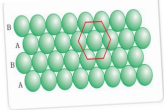
Flow Chart Of Complete Chapter (NCERT)

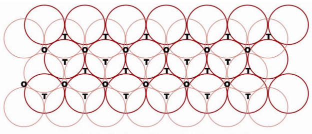
Solid State

- Classification of cystalline Solid
  - Crystal lattice
  - Unit cell
- No. of atoms in a unit cell
- Closed Packed Structure
  - In 1 D

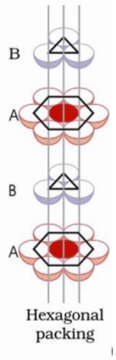

Close packing of spheres in one dimension

  - In 2 D
    - Square
    - Hexagonal

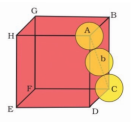



A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

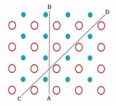
  - In 3 D
    - Tetrahedral void
    - octahedral void
    - HCP
    - CCP / FCC



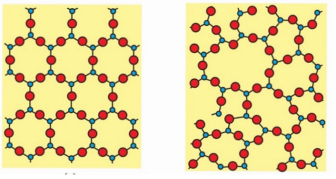
- Packing Efficiency



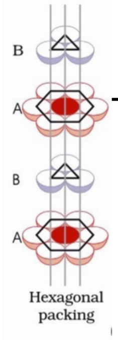
- Magnetic Properties
  - Paramagnetic / Diamagnetic
  - Ferromagnetic / Ferrimagnetic
  - Antiferromagnetic
- Characteristics of Solid State



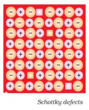
- Amorphous & Crystalline solid

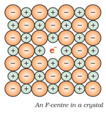


- Defects in Solids

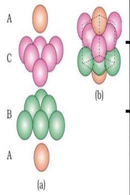


  - Stoichiometric Defect
    - Vacancy
    - Interstitial
    - Frenkel
    - Schottky

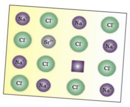

Schottky defects


An F-centre in a crystal

  - Impurity Defect



  - Non Stoichiometric Defect
    - Metal Excess Defect
    - Metal Deficiency Defect



- Electrical Properties
  - Insulator
  - Conductor
  - Semiconductor

The Solid State

→ As we know, matter can exist in three states : Solid , liquid and gas. In this chapter we will focus only on solid state.

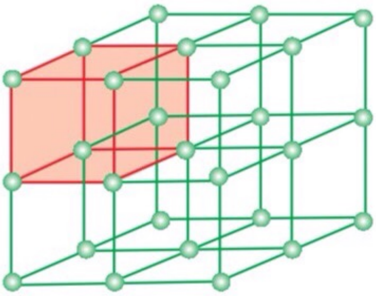
→ Every substances have two opposing forces in it :→

(i) The attractive forces between the particles which tend to keep the particles closer.

(ii) The thermal energy which tends to keep them apart by making them move faster.

→ At sufficiently low temperature , the thermal energy is low and intermolecular forces bring them close and particles occupy fixed positions. Particles can still oscillate about their mean positions. This substance exists in solid state.

General characteristics of solid state :—



(i) They have definite mass , volume and shape.

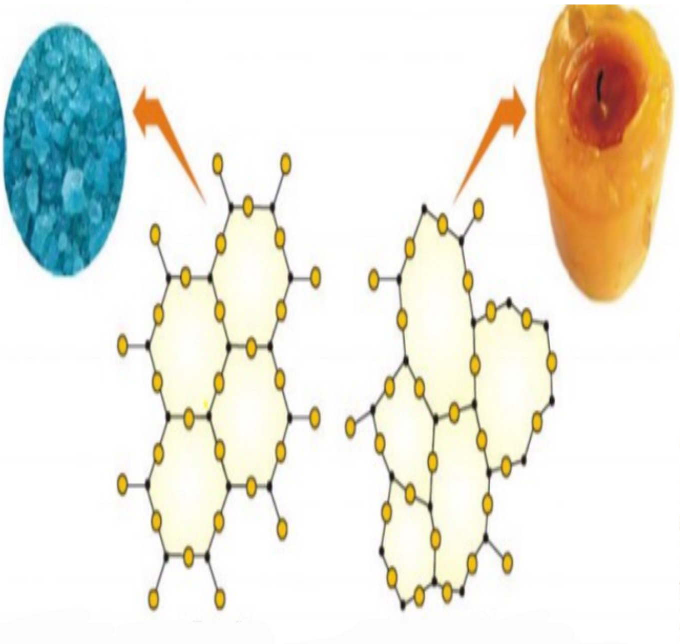
(ii) Intermolecular distances are short.

(iii) Intermolecular forces are strong.

(iv) Their constituent particles [atoms, molecules or ions] have fixed positions and can only oscillate about their mean positions.

(v) They are incompressible and rigid.

Types of solids [Based on arrangement of particles] :— There are two types of solid.



(i) **Crystalline Solid** —: It consist of a large no. of small crystals, each of them having a definite characteristic geometrical shape. It has long range regular pattern of arrangement of particles.

Example → NaCl Crystal | Quartz

(ii) **Amorphous Solid** —: It consist of particles of irregular shape. And has short range order. Example → Quartz glass.

Anisotropic Properties :- [Anisotropy]

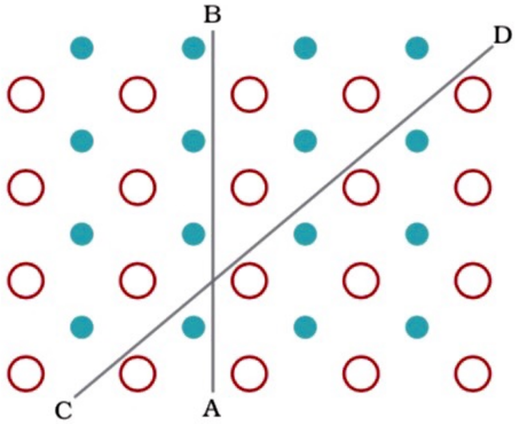
→ It can be defined as a difference in material's physical or mechanical properties (like refractive index, Conductivity, tensile strength) in different directions.

→ Cystalline solids are anisotropic in nature. This anisotropy in crystals is due to different arrangement of particles along different directions.

[CBSE 2014C | Delhi 2011] (1M)

A → B : Regular Pattern

C → D : Regular Pattern



But Pattern in A – B is different from C – D.

Isotropic :- Amorphous solids are isotropic in nature. It is because there is no long range order in them and arrangement is irregular along all the directions. so value of any physical property would be same along any directions.

Difference between Crystalline and Amorphous Solids

(CBSE 2000C | Delhi 2017) (2M)

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Classification of crystalline Solids [Based on interparticle forces] :-

Crystalline Solids

- Ionic Solids
- Covalent | Network Solids
- Metallic Solids
- Molecular Soli

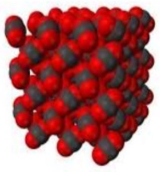
Molecular Solids :-

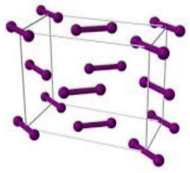
(i) **Non - Polar molecular solids** :- This solid is formed by either atoms (Ar, He) or molecules formed by non - polar covalent bonds (H_2, Cl_2).

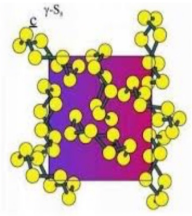
→ In these solids atoms or molecules are held by weak dispersion forces or London forces. These solids are soft and non-conduc of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) **Polar molecular solids** -: The molecules of substances [like CO_2 , HCl] are formed by polar covalent bonds. Molecules are held together by dipole dipole interactions.

→ These solids are soft and non conductors of electricity.


Carbon Dioxide

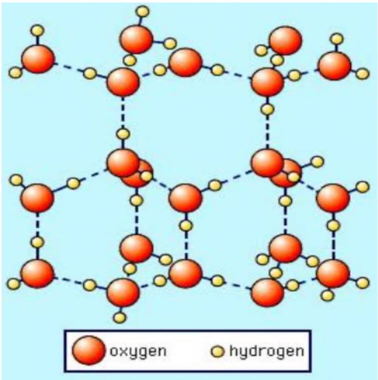

Iodine (I_2)


Sulfur (S_8)

→ Melting Points : PMS > NPMS

→ At room temperature, most of them are gases or liquids.

(iii) **Hydrogen bonded molecular solids** -: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms.



→ Strong H-bonding is present in H_2O (solid) : Ice

→ They are non-conductors of electricity.

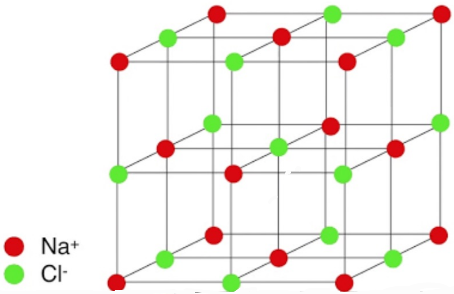
→ At room temperature they are volatile liquids or soft solids.

Ionic Solids :- Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by electrostatic forces. These solids are hard and brittle in nature.

→ They have high M.P. and B.P.

→ In these solids, ions are not free to move. So, they are electrical insulators in solid state.

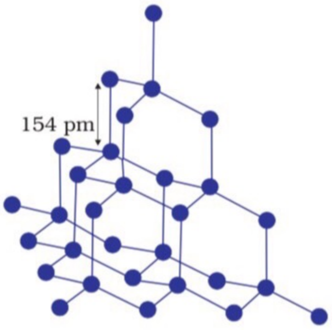
→ But in molten state or when dissolved in water the ions become free to move about and they conduct electricity.



