Welcome to

Aakash + BYJU'S LIVE

Solid State Notes

Properties of Solids

01 Have a definite mass, volume, and shape.

02 Least interparticle distances in solids as compared to liquids and gases.

03 Strong interparticle forces of attraction.

04 They are rigid and incompressible and their particles cannot flow.

Classification of Solids

Classification of Solids Based on Arrangements of Particles

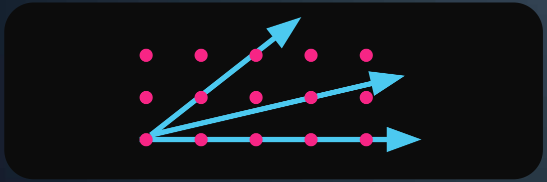
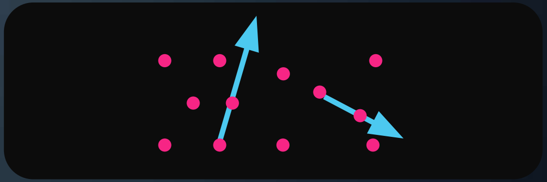
Crystalline

A solid material whose constituents are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions.

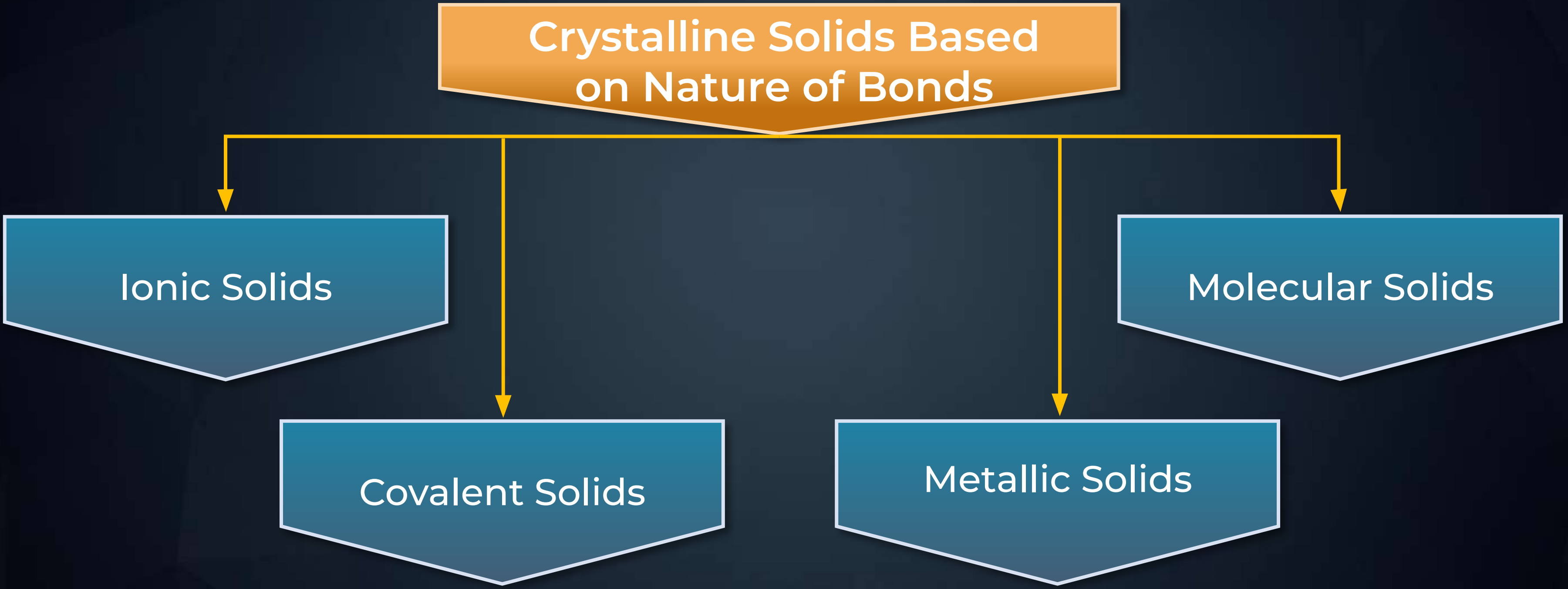
Amorphous

Solids, which do not have a definite geometrical arrangement are known as amorphous solids.

Crystalline Solid	Amorphous Solid
Definite characteristic geometrical shape	Irregular shape
True solids	Pseudo solids or super cooled liquids
Long-range order in the arrangements	Don’t show any long-range order
Have fixed or sharp melting point.	Have a range of temperature for melting.
They can show isomorphism and polymorphism.	They can’t show isomorphism and polymorphism.

Crystalline Solid	Amorphous Solid
Anisotropic: Different values of physical properties in different directions. 	Isotropic: Same values of all physical properties in all the directions. 
Ag, Fe, Cu, NaCl, Copper sulphate, $NiSO_4$, $H_2O(s)$, Diamond, Graphite, Quartz, Sucrose (Sugar) are the examples	Coal, Coke, Glass, Plastic, Amorphous silica, Rubber, Starch are the examples

Classification of Solids



Crystalline Solids Based on Nature of Bonds

Ionic Solids

Covalent Solids

Metallic Solids

Molecular Solids

Ionic Solids

Ions are the constituent particles formed by the 3D arrangements of cations and anions.

