.96 \times 10^{13} = 3.92 \times 10^{13}$$

Ex.5 *An atom crystallises in hexogonal closed pack arrangement. Determine dimensions (radius and length) of a large cyclindrical atom that can be accommodated in the centre of HCP, in terms of radius of host atom.*

Sol. The cylinder will pass through centre of middle layer and will lie between the face centres.
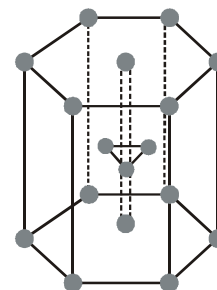
Therefore,

Height of cylinder (h) = height of hexagon (h) = 2r

Since, in HCP : $H = 4\sqrt{\dfrac{2}{3}}\,r$, where r = radius of atoms.

$$\Rightarrow \qquad h = \left(4\sqrt{\frac{2}{3}} - 2\right)\,r = 1.266\ r$$

Also, if R is the radius of cylinder, then in the case of closet contact :

$$\frac{R}{r} = 0.155 \quad \Rightarrow \quad R = 0.155\ r$$
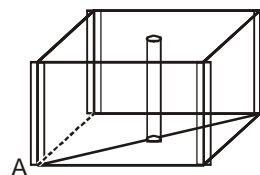$$\Rightarrow h = 1.266\ r$$

Ex.6   *A uniform cylindrical, polymer molecule crystallizes in body centred cubic array. Determine the packing fraction of this polymer in solid state assuming that molecules are in their closest contact.*

Sol.   The arrangement of molecules can be represented as follows :

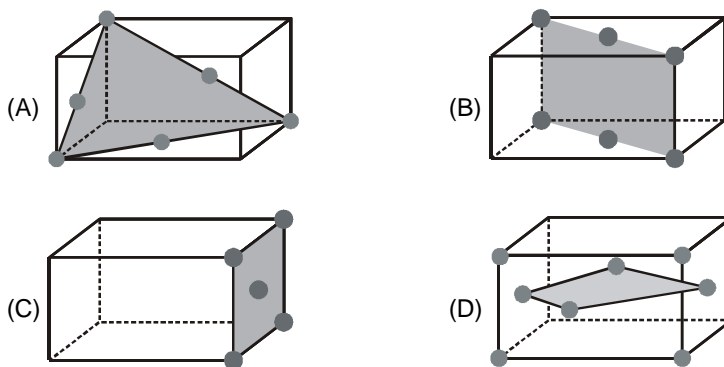Here, $4r = \sqrt{2}\, l$ $\Rightarrow$ $I = 2\sqrt{2}r$

Packing fraction (ϕ) = $\dfrac{2\pi r^2 l}{I^3} = \dfrac{2\pi r^2}{I^2}$

$= \dfrac{\pi}{4} = 0.785$

Ex.7   *Show the following arrays of atoms on a plane in an atomic FCC.*

(A)   (B)   (C)   (D)

Sol.   (A)   (B)

(C)   (D)

Ex.8   *Cesium bromide crystallizes in cubic arrangement like CsCl. Given the ionic radii of Cs⁺ and Br⁻ are 1.88 Å and 1.82 Å respectively, determine the packing fraction.*

Sol.   Here Cs^+ ion is at body centre and Br^- at the corners, therefore the relationship is

$2(r_+ + r_-) = \sqrt{3}\, a\ = 2\,(1.88 + 1.82)$ Å

$\Rightarrow$ $a = 4.27$ Å

Packing fraction (ϕ) = $\dfrac{4}{3}\pi\left(\dfrac{r_+^3 + r_-^3}{a^3}\right) = \dfrac{4}{3}\pi\left(\dfrac{(1.88)^3 + (1.82)^3}{(4.27)^3}\right) = 0.6807$

Ex.9   *Titanium metal crystallises in a BCC arrangement and radius of an atom is 142 picometre. Determine atomic weight of titanium if density is 16.6 g/cm³. Also determine the number of unit cells present in a 5 cm³ block of titanium metals.*

Sol.   In BCC arrangement of atoms the relatioship between edge length radius of atom is

$4r = \sqrt{3}a$

Density (ρ) = $\dfrac{NM}{N_A V}$

Where,   N = Number of atoms per unit cell,
M = Molar mass, N_A = Avogadro's number
V = Volume of unit cell

$\Rightarrow 16.6 = \dfrac{2M}{6.023\times10^{23}\left(\dfrac{4}{\sqrt{3}}\times 142\times10^{-10}\right)^3}$

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Here, radius is taken in cm unit since, density is in g/cm^3 unit.