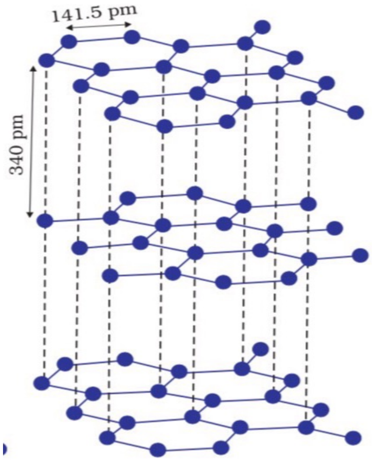
Metallic solids :- Metals are collection of ⊕ve ions surrounded by and held together by a sea of free electrons. Example → Na metal crystal. [CBSE 2016/2014C Delhi 2010] (1M)

Covalent / Network solids -: Crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms.

→ For example : Diamond, Silicon Carbide graphite etc.

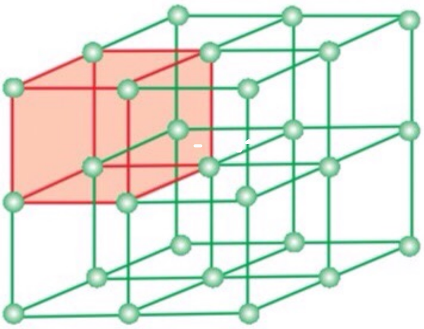


Network structure of diamond



Structure of graphite

Type of Solid	**Constituent Particles**	**Bonding/ Attractive Forces**	**Examples**	**Physical Nature**	**Electrical Conduc-tivity**	**Melting Point**
(1) Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$	Hard Soft	Insulators Conductor (exception)	Very high



Crystal lattice :- A regular 3D arrangement of points [Constituent particles] in space is called a crystal lattice.

Characteristics of a crystal lattice :-

(i) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule or an ion.

(ii) Each point in a lattice is called lattice point | lattice site.

(iii) Lattice points are joined by straight lines to bring out the geometry of lattice.

Unit Cell :- It is the smallest portion of a crystal lattice. When it repeate in different directions generates the entire lattice. [Delhi 2011 / CBSE 2011] (1M)

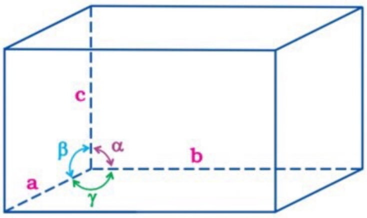


Illustration of parameters of a unit cell

→ a, b, c : Three edges [length]

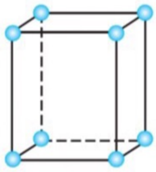
→ α, β, γ : Angles between edges

→ Six Parameters.

[CBSE 2015 / 2011
Delhi 2009] (1M)

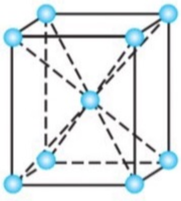
Types of unit cell -:

(i) **Primitive Unit cells -:** Constituent particles are present only on the corner of unit cell.

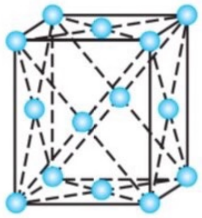

Primitive

(ii) **Centered unit cells -:** When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners.

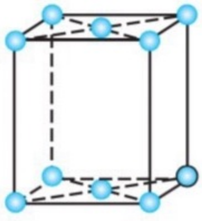
(a) Body - centered unit cells -: When a unit cell contains one particle at its body centre besides the ones that are at its corners.

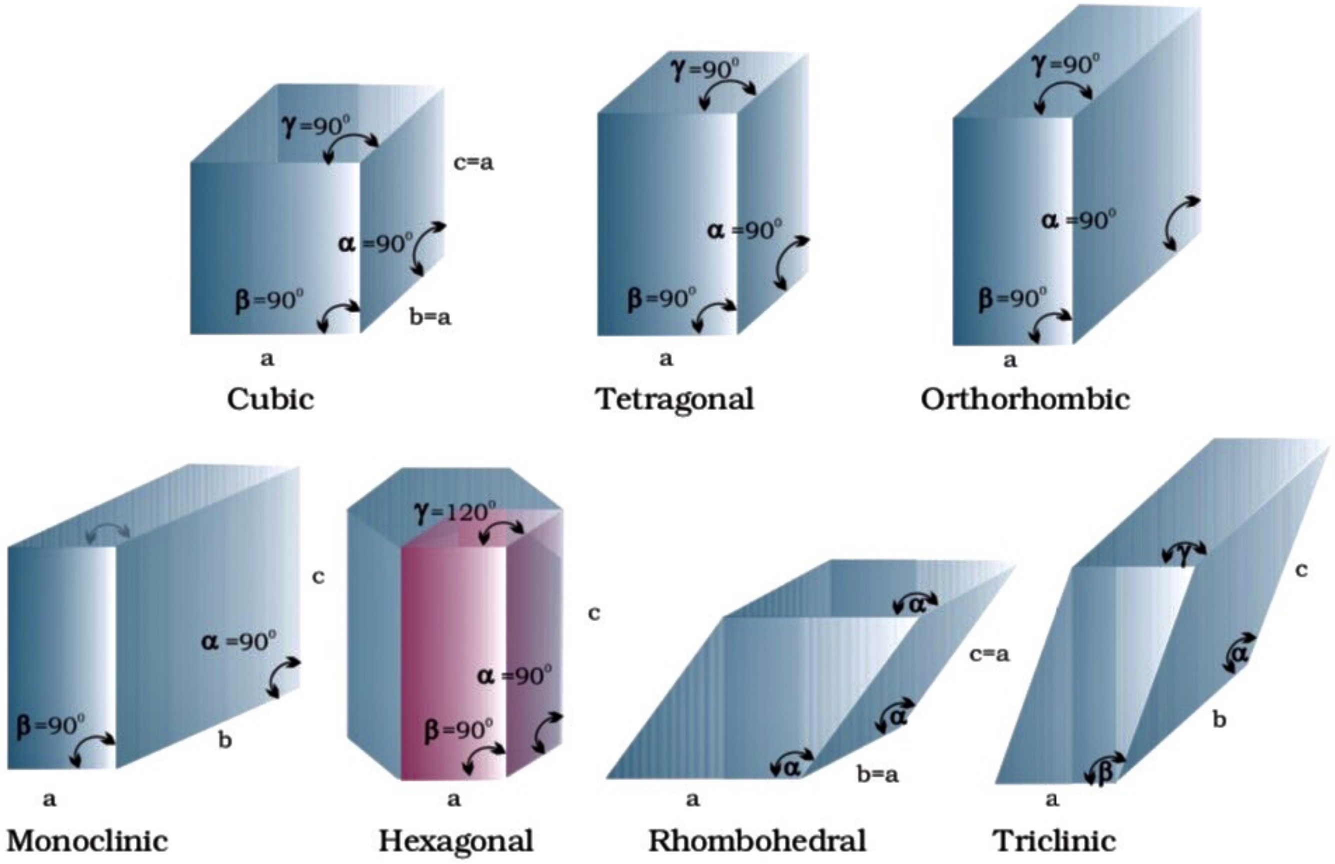

Body-centred

(b) Face - centered unit cells -: When a unit cell contains one particle at centre of each face besides the ones that are at its corners.

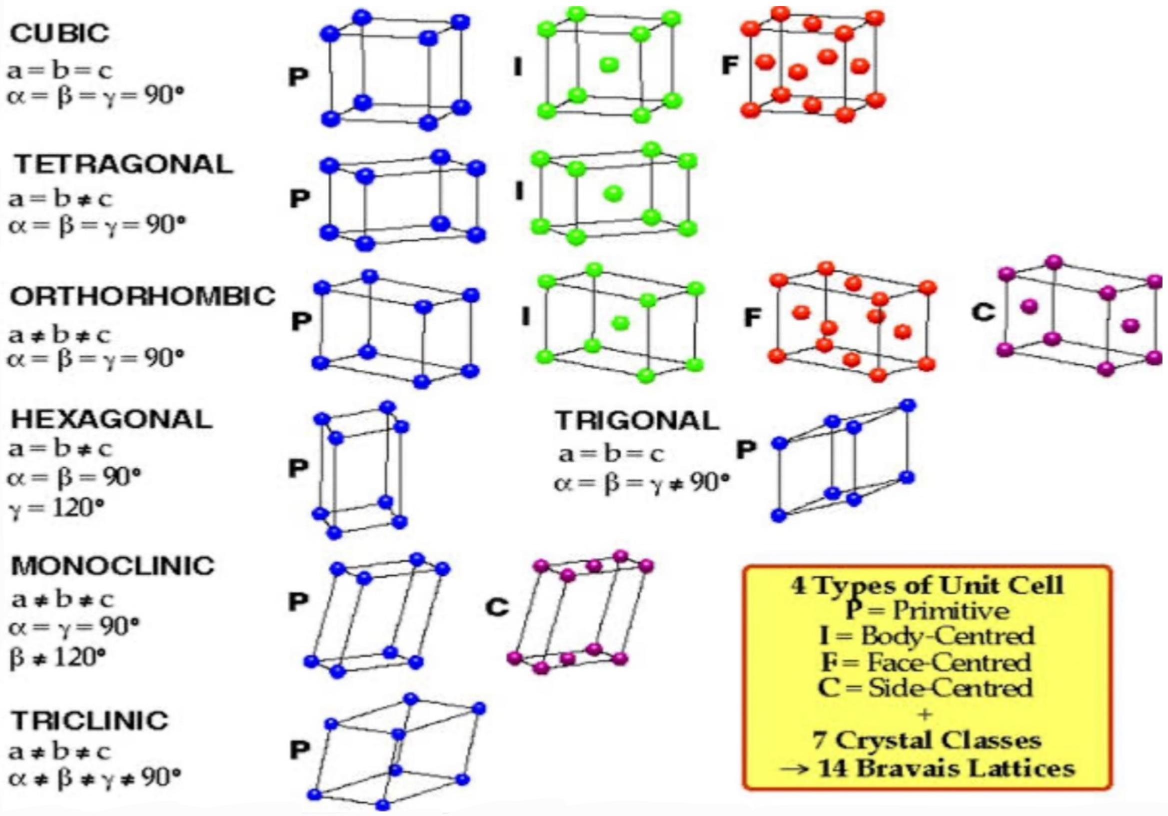

Face-centred

(c) End - centered unit cells -: In such a unit cell, one particle is present at the centre of any two opposite faces besides the ones present at its corners.