(i) Hard and brittle in nature

(ii) Have high melting and boiling points

Characteristics

(iii) In the solid state, they act as electrical insulators

(iv) In the molten state, they act as electrical conductors

(v) Ex: NaCl, ZnS, CsCl, CaF_4 etc.

Covalents Solids

The atoms or chemical subunits are bonded by conventional covalent bonds in a continuous network. Also called giant molecules or network solid.

(i) Very hard and brittle

(ii) Have extremely high melting points

Characteristics

Due to strength and directional nature of covalent bonds.

(iii) Atoms held very strongly

(iv) They are insulators

(v) e.g. Diamond, graphite, Silicate (SiO_2) and Silicon carbide

Metallic Solids

Composed of positively charged metal ions in a 3D array. Positive ions surrounded by and held together by a sea of free electrons.

(i) Possess lustre and are coloured in certain cases.

(ii) Highly malleable and ductile.

Characteristics

(iii) Have a wide range of melting points

(iv) Show high thermal and electrical conductivity

Molecular Solids and its Characteristics

Molecules are the **constituent particles** of molecular solids.

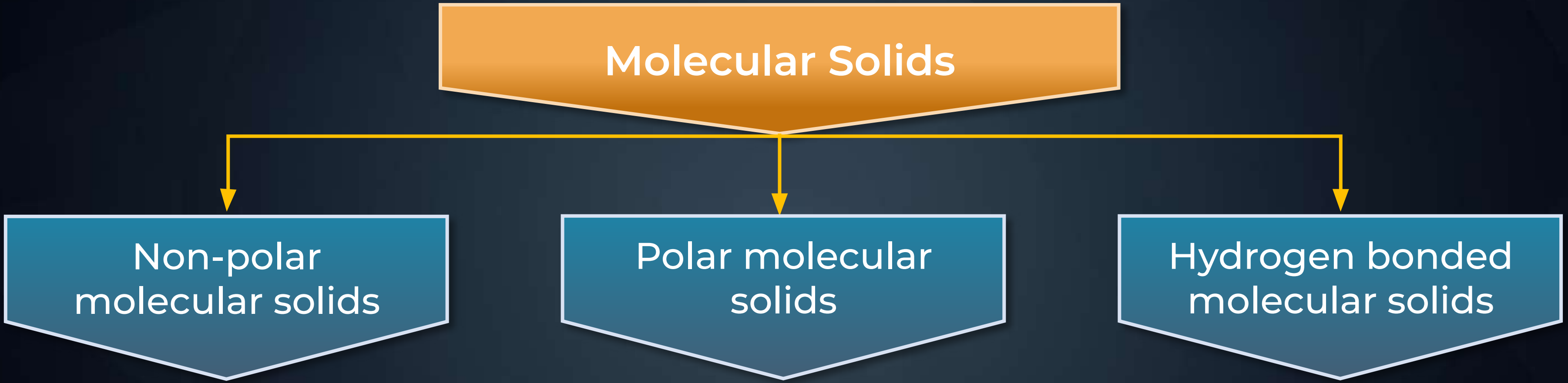
01 Molecular solids contain both intramolecular bonds and intermolecular forces

02 The forces between these molecules are relatively weak(van der Waal Forces).

03 Often soft substances with low melting points.

04 Ex: dry ice, I_2 (s), HCl (s), H_2O (s), H_3BO_3 (s)

Classification of Molecular Solids



Molecular Solids

Non-polar molecular solids

Polar molecular solids

Hydrogen bonded molecular solids

Non-Polar Molecular Solids

The atoms or molecules are held by weak dispersion forces or London forces.

Ex: H_2(s), Cl_2(s) and I_2(s).

Polar Molecular Solids

The molecules have dipole moment.

Held together by relatively stronger dipole-dipole interactions.

Ex: $HCl(s)$, $SO_2(s)$ and $NH_3(s)$

Hydrogen Bonded Molecular Solids

The molecules contain polar covalent bonds between H and F/O/N atoms.

Strong hydrogen bonding binds molecules of such solids like $H_2O(s)$.