Solving : M = 176. Also mass of 5 cm^3 block = 5 × 16.6 = 83 g

$\Rightarrow$ Number of atoms is 5 cm^3 block = $\dfrac{83}{176}$ × 6.023 × 10^{23}

$\Rightarrow$ Number of unit cells = $\dfrac{\text{No. of atoms}}{2}$ = $\dfrac{83 \times 6.23 \times 10^{23}}{176 \times 2}$ = 1.42 × 10^{23}

Ex.10 *Copper metal crystallizes in face-centred cubic arrangement and surface of adjacent atoms along the edge of unit cell are 106 picometre apart. Determine the density of metal. Atomic mass of copper metal is 63.5 u.*
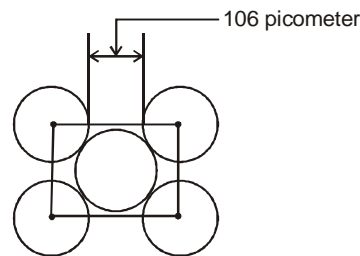
Sol. According to the given information, a view of one face of the unit cell will be as shown below.

In FCC; $4\sqrt{2}\,a$

The given distance is $a - 2r = a - \dfrac{a}{\sqrt{2}}$

$$= a\left[\dfrac{\sqrt{2}-1}{\sqrt{2}}\right] = 106 \text{ pm}$$

$\Rightarrow$ $\qquad$ a = 362 pm = 3.62 × 10^{-8} cm

$\Rightarrow$ $\qquad$ Density $(\rho) = \dfrac{4 \times 63.5}{6.023 \times 10^{23}(3.62 \times 10^{-8})^3}$ = 8.89 g/cm^3

Ex.11 *Potassium crystallizes in "body centred cubic" arrangement and the surfaces of adjacent atom along the edges of unit cells are 71.4 picometre apart. Determine the density of metal. Atomic weight of K = 39.*

Sol. In BCC, the relationship between edge length and radius of atom is

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

Also, given $\qquad$ $a - 2r = 71.4 \times 10^{-10}$ cm

$\Rightarrow$ $\qquad$ $a - \dfrac{\sqrt{3}}{2}a = a\left[\dfrac{2-\sqrt{3}}{2}\right]$ = 71.4 × 10^{-10} cm

$\Rightarrow$ $\qquad$ a = 5.329 × 10^{-10} cm

$\Rightarrow$ $\qquad$ Density $(\rho) = \dfrac{2 \times 39}{6.023 \times 10^{23}(5.329 \times 10^{-8})^3}$ = 0.855 g/cm^3

Ex.12 *Magnesium oxide has the NaCl structure and radii of Mg^{2+} and O^{2-} ions are 0.86 A and 1.24 A. Determine the density of magnesium oxide solid.*

Sol. In a unit cell, there are four unit of MgO and edge-length of the unit cell is

a = 2 (radius of cation + radius of anion)

= 2 (0.86 + 1.24) = 4.2 Å

Density $(\rho) = \dfrac{4 \times 40}{6.023 \times 10^{23}(4.2 \times 10^{-8})^3} = 3.585$ g/cc

Ex.13 *An unknown substance that uses gas at room temperature can be condensed to a solid at –80°C. As a solid, it is found to have cubic unit cell, 5.15 Å on each side, containing four molecules. The density of solid is 0.73 g/cm^3. What is the density of the substance as a gas at 27°C and at a pressure of 1.00 atmopshere ?*

Sol. For a cubic unit cell :

$$\text{Density } (\rho) = \dfrac{nM}{N_A a^3}$$

Where, n : No. of molecules per unit cell,

$\qquad$ M = Molar mass

$\qquad$ N_A = Avogadro's constant,

a = Edge length of unit cell.

$$\Rightarrow \quad 0.73\,g/cm^3 = \frac{4 \times M}{6.023 \times 10^{23}(5.15 \times 10^{-6}\,cm)^3}$$

M = 15 g/mol M

Molar mass of a substance is independent of state.

$$\Rightarrow \quad \text{As a gas, Density } (\rho) = \frac{pM}{RT} = \frac{1.05 \times 15}{0.082 \times 300} = 0.6097 \text{ g/L.}$$

Ex.14 ***Aluminium crystallizes in a cubic lattice with an edge of 404 pm and density of metal is 2.70 g/cm³. What type of cubic is formed by aluminium ?***
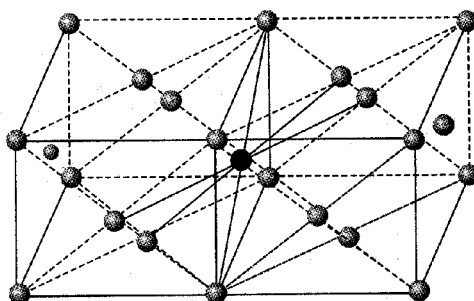
Sol. If there is "n" aluminium atoms per unit cell :

$$\text{Density } (\rho) = \frac{nM}{N_A a^3}$$

$$\Rightarrow \quad 2.70 = \frac{n \times 270}{6.023 \times 10^{23}(4.04 \times 10^{-8}\,cm)^3}$$

$\Rightarrow$ n = 6.023 × 10²² (4.04 × 10⁻⁸)⁻³ = 3097 ≈ 4

Hence, Al forms face-centred cubic (FCC) lattice.

the coordination number of Al in FCC is 12 i.e., each Al atom has twelve other Al atoms in its nearest neighbour.