End-centred

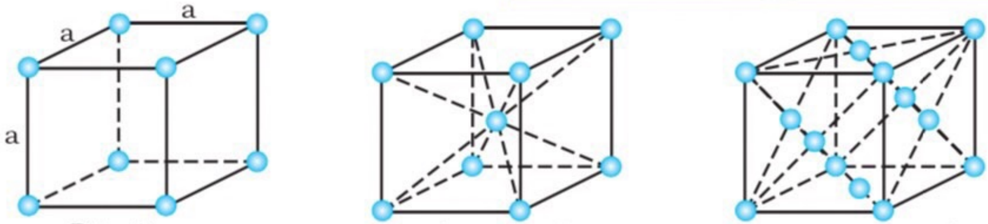


Seven primitive unit cells in crystals



→ There are 7 primitive unit cells. And 14 possible 3D lattices. → [Bravais Lattices

Unit Cells of 14 Types of Bravais Lattices

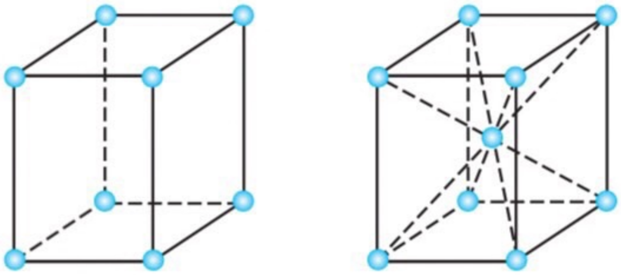


Primitive (or simple)

Body-centred

Face-centred

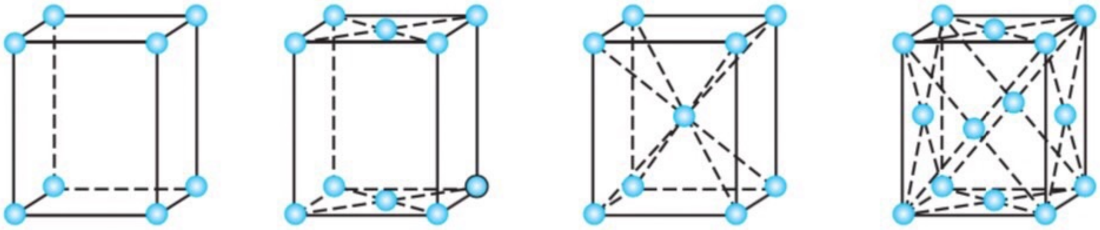
The three cubic lattices: all sides of same length, angles between faces all 90°



Primitive

Body-centred

The two tetragonal: one side different in length to the other, two angles between faces all 90°



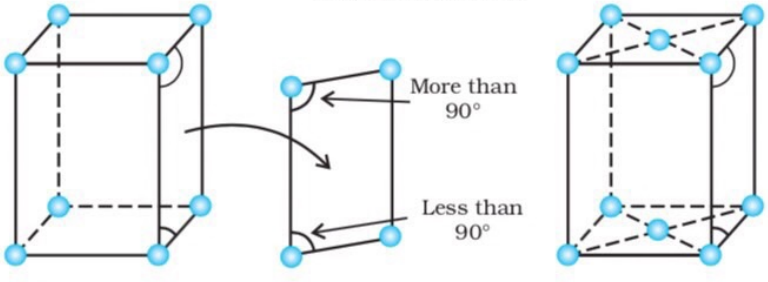
Primitive

End-centred

Body-centred

Face-centred

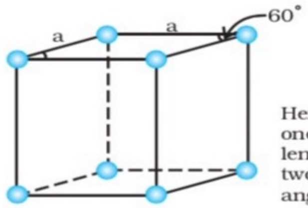
The four orthorhombic lattices: unequal sides, angles between faces all 90°



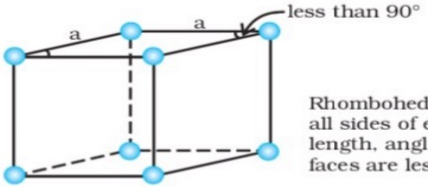
Primitive

End-centred

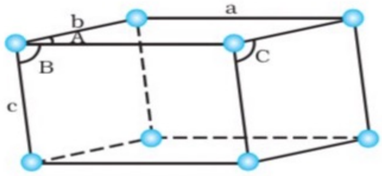
The two monoclinic lattices: unequal sides, two faces have angles different to 90°



Hexagonal lattice– one side different in length to the other two, the marked angles on two faces are 60°

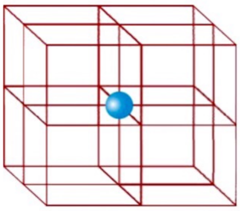


Rhombohedral lattice– all sides of equal length, angles on two faces are less than 90°



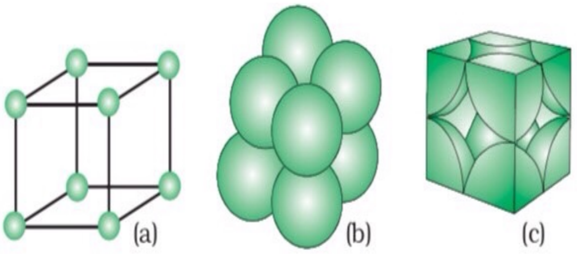
Triclinic lattice– unequal sides a, b, c, A, B, C are unequal angles with none equal to 90°

Number of atoms in Unit Cell -:



(i) Primitive cubic Unit cell -:

→ In a simple cubic unit cell, each corner atom is shared between 8 unit cells. So contribution of a particle which is at corner = $\frac{1}{8}$ for a unit cell.

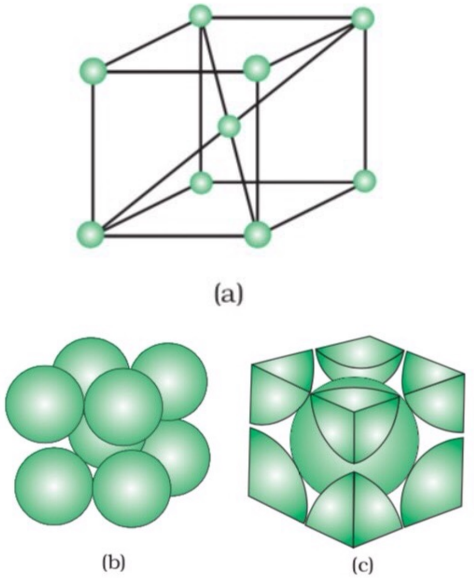


→ Total no. of atoms in one unit cell

= No. of atoms at corner x contribution of a particle at corner

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

(ii) Body centered cubic unit cell :- [BCC]



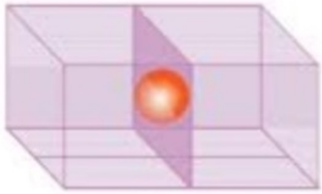
→ Body centre wholly belongs to the unit cell in which it is present.

a.) 8 corners x $\frac{1}{8}$ per corner atom = 1 atm

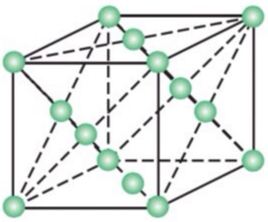
b.) 1 body centre atom = 1 atom

[Delhi 2014|2015c] (1M) Total no. of atoms per unit cell = 2 atoms

(iii) face centered cubic unit cell -: [FCC]



→ Each atom located at the face centre is shared between two adjacent unit cells and only $\frac{1}{2}$ of each atom belongs to unit cell.



a.) 8 corner atoms x $\frac{1}{8}$ per carbon atom = 1 atom

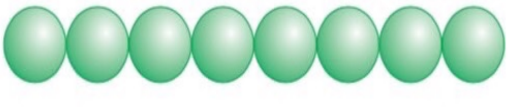
b.) 6 face centered atoms x $\frac{1}{2}$ atom per unit cell = 3 atoms

Total no. of atoms per unit cell = 4 atoms

[Delhi 2008|2012|CBSE 2008|2009] (1M)

Close Packed structures :- In solids, constituent particles are close packed, leaving the minimum vacant space [Void].

(i) close packing in one dimension :- There is only one way of arranging spheres in one dimensional close packed structure that is to arrange them in a row and touching each other.