General Features of Molecular Solids

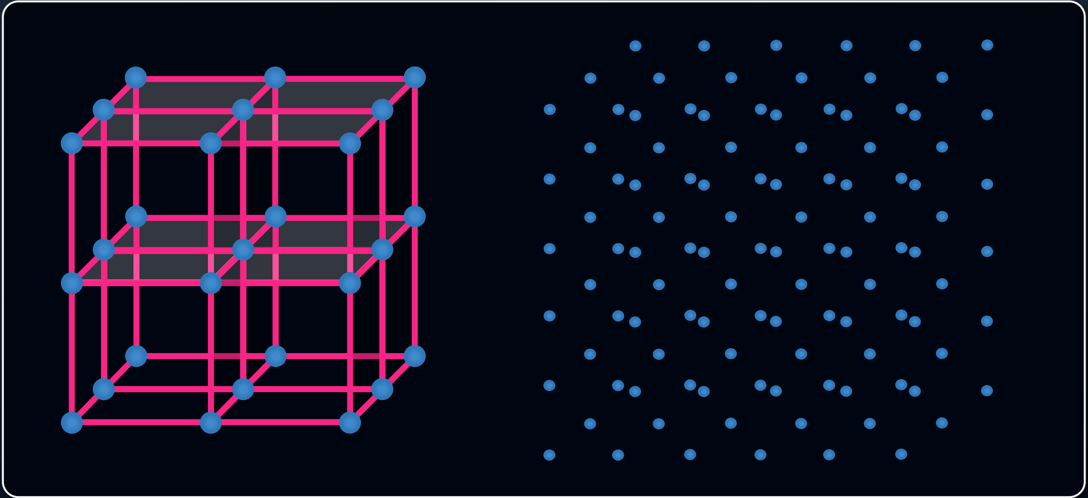
(1) Generally, nonconductors of electricity

(2) Non-polar and polar molecular solids are soft, whereas H-bonded solids are hard.

(3) Have low melting point.

Crystal

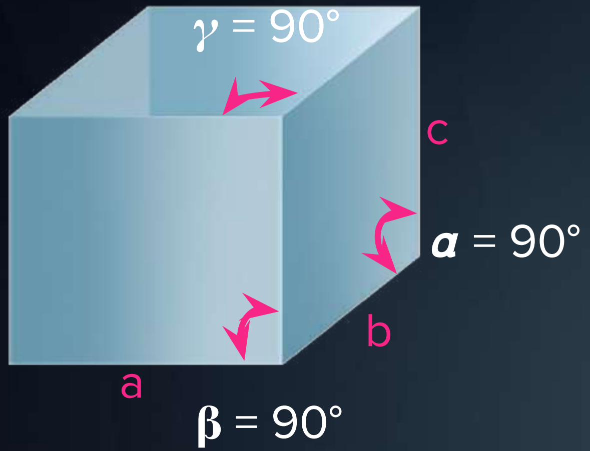
A solid material in which the constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions.



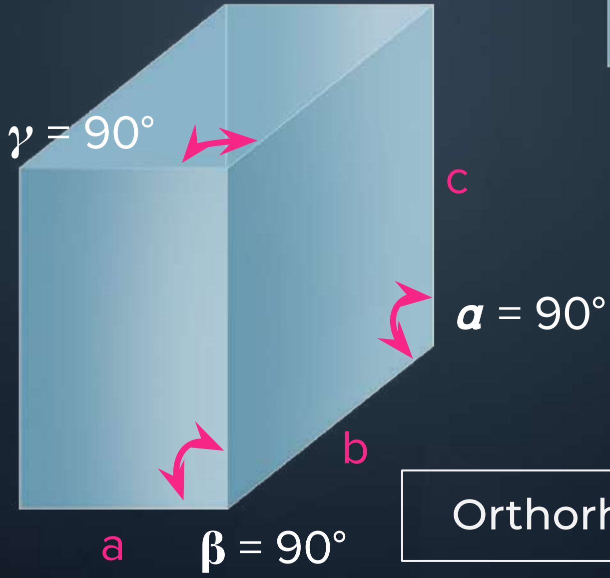
3-D Space Lattice

Seven crystal systems

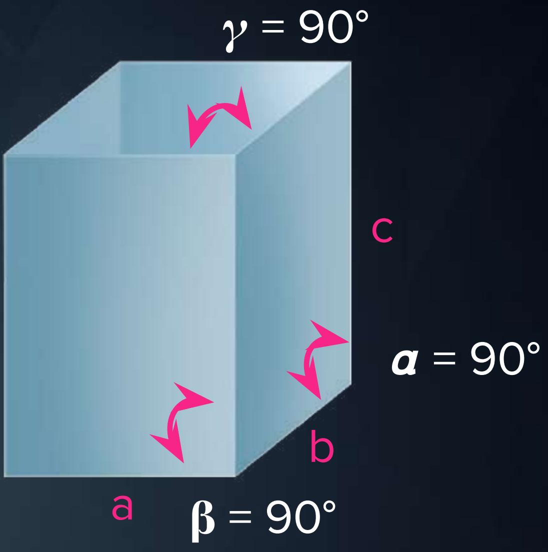
There are seven unique crystal systems with varying elements of symmetry in a three-dimensional space.