An atom of aluminium (solid black) present on the centre of middle vertical face is equidistant from the twelve adjoining atoms, hence, coordination number of an atom in FCC arrangement is twelve.

Ex.15 ***Except helium, all the noble gases crystallize with cubic close packed structures. Derive an equation relating atomic radius to the density of cubic close packed solid of given mass and apply it to deduce the relative size of Ar and Xe if their densities are 1.4 g/cm and 2.83 g/cm³ respectively.***

Sol. For a CCP solid : $\rho = \dfrac{nM}{n_A a^3}$

Where, ρ = Density, n = No. of atoms/unit cell

M = Molar mass, N_A = Avogadro constant,

and   a = Edge length

$$\Rightarrow \quad \rho = \frac{4M}{N_A(2\sqrt{2}\,r)^3} = \frac{M}{4\sqrt{2}\,N_A r^3}$$

$$\Rightarrow \quad \frac{\rho_{x_e}}{\rho_{Ar}} = \frac{2.83}{1.40} = \frac{131}{40}\left(\frac{r_{Ar}}{r_{Xe}}\right)^3 \quad \Rightarrow \quad \frac{r_{Xe}}{r_{Ar}} = \left(\frac{131 \times 1.4}{40 \times 2.83}\right)^{1/3} = 1.174$$

Ex.16 ***All alkali metals crystallize into BCC strucutres.***

(a) Find an equation relating the metallic radius to the density of a BCC solid in terms of its molar mass.

(b) Determine the relative size of Cs atom compared to a Li atom, if their densities are 1.87 g/cc and 0.53 g/cc, respectively.

Sol.   (a) For a BCC solid of an element, there are two atoms per unit cell.

$\Rightarrow$ Density (ρ) = $\dfrac{2 \times M}{6.023 \times 10^{23} \, a^3}$

Also; in BCC of an atomic solid,

$$\rho = \dfrac{2M \times 3\sqrt{3}}{6.023 \times 10^{23} \times 64 \, r^3} = 2.696 \times 10^{-23} \, \dfrac{M}{r^3}$$

(b) $\dfrac{\rho_{Cs}}{\rho_{Li}} = \dfrac{1.87}{0.53} = \dfrac{133}{7}\left(\dfrac{r_{Li}}{r_{Cs}}\right)^3$

$\Rightarrow$ $\dfrac{r_{Cs}}{r_{Li}} = 1.753$ $\Rightarrow$ $r_{Cs} = 1.753 \, r_{Li}$

Ex.17   *Some of the metals with BCC structures are not close packed. Therefore, their densities would be greater if they were to change to a cubic close packed structure. What would be density of a metal if it had a cubic close packed structure rather than BCC? Its actual density is 19.3 g/cc.*

Sol. $\rho_{CCP} = \dfrac{4M}{N_A a_{CCP}^3}$ and $\rho_{BCC} = \dfrac{2M}{N_A a_{BCC}^3}$

$\Rightarrow$ $\dfrac{\rho_{CCP}}{\rho_{BCC}} = 2\left(\dfrac{a_{BCC}}{a_{CCP}}\right)^3$: Also in FCC $4r = \sqrt{2}\, a_{CCP}$

in BCC, $4r = \sqrt{3}\, a_{BCC}$

$\Rightarrow$ $\dfrac{\rho_{CCP}}{19.3} = 2\left(\dfrac{2}{3}\right)^{3/2} = 1.08867$ $\Rightarrow$ $\rho_{CCP} = 21 \, g/cc$

Ex.18   *How many unit cells of KBr are present in a 1.00 mm³ of KBr, KBr crystallizes in NaCl type of crystal lattice and its density is 2.75 g/cm³.*

Sol.   In a unit cell of KBr, there are four formula units of KBr.

Therefore, density (ρ) = $\dfrac{4 \times 119}{6.023 \times 10^{23} \times a^3} = 2.75$

$\Rightarrow a^3 = 2.778 \times 10^{-22} \, cm^3 = 2.778 \times 10^{-19} \, mm^3$

$\Rightarrow$ No. of unit cells per mm³ = $\dfrac{10^{19}}{2.778} = 3.6 \times 10^{18}$