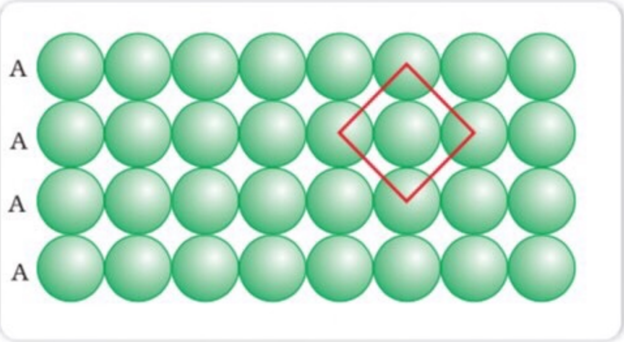


Coordination Number -: No. of nearest neighbours of a particle [CBSE 2011 | Delhi 2009C (1M)

→ Here CN = 2.

(ii) Close packing in two dimensions :-

(a)→ **A A A Type** :- Second row is exactly same as first row.

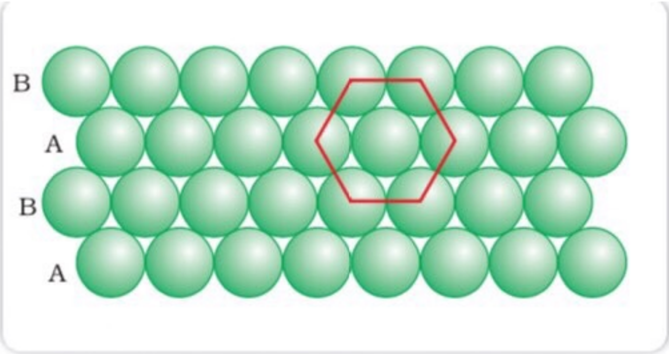


→ C.N. = 4 [In this arrangement, each sphere is in contact with four of its neighbours]

→ If the centre of above four immidiate neighbouring spheres are joined, a square is formed. Hence this packing is called square close packing in 2D

(b)→ **A B A B Type** -: If second row of spheres ar placed above first row in a staggered manner in such a way that spheres are fit in depressions of first row.

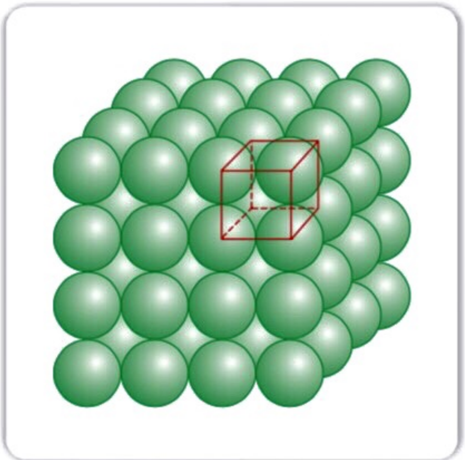
→ C.N. = 6



→ The centres of 6 spheres are at the corners of a regular hexagon. Hence this packing is called 2D hexagonal close packing.

(iii) **Close packing in 3D** -: This packing can be obtained by putting two dimensional layers one above the other.

[a] 3D close packing from two 2D square close packed layers (AAA--- type)



Simple cubic lattice formed by A A A .... arrangement

→ If the arrangement of spheres in the first layer is called A type. Then this lattice has AAA--- type arrangement because all layers have same arrangement.

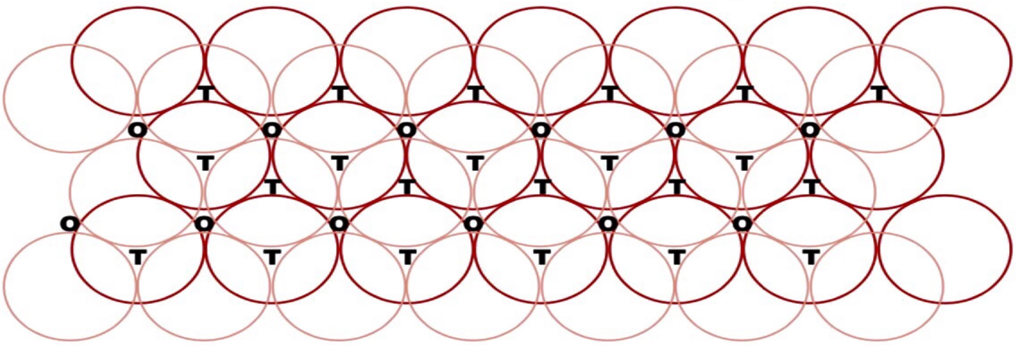
b→ Three dimensional close packing from two dimensional hexagonal close packed layers.

ⓘ **Placing second layer over the first layer :—** Let us take a 2D hexagonal close packed layer A and place a similar layer above it such that the spheres of second layer are placed in depressions of the first layer.

→ All the triangular voids of first layer are not covered by spheres of the second layer [B].

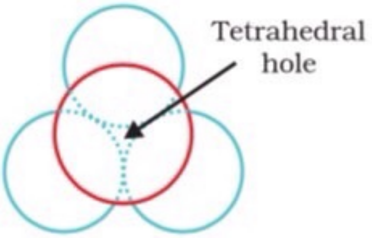
T : Tetrahedral

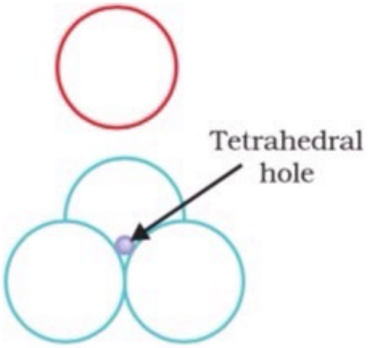
O : Octahedral

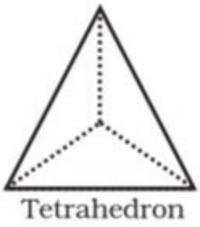


A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

Tetrahedral Voids :- Whenever a sphere of second layer (HCP) is above the void of first layer, a tetrahedral void is formed. These voids are surrounded by four spheres which lie at the corners (vertices) of regular tetrahedron.

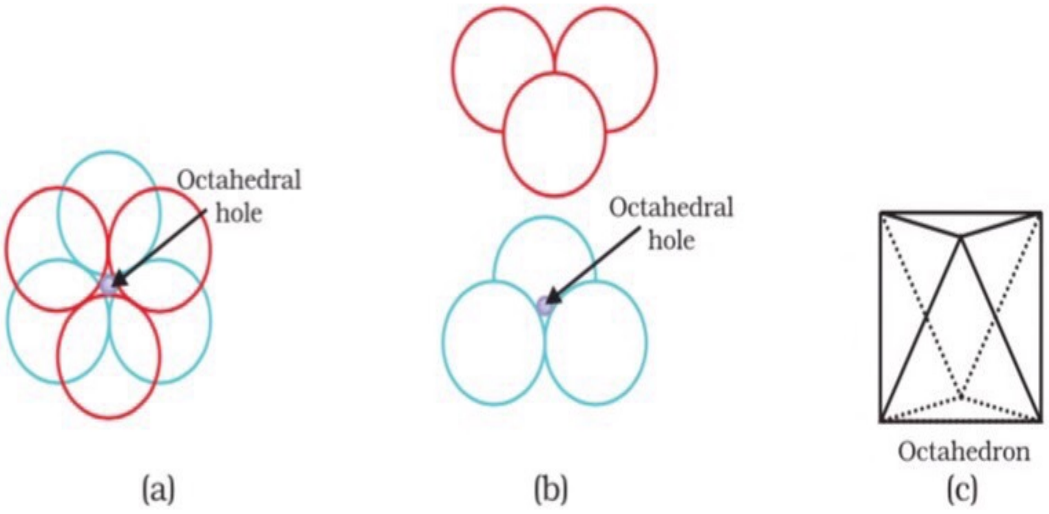






Octahedral Voids -: These are formed, whenever the trigonal voids in the second layer (HCP) are above the trigonal voids of the first layer. One trigonal void has the apex of triangle pointing upwards but another apex pointing downwards

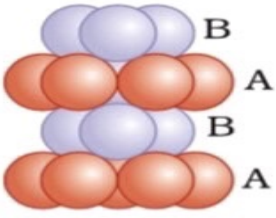
→ For N close packed spheres, there are N octahedral voids and 2N tetrahedral voids.



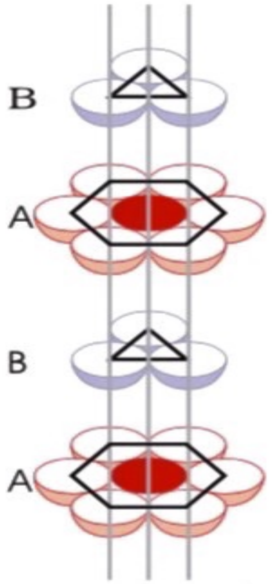
octahedral voids
(a) top view
(b) exploded side view and
(c) geometrical shape of the void.

(ii) Placing third layer over the second layer -:

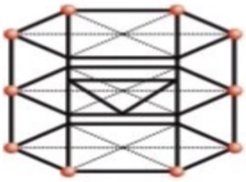
a.) Covering tetrahedral voids :- Tetrahedral voids of second layer may be covered by the spheres of third layer. The spheres of the third layer are exactly aligned with those of first layer. This ABAB.... type pattern is calle HCP [Hexagonal close packed] structure.