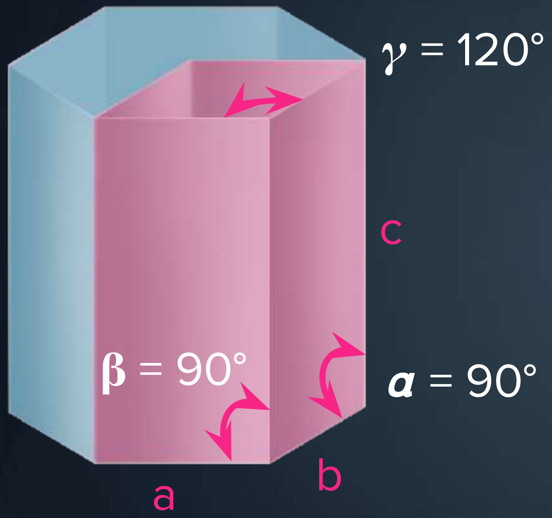
Cubic



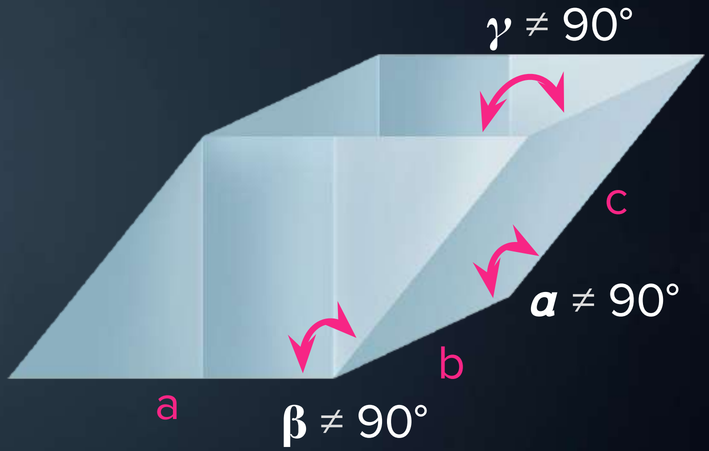
Orthorhombic



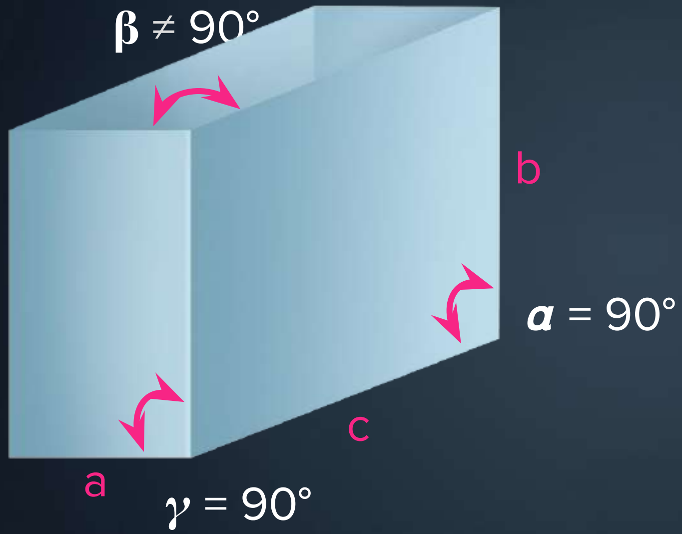
Tetragonal



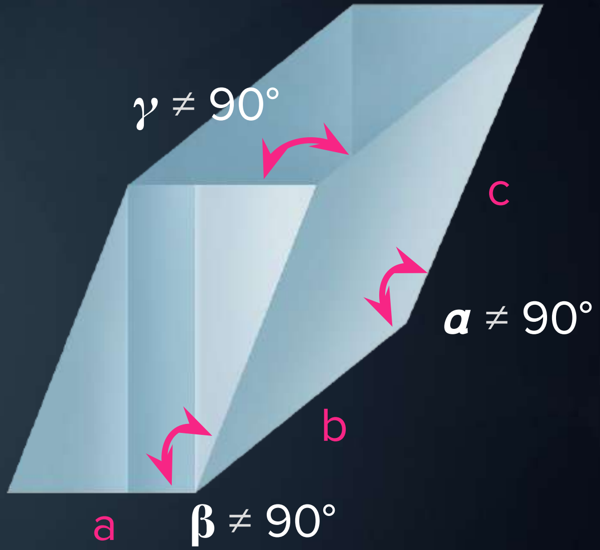
Hexagonal



Rhombohedral or trigonal



Monoclinic



Triclinic

Crystal systems and their Variations

Crystal System	Edge Length	Angles	Unit Cells Found
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BC, FC
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BC
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BC, FC, EC

Crystal systems and their Variations

Crystal System	Edge Length	Angles	Unit Cells Found
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$, 120°, 60°	Primitive, EC
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Primitive