Hexagonal



Hexagonal packing

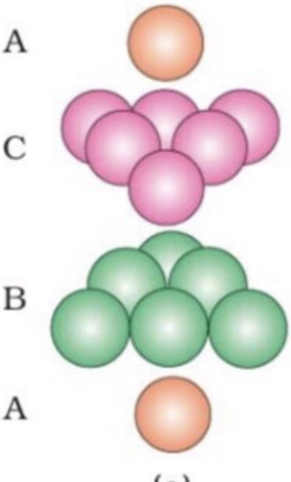


hcp

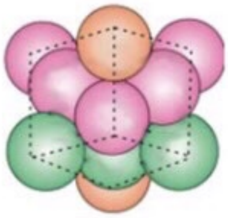
b.) Covering octahedral voids :- The third layer may be placed above second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, third layer are not aligned with those of either the first or the second layer.

→ Only when 4th layer is placed, its spheres are aligned with those of first layer.

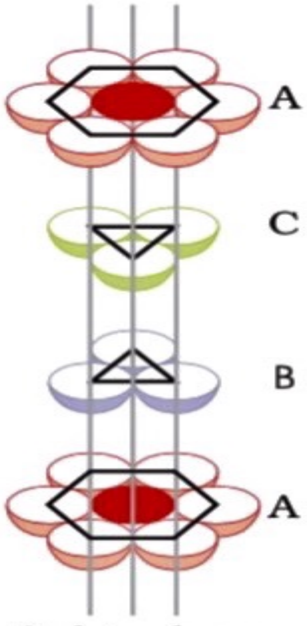
→ This ABCABC... type pattern is called FCC [Face centred cubic] or CCP [Cubi closed packed] structure.



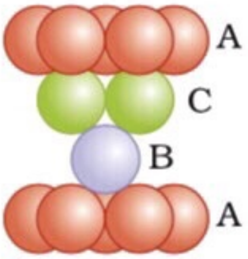
(a)



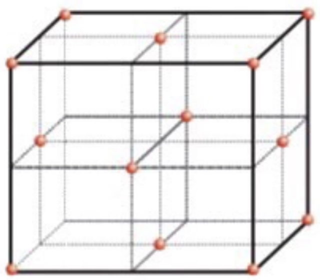
(b)



Cubic close packing



cubic



fcc

NOTE :- In HCP | FCC : CN = 12 [each sphere is in contact with 12 spheres]

Formula making -:

Question -: What is the formula of a compound in which the element Y forms ccp lattice and atoms of X element occupy $\frac{2}{3}$ rd of octahedral void?

[CBSE 2015] (1M)

Answer -: No. of atoms of element Y in ccp | fcc unit cell = 4

→ No. of octahedral voids = No. of atom present in unit cell = 4

→ No. of atoms of element X in unit cell = $\frac{2}{3}$ × No. of octahedral voids

$$= \frac{2}{3} \times 4 = \frac{8}{3}$$

→ Ratio of X and Y = $\frac{8}{3} : 4 = 8 : 12$

$= 2 : 3$ Then formula = X_2Y_3

Question -: What is the formula of a compound in which the element Y forms ccp lattice and atom of X occupy $\frac{1}{3}$ rd of tetrahedral voids?

[Delhi 2015] (1M)

Answer -: No. of Y atoms per unit cell of ccp | fcc lattice = 4

→ No. of tetrahedral voids = 2 × No. of atoms present per unit cell = 2×4 = 8

→ No. of tetrahedral voids × $\frac{1}{3}$ = No. of X atoms = $8 \times \frac{1}{3}$

→ $X : Y = \frac{8}{3} : 4 = 2 : 3$ Formula = X_2Y_3

Question :- Calculate the no. of unit cells in 8.1 g of aluminium, if it crystallises in a face centered cubic structure. (Atomic mass of Al = 27 g mol⁻¹)

[CBSE 2017] (2M)

Answer -: 27 g of Al (1 mole) = 6.023×10^{23} atoms

8.1 g of Al $= \frac{6.023 \times 10^{23}}{27} \times 8.1$ atoms.

→ No. of atoms in fcc unit cell = 4

Then no. of unit cell in 8.1 g Al $= \frac{6.023 \times 10^{23} \times 8.1}{4 \times 27} = 4.52 \times 10^{22}$

Question :- A compound forms HCP structure. What is the total no. of voids in 0.5 mol of it? How many of these are tetrahedral voids? [CBSE 2013 C] (2M)

Answer -: No. of atoms in 1 mol HCP lattice = 6.022×10^{23} atoms

No. of atoms in 0.5 mol = $\frac{6.022 \times 10^{23}}{2}$ atoms = N

→ No. of octahedral void = N = 3.011×10^{23}

→ No. of tetrahedral void = 2N = $2 \times (3.011 \times 10^{23})$ = 6.022×10^{23} voids.

→ Total voids = $(3.011 \times 10^{23}) + (6.022 \times 10^{23})$ = 9.033×10^{23} voids

Question -: An alloy of gold and cadmium crystallises with a cubic structure in which gold atoms occupy the corners and cadmium atoms fit into the face centeres. Assign formula for this alloy? [CBSE 2011 C] (2M)

Answer -: No. of gold atoms in a unit cell = 8 corners × $\frac{1}{8}$ atom per corner

= 1 atom of gold.

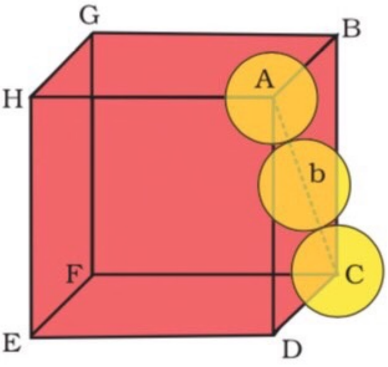
→ Cadmium at face centre then no. of Cadmium in a unit cell = 6 face centre × $\frac{1}{2}$ atom perface

= 3 atoms

Ratio of no. of atoms of Au : Cd = 1 : 3, Then formula Au_1Cd_3.

Packing Efficiency :- It is the percentage of total space filled by particles.

Packing efficiency in hcp and ccp structures :- Both types of close packing (HCP and CCP) are equally efficient.



→ a : Edge length of unit cell

b : Face diagonal [AC]

→ In Δ ABC : $AC^2 = BC^2 + AB^2$

$b^2 = a^2 + a^2$ then $b = \sqrt{2}a$

→ If r is the radius of sphere then $AC = b = 4r = \sqrt{2}a$

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

→ No. of atoms [spheres] in each unit cell of ccp = 4

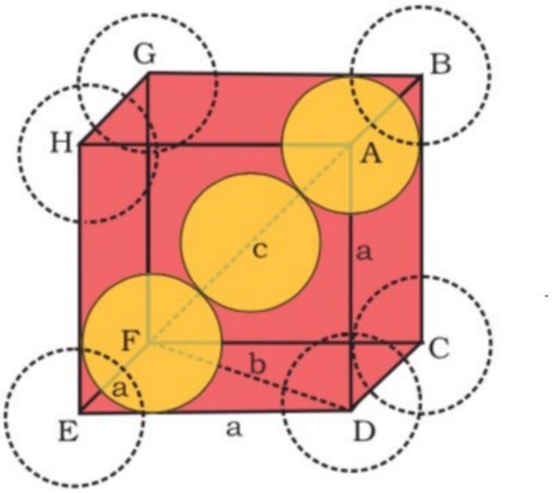
Total volume of four spheres $= 4 \times \left[\frac{4}{3} \pi r^3\right]$

Volume of cube $= a^3 = [2\sqrt{2}r]^3$

→ Packing Efficiency $= \dfrac{\text{Volume occupied by 4 spheres}}{\text{Total volume of unit cell}} \times 100$

$$= \frac{4 \times (4/3 \, \pi r^3)}{(2\sqrt{2} r)^3} \times 100 = 7.4 \times 100 = \boxed{74\%}$$

Efficiency of packing in BCC :—



→ The atom at the centre will be in touch with the other two atoms which are diagonally arranged.

→ In ΔEFD : $b^2 = a^2 + a^2 = 2a^2$ then $b = \sqrt{2}a$

→ In ΔAFD : $c^2 = a^2 + b^2 = a^2 + 2a^2$ then $c = \sqrt{3}a$

→ The length of body diagonal $c = 4r$ (r : radius of sphere)

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

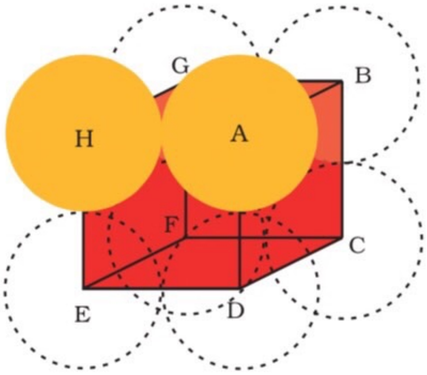
→ Total no. of atom per unit cell of BCC = 2 then volume of 2 atoms $= 2 \times \frac{4}{3}$

→ Volume of the cube $= a^3 = \left(\dfrac{4r}{\sqrt{3}}\right)^3$

Packing Efficiency $= \dfrac{\text{Volume occupied by 2 spheres}}{\text{Total volume of unit cell}} \times 100$

$$= \frac{2\left(\frac{4}{3}\pi r^3\right)}{\left(\frac{4}{\sqrt{3}} r\right)^3} = \boxed{68\%}$$

Packing efficiency in simple cubic lattice -: (2M) [Delhi 2011C CBSE 2011 2009C]



→ The edge length $a = 2r$ (r : Radius of sphere)

→ Volume of cubic unit cell $= a^3 = 8r^3$

→ No. of atoms in simple cubic unit cell = 1 So, Volume of occupied space $= \frac{4}{3}\pi r^3$

→ Packing Efficiency $= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100$

$$= \frac{\left(\frac{4}{3}\pi r^3\right)}{8r^3} \times 100 = \frac{\pi}{6} \times 100 = 52.36\% = \boxed{52.4\%}$$

Calculation involving unit cell dimensions :— [CBSE 2011] ②M

If a : Edge length of unit cell , d : Density of solid substance.