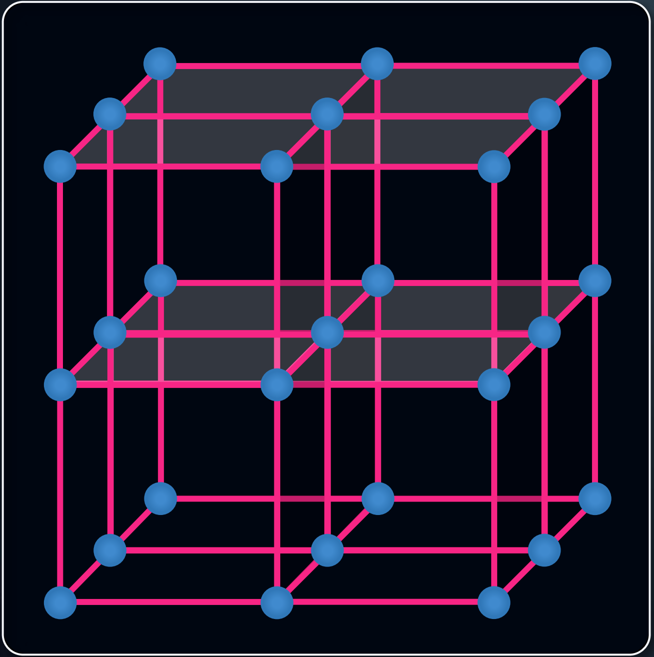
Bravais Lattices

On combining the 7 crystal systems with the 4 possible unit cell types (SCC, BCC, FCC, and End Centered)

Only 14 3D lattices are possible

These are called **Bravais lattices**

Internal arrangement of particles in a crystal



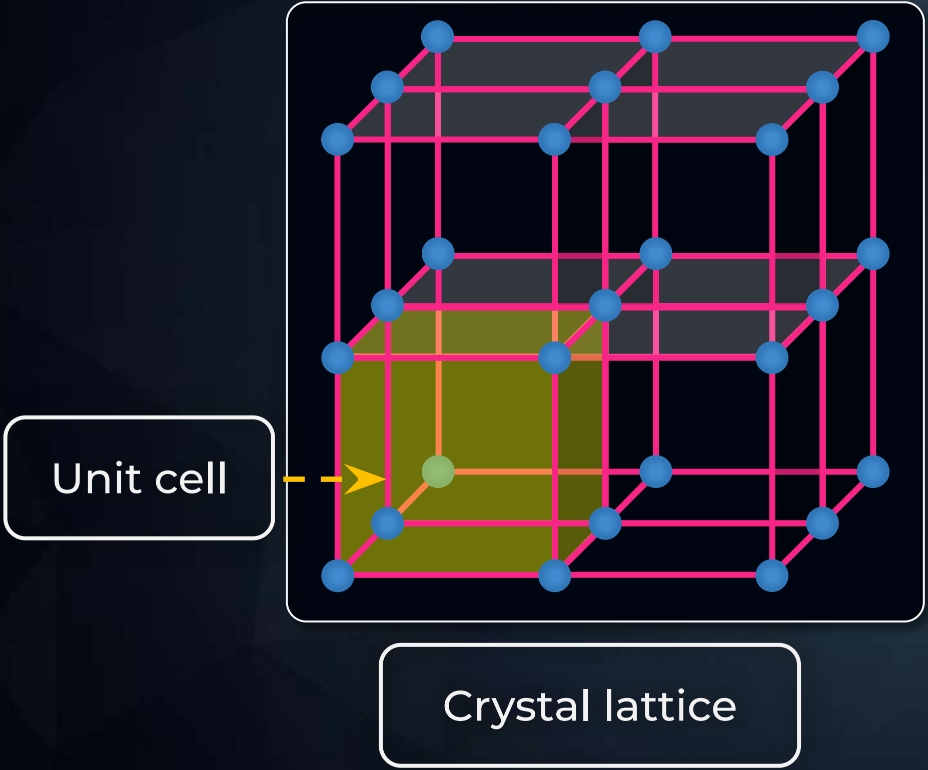
Each constituent particle (molecule, atom, and ion) will be represented by a dot(.)

Each dot is called a lattice point

Lattice / Crystal Lattice / Space Lattice

A regular arrangement of the constituent particles(molecules, atoms or ions) of a crystal in a three-dimensional space.

Unit Cell


Unit cell

Crystal lattice

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

Types of Unit Cell

- Unit Cell
  - Primitive Unit Cell
  - Centred Unit Cell

Constituent particles are present only on the corner positions of a unit cell.

A unit cell contains one or more constituent particles present at positions other than corners, along with the corner particles.

Centred Unit Cell

- **Centred Unit Cell or Non-Primitive Unit Cell**
  - Body-Centred Unit Cell (BCC)
  - Face-Centred Unit Cell (FCC)
  - End-Centred Unit Cell (ECC)

Number of Particles in a unit cell

Not all particles/lattice points contribute fully to a unit cell

Effective number of particles (Z_{eff}) depends upon the contribution of particles to a unit cell

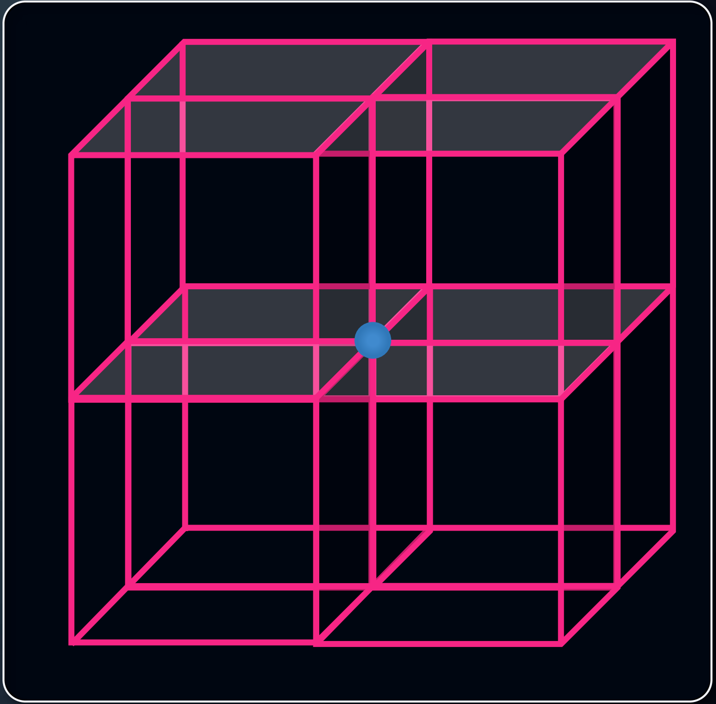
Contribution of particles to a unit cell

Depends upon the position of constituent particles in a unit cell

Contribution of Corner Particles

(1) A particle at the corner of a unit cell is shared by eight-unit cells.

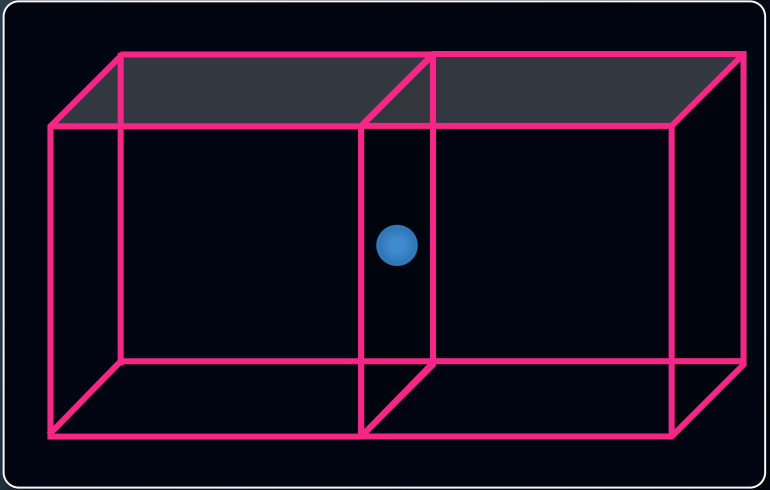
So, each particle contributes ⅛ part to the unit cell.



Contribution of Face-Centred Particles

(2) A particle at the face-centre is shared by two-unit cells.

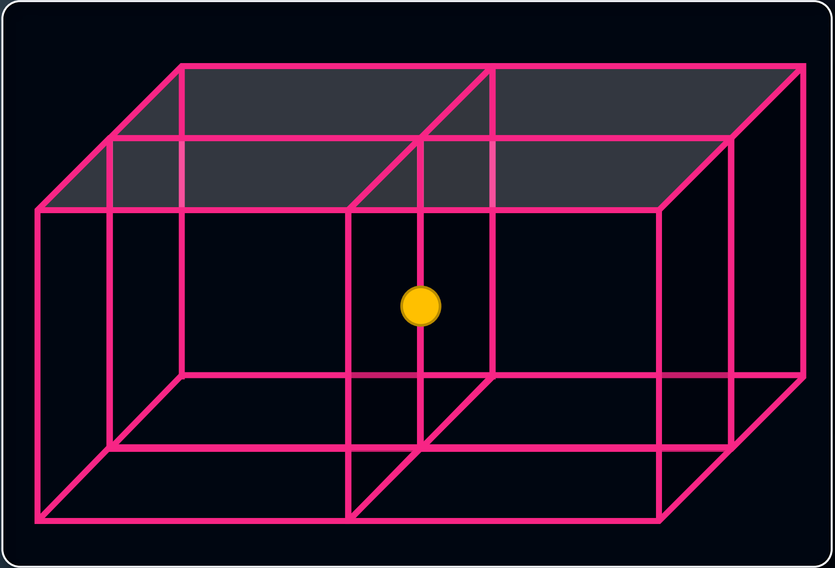
Contributes ½ part to the unit cell.



Contribution of Edge-Centred Particles

(3) A particle present at the edge-centre is shared by four-unit cells.

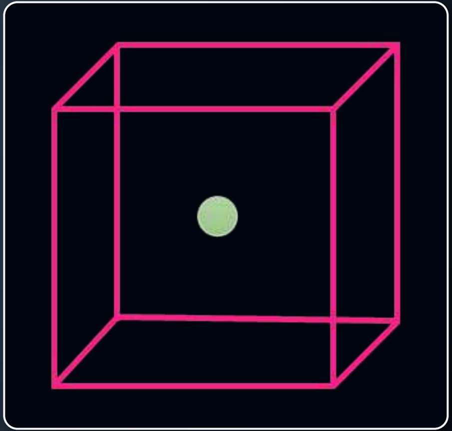
Contributes ¼ part to the unit cell.