M : Molar Mass , Z : No. of atoms present in one unit cell.

→ Volume of unit cell $= a^3$

→ Mass of unit cell $= Z \times$ mass of each atom

$$= Z \times \frac{M}{N_A} \qquad \left[\text{Mass of an atom} = \frac{\text{Molar Mass}}{N_A}\right]$$

→ Density of unit cell $= \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{(ZM/N_A)}{a^3} = \boxed{\frac{ZM}{a^3 N_A} = d}$

Question :- Aluminium crystallises in fcc structure. Atomic radius of metal is 125 p
What is the length of the side of unit cell of the metal ? [CBSE 2013] ①M

Answer -: length of side $a = \frac{4r}{\sqrt{2}}$ $[4r = \sqrt{2}a : \text{fcc}]$

$$= \frac{4 \times 125 \text{ pm}}{\sqrt{2}} = 353.61 \text{ pm}$$

Question :— An element with density 11.2 g cm^{-3} forms a fcc lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of element?
[CBSE 2014] ②M

Answer -: $d = 11.2$ g cm^{-3} , $a = 4 \times 10^{-8}$ cm , $N_A = 6.022 \times 10^{23}$

For fcc : Z = 4

$$d = \frac{ZM}{a^3 N_A}$$

$$\rightarrow M = \frac{d\,a^3 N_A}{Z} = \frac{11.2 \times (4\times10^{-8})^3 \times 6.022\times10^{23}}{4} = 107.9 \text{ g mol}^{-1}$$

$$= 108 \text{ g mol}^{-1}$$

Question :- Silver crystallises in fcc lattice. If edge length of unit cell is 4.077×10^{-8} cm. Then calculate the radius of silver atom. [CBSE 2015C] (3M)

Answer -: $a = 4.077 \times 10^{-8}$ cm , For fcc $Z = 4$; $\boxed{4r = \sqrt{2}a}$

then $r = \dfrac{\sqrt{2}\,a}{4} = \dfrac{\sqrt{2}}{4} \times 4.077 \times 10^{-8} = 1.44 \times 10^{-8}$ cm

Question :- Tungsten crystallises in BCC unit cell. If edge length of unit cell is 316.5 pm, what is the radius of tungsten atom? [Delhi 2012] (3M)

Answer -: For BCC $\boxed{r = \dfrac{\sqrt{3}}{4}a}$ $a = 316.5$ pm

$$r = \frac{\sqrt{3}}{4} \times 316.5 = 137.04 \text{ pm.}$$

Question :- The density of copper metal is $8.95\ g\ cm^{-3}$. If the radius of copper atom is 127.8 pm. Is the copper unit cell a simple cubic, a BCC or FCC structure? [Atomic mass of Cu = $63.54\ g\,mol^{-1}$, $N_A = 6.02 \times 10^{23}\ mol^{-1}$]

Answer -: Given $d = 8.95\ g\ cm^{-3}$, $r = 127.8$ pm [CBSE 2010 | Delhi 2010] (3M)

$M = 63.54\ g\,mol^{-1}$

① Simple cubic : $a = 2r = 2 \times 127.8 = 255.6$ pm and $Z = 1$

Density $d = \dfrac{ZM}{a^3 N_A} = \dfrac{1 \times 63.54}{(255.6 \times 10^{-10} cm)^3 \times 6.02 \times 10^{23}} = 6.34\ g\,cm^{-3}$

→ But given density is different. So copper unit cell is not simple cubic.

② BCC : $4r = \sqrt{3}a$ then $a = \dfrac{4}{\sqrt{3}} r = \dfrac{4}{\sqrt{3}} \times 127.8 = 295.15$ pm

↳ $Z = 2$

Density $d = \dfrac{ZM}{a^3 N_A} = \dfrac{2 \times 63.54}{(295.15)^3 \times 6.02 \times 10^{23}} = 8.21\ g\,cm^{-3}$: Not BCC

③ FCC : $\sqrt{2}a = 4r$ then $a = \dfrac{4}{\sqrt{2}} \times 127.8 = 361.4$ pm.

↳ $Z = 4$

Density $d = \dfrac{ZM}{a^3 N_A} = \dfrac{4 \times 63.54}{(361.4 \times 10^{-10})^3 (6.02 \times 10^{23})} \Rightarrow \boxed{8.94\ g\,cm^{-3}}$

Hence copper unit cell is fcc.

Question :– An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell

Answer –: $M = 93 \text{ g mol}^{-1}$, $d = 11.5 \text{ g cm}^{-3}$, $a = 300 \text{ pm}$ [Delhi 2017] (3M)

→ Density $d = \frac{ZM}{a^3 N_A}$. then $Z = \frac{d a^3 N_A}{M} = \frac{(11.5)(300\times10^{-10}\text{cm})^3 (6.022\times10^{23})}{93}$

$\boxed{BCC} \leftarrow \boxed{Z = 2}$

Question –: Niobium crystallises in BCC structure. If it's density is 8.55 g cm^{-3}. Calculate the atomic radius of niobium. (Atomic mass 93U)

Answer –: $d = 8.55 \text{ g cm}^{-3}$, $M = 93 \text{ g mol}^{-1}$ [Delhi 2013C] (3M)

for BCC $Z = 2$

Density $d = \frac{ZM}{a^3 N_A}$

$$a = \sqrt[3]{\frac{ZM}{d N_A}} = \sqrt[3]{\frac{2\times 93}{8.55 \times 6.023\times10^{23}}} = 3.3\times10^{-8} \text{ cm}$$

→ for BCC $4r = \sqrt{3}\,a$ then $r = \frac{\sqrt{3}}{4} \times (3.3\times10^{-8}) = 1.42\times10^{-8}$ cm

Question :– The well known mineral fluoride is chemically calcium fluoride. I is known that in one unit cell of this mineral, there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a fcc lattice. The F^- fill all tetrahedral holes in fcc lattice of Ca^{+2} ions. The edge of unit cell is 5.46×10 cm in length. The density of solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro no. [Molar mass of CaF_2 = 78.08 g mol^{-1}] (3M) [Delhi 2010]

Answer –: $a = 5.46\times10^{-8}$ cm , $d = 3.18 \text{ g cm}^{-3}$

$M = 78.08 \text{ g mol}^{-1}$, for FCC : $Z = 4$

$$d = \frac{ZM}{a^3 N_A} \Rightarrow N_A = \frac{ZM}{a^3 . d} = \frac{4\times78.08}{(5.46\times10^{-8})^3 \times 3.18} = 6.03\times10^{23} \text{ mol}^{-1}$$

$$\boxed{NA = 6.03\times10^{23}}$$

Imperfections in solid

→ Any deviation from the perfecly ordered arrangement of constituent particl in a crystal is called defects (imperfections) in solids.

Point and line defect :– Deviation from ideal arrangement around a point in a crystalline substance is called point defects.

→ Line defects are deviation from ideal arrangement in entire row of lattice points.

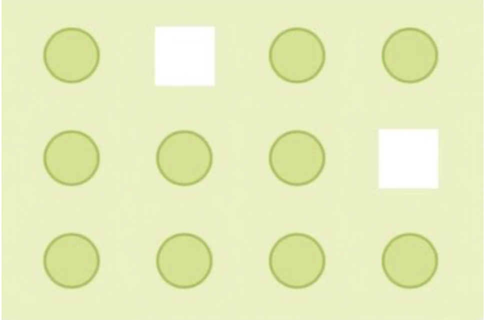
→ Above irregularities are also known as crystal defect.

Point Defects
- Stoichiometric defects
  - Vacancy defects
  - Interstitial defects
- Impurity defects
- Non - stoichiometric defect
  - Metal excess defects
  - Metal deficiency defects.

Stoichiometric Defects :–

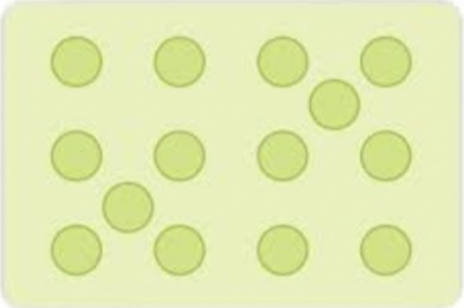
→ These are the point defects that do not disturb the stoichiometry of solid. They are also called intrinsic or thermodynamic defects.

(i) **Vacancy Defect :-** When some of the lattice sites are vacant, the crystal is said to have vacancy defect.



→ This results in decrease in density of substance. This defect can also develop when a substance is heated.

(ii) **Interstitial Defect –:** When some particles occupy an interstitial site, the crystal is said to have interstitial defect.



→ This defect increases the density of substance.

[CBSE 2012 | Delhi 2009, 2011] IM

\# Above both are found in non-ionic solids.

(iii) Frenkel Defect :- It occurs when smaller ions (usually cations) are displaced from its normal site to an interstitial site.