Contribution of Body-Centred Particles

(4) A particle present at the body-centre wholly belongs to the unit cell in which it is present.

Contributes 1 part (fully) to the unit cell.



Effective number of Particles (Z_{eff}) in a unit cell

$$Z_{eff} = n_c \times \frac{1}{8} + n_f \times \frac{1}{2} + n_b \times \frac{1}{1} + n_e \times \frac{1}{4}$$

Where,

- n_c = no. of particles at corners of a unit cell
- n_f = no. of particles at face-centre of a unit cell
- n_b = no. of particles at body-centre of a unit cell
- n_e = no. of particles at edge-centre of a unit cell

Packing Efficiency

The percentage of total space filled by the particles is called packing efficiency.

$$\text{Packing Efficiency (f)} = \frac{\text{Area or Volume occupied by particles}}{\text{Total area or volume of the unit cell}} \times 100$$

Nearest Neighbor

Particle, closest to any reference particle is defined as nearest neighbor w.r.t. that reference particle.

Coordination Number

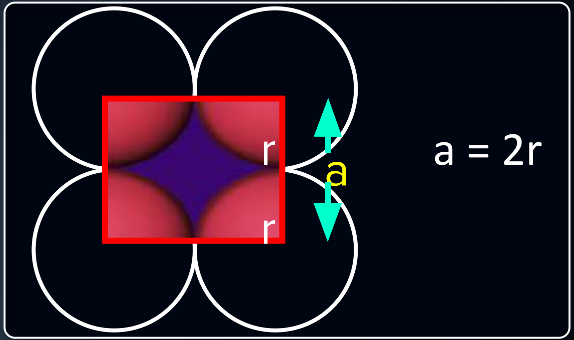
Number of particles nearest to a reference particle in a crystalline structure, is called it’s **coordination number.**

Simple Cubic Unit Cell

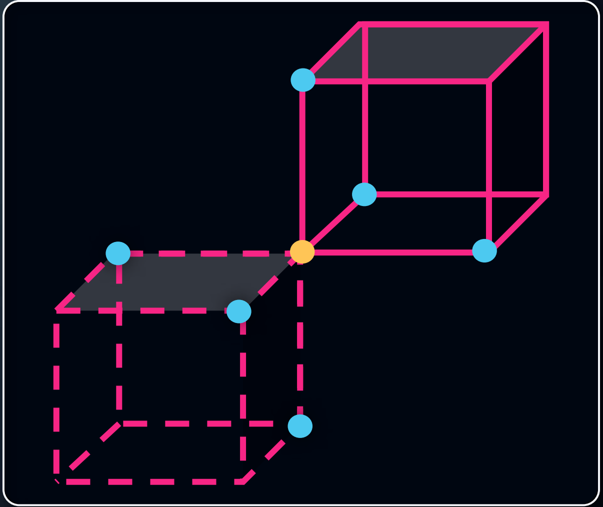
Distance of the nearest particle (d) = a = 2r

Number of nearest particles = 6

Coordination Number = 6



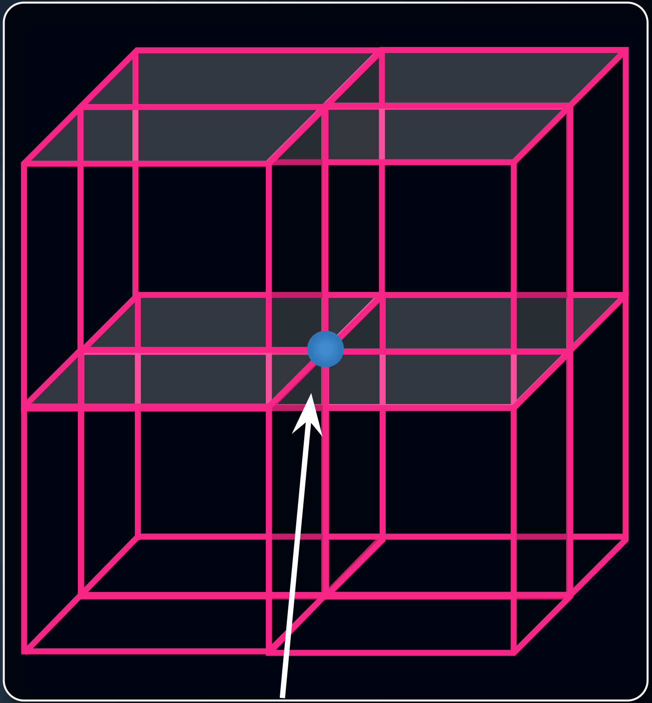
a = 2r



Simple/Primitive Cubic Unit Cell

Primitive cubic unit cell has particles only at its corners.