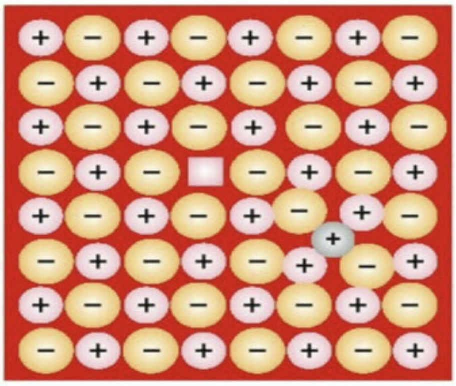
→ It is also known as dislocation defects.

→ It does not change the density of solid.

Example → Ionic solids [ZnS, AgCl, AgBr, AgI]

→ Large size difference between cations and anions.

[CBSE 2015C | 2012 | 2010C / Delhi 2013] (1M)



Frenkel defects

(iv) Schottky Defect :- This defect is a vacancy defect in ionic solids that occur due to, both cations and anoins.

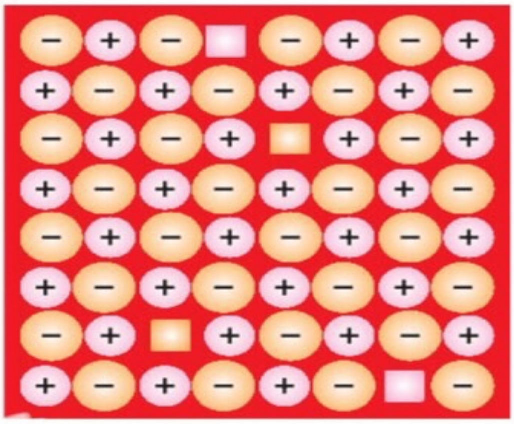
↳ missing of

→ It decreases the density of substance.

Example → NaCl, KCl, CsCl, AgBr.

→ AgBr shows both Frenkel and Schottky defect.

[Delhi 2014C]
2015

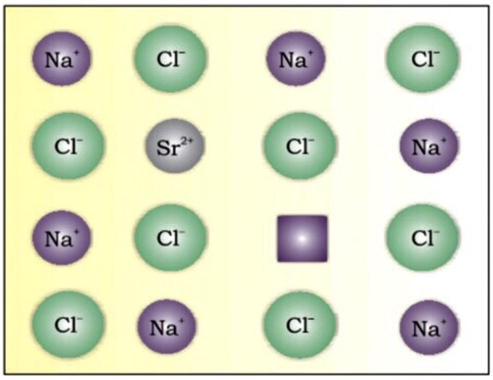


Schottky defects

NOTE :- ① Density decreases in Schottky Defect / Vacancy defect. [Delhi 2010 CBSE 2009] (1M)

② Density does not change in Frenkel Defect. [Delhi 2009 | 2010] (1M)

③ Density increases in Interstitial Defect. [Delhi 2009 | 2011, CBSE 2012] (1M)



Impurity Defects :- If molten NaCl containing a littre amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{+2}. (Each Sr^{+2} replaces two Na^+ ions. It occupies the site of one ion and other site remains vacant)

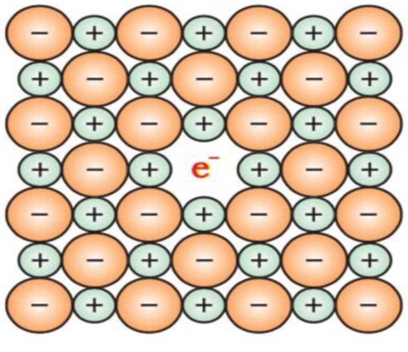
Other example : $CdCl_2$ + AgCl [CBSE 2013 | 1M]

[No. of cationic vacancies = No. of Sr^{+2} ions]

Non-stoichiometric Defects :- These defects are of two types.

ⓘ Metal excess defect -:

→ Metal excess defect due to anionic vacancies : Alkali halides like NaCl and KCl show this type of defect.



An F-centre in a crystal

→ When crystals of NaCl are heated in an atmosphere of sodium vapour. The Na atoms are deposited on surface of crystals.

→ The Cl⁻ ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by Na atoms to form Na⁺ ion. The released electron diffuse into crystal and occupy anionic sites. As a result the crystal now has an excess of sodium.

→ The anionic sites occupied by unpaired electrons are called F Centres.

[Delhi 2015] (1M)

→ Due to presence of F centres NaCl crystal shows yellow colour.

→ Similarly excess of Li makes LiCl crystal pink.

[CBSE 2013] (1M)
Delhi 2014

→ Excess of K makes KCl crystals voilet.

Reason of colour :-
The colour results by excitation of unpaired electrons when they absorb energy from the visible light falling on the crystal.

Metal excess defect due to presence of extra cations at interstitial site.

↳ Zinc oxide is white in colour at room temperature. on heating it loses oxygen and turns yellow.

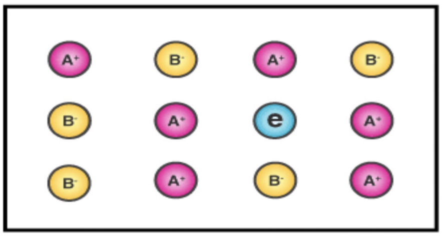
[CBSE 2017] (1M)

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

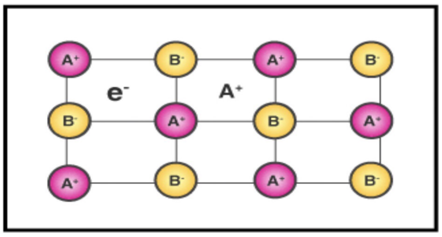
→ After removal of oxygen, there is excess of zinc in crystals. and its formula becomes $Zn_{1+x}O$.

→ Zn^{+2} and electrons move to interstitial site.

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



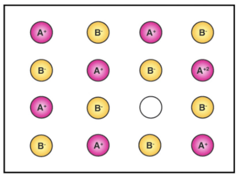
Metal excess defect due to anionic vacancy



Metal excess defect due to the presence of interstitial cation:

(ii) **Metal Deficiency Defect** :- There are many solids which contain less amount of metal as compared to the stoichiometric proportion.

Example → FeO → $Fe_{0.96}O$ → Some Fe^{+2} cations are missing and loss of positive charge is made up by the presence of required no. of Fe^{+3} ions.



Metal Deficiency Defect

Question :- If NaCl is doped with 10^{-3} mole percent $SrCl_2$. What will be the concentration of cationic vacancies?

[CBSE 2013C] (2M)

Answer -: The no. of cationic vacancies created in the lattice of NaCl is equal to the no. of divalent Sr^{+2} ions added.

→ Concn of Sr^{+2} = 10^{-3} mol percent $= \frac{10^{-3}}{100} = 10^{-5}$ mol

→ 1 mole of Sr^{+2} $= 6.023 \times 10^{23}$ Sr^{+2} ions

10^{-5} mole of Sr^{+2} $= 6.023 \times 10^{23} \times 10^{-5} = 6.023 \times 10^{18}$ Sr^{+2} ion.

then concn of cation vacancies $= 6.023 \times 10^{18}$

Question :- A metal crystallises in FCC unit cell with $a = 0.560$ nm. Calculate the density of metal if it contains 0.1 % Schottky defects.

Given: Atomic mass of metal = 40 g mol^{-1}.

[CBSE 2008C] (3M)

Answer :- Due to Schottky defects, the vacant spaces will increase resulting in decrease in no. of atoms per unit cell.

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996 \text{ atom.}$$

$$d = \frac{ZM}{a^3 N_A} = \frac{3.996 \times 40}{(0.56 \times 10^{-7})^3 (6.022 \times 10^{23})} = 1.51 \text{ g cm}^{-3}$$

Electrical Properties

[CBSE2008C]

→ Solid has large range of conductivity [10^{-20} to 10^{7} ohm^{-1} m^{-1}].

→ Solids can be classified into three types on the basis of their conductivity

(i) **Conductors** –: Conductivity range between 10^{4} – 10^{7} ohm^{-1} m^{-1}.

→ Metals have conductivities in order of 10^{7} ohm^{-1} m^{-1} are good conductors.

(ii) **Insulators** –: Low conductivity range [10^{-20} to 10^{-10} ohm^{-1} m^{-1}]