$$Z_{eff} = \underbrace{1/8}_{\text{contribution}} \times \underbrace{8}_{\text{Number of lattice points}} = 1$$



shared among 8 unit cells

Packing Efficiency in Simple Cubic

Z_{eff} for SCC $= 1$

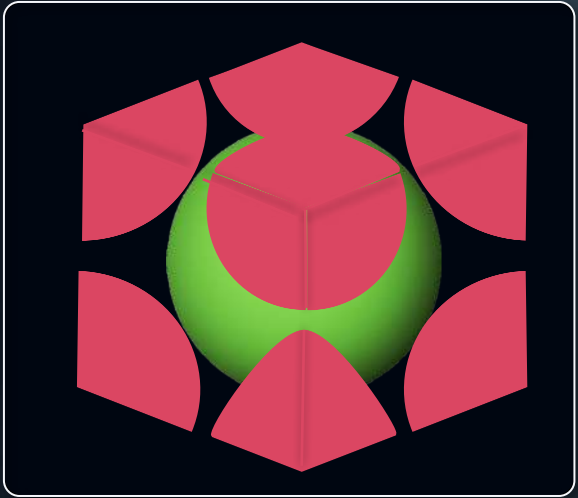
Total volume occupied by particles $= 1 \times \frac{4}{3}\pi r^3$

Volume of the cube/unit cell $= a^3 = (2r)^3$

Packing efficiency $= \frac{1 \times (4/3)\pi r^3}{(2r)^3} \times 100$

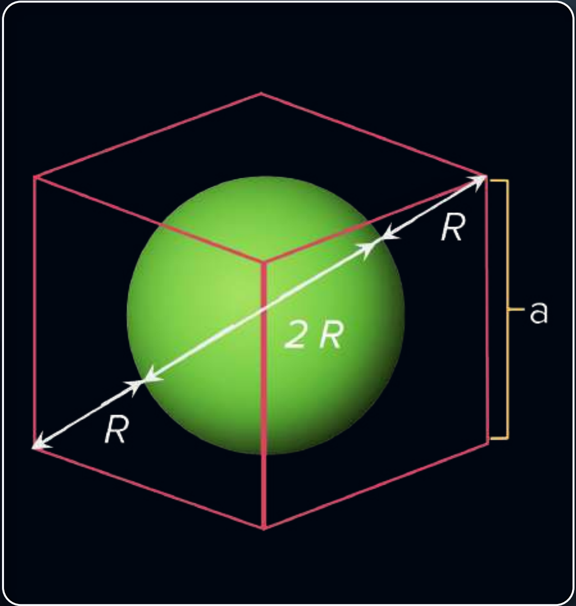
$\approx$ **52.33%**

Body-centred Cubic Unit Cell



In BCC unit cell, constituent particles touch each other along the body diagonal of cube/ unit cell

Body-centred Cubic Unit Cell



For a BCC unit cell

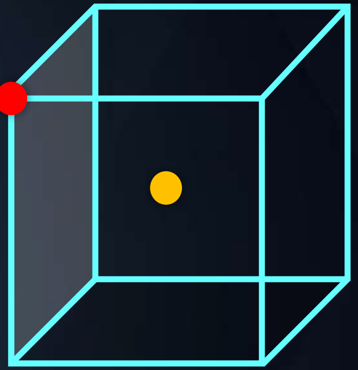
$\sqrt{3}a = 4r$

- a = Edge length of a BCC unit cell
- r = Radius of a particle present in that unit cell

Nearest Neighbor in BCC

Distance of nearest particle in BCC (d) $= \frac{\sqrt{3}a}{2} = 2r$

w.r.t corner particle and w.r.t body-centred particle

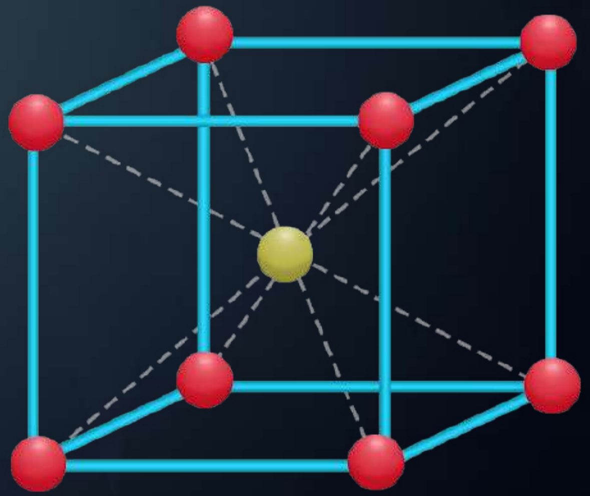


● Reference particle

● Nearest particle

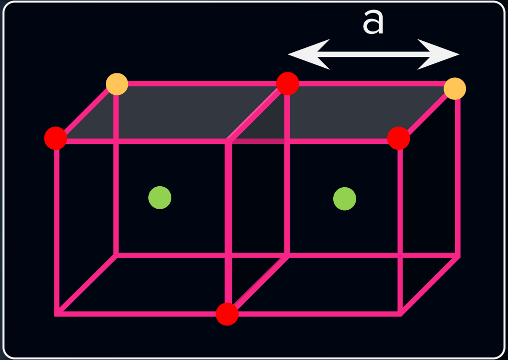