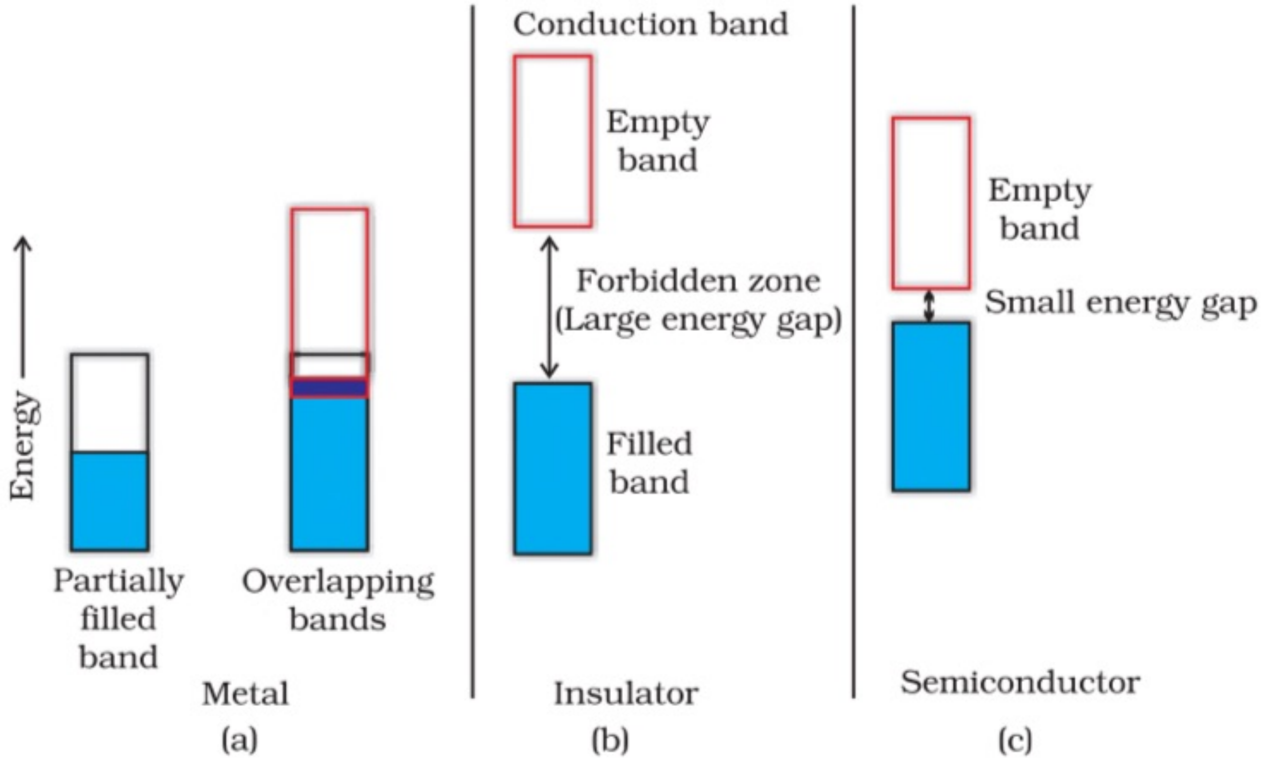
(iii) **Semiconductors** –: Intermidiate range of conductivity [10^{-6} to 10^{4} ohm^{-1}m^{-1}

Conduction of electricity in metals :– Metals conduct electricity in solid as well as molten state. Conductivity of metals depend upon number of valence electrons available per atom.

→ The atomic orbitals of metal atoms form molecular atoms which are so close in energy to each other as to form a band.

→ If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field. and metal shows conductivity.

⇒ If the gap between filled valence band and the next higher unoccupied band [Conduction band] is large, electrons can not jump to it and such a substance has very small conductivity and it behaves as an insulator.



Conduction of electricity in semiconductors :-

→ In case of semiconductors, the gap between valence band and conduction band is small. Therefore some electrons may jump to conduction band and show conductivity.

→ Electrical conductivity of semiconductors increases with rise in temperature since more electrons can jump to the conduction band.

→ Pure semiconductors [like silicon, germanium] are called intrinsic semiconductors.

→ The conductivity of intrinsic semiconductors is too low for practical use.

Doping :- To increase the conductivity of intrinsic semiconductors, we add some amount of suitable impurity. This process is called doping.

[Delhi 2012 / CBSE 2012] 1M

n - type Semiconductors :-

→ Si and Ge belong to group 14 of periodic table and have 4 valence electrons. In their crystals Si and Ge forms 4 covalent bonds with its neighbours.

→ When pure crystal of Si and Ge is doped with a group 15 element [like P or As] which contains 5 valence electrons. They occupy some of the lattice sites in Si or Ge crystal.

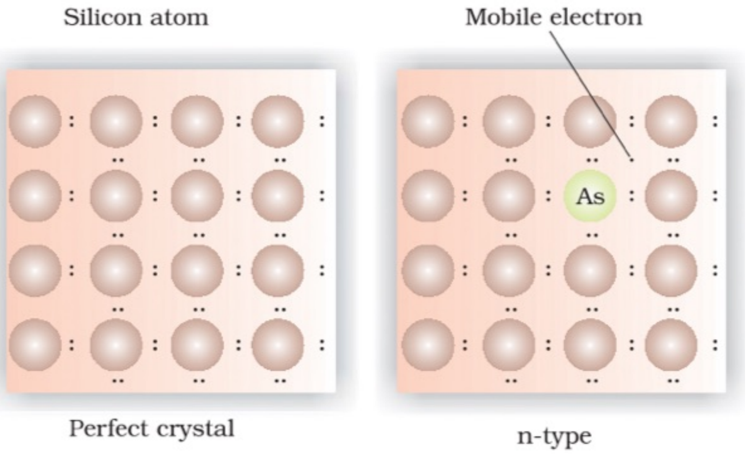
→ 4 out of 5 electrons are used in the formation of four covalent bonds with 4 neighbouring silicon | Ge atoms. 5th electron is extra and becomes delocalised.

→ These delocalised electrons increase the conductivity of doped Si | Ge.

→ Increase in conductivity is due to negatively charged electrons. So this doped semiconductor [with electron rich impurity] is called n - type semiconductor.

[Delhi 2017 / 2008C
CBSE 2013]

1M



Perfect crystal

n-type

[Delhi 2008 / 2008C]

→ n type + p type : [CBSE 2009C / 2008 / 2008C]

p- type Semiconductor :-

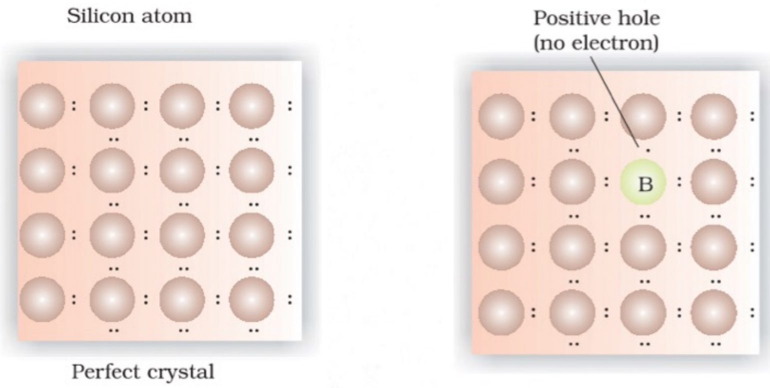
→ Si | Ge can also be dopped with group 13 element [B | Al | Ga] which contains only 3 valence electrons. The place where 4th valence electron is missing is called electron hole | vacancy.

→ An electron from neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position.

→ These holes can move through the crystal like a positive charge and increase the conductivity of Si | Ge crystal.

→ Silicon | Ge doped with electron deficient impurity is called p- type semiconductor.

CBSE 2013



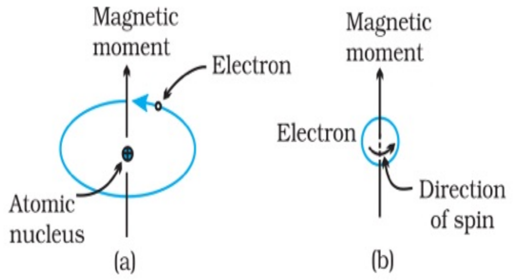
Magnetic Properties :-

→ Every substance has some magnetic properties associated with it.

→ This magnetic moment generates due to two types of motion of electron.

a.> Its orbital motion around the nucleus.

b.> It spin around its own axis.



→ Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment.

→ On the basis of their magnetic properties. substances can be classified into five catagories.

ⓘ Paramagnetic [Paramagnetism] :- Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in absence of magnetic field.

→ It is due to presence of unpaired electrons.

→ Examples: O_2 | Cu^{2+} | Fe^{3+} | Cr^{+3} [Delhi 2010C]

1M

(ii) **Diamagnetism** :- Diamagnetic substances are weakly repelled by a magnetic field. Example -: H_2O, NaCl, C_6H_6.

→ Diamagnetic substances have paired electrons. There are no unpaired electrons.

→ Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) **Ferromagnetism** -: A few substances [Fe, Co, Ni, Gd, CrO_2] are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances.

→ In solid state the metal ions of ferromagnetic substances are grouped together into small regions called domains. Each domain acts as a tiny magnet. When the substance is placed in a magnetic field all the domains get oriented in direction of magnetic field and becomes a permanent magnet even when magnetic field is removed. [Delhi 2011C | 2010C | 2008 | 2016] (1M)

(iv) **Antiferromagnetism** -: Substances [like MnO] showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

(1M) [Delhi 2008 | 2014 / 2011C | CBSE 2014C | 2014]

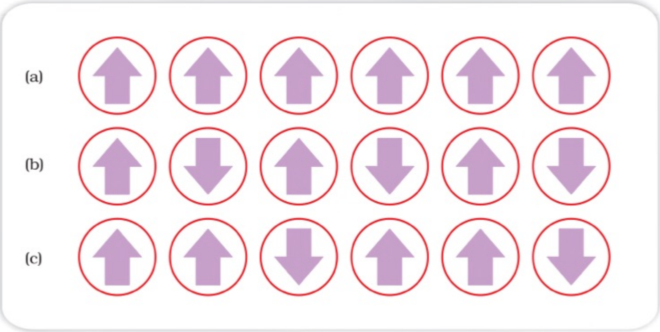
(v) **Ferrimagnetism** -: It is observed when the magnetic moments of domains in substance are aligned in parallel & anti parallel directions in unequal no.

→ They are weakly attracted by magnetic field as compared to ferromagnetic substances.

→ Example :- Fe_3O_4 [Magnetite]

Ferrites [$MgFe_2O_4$, $ZnFe_2O_4$]

→ Ferrimagnetic $\xrightarrow[\text{Heat}]{\Delta}$ Paramagnetic



Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.

[CBSE 2014 | (1M)
Delhi 2008 | Delhi 2017]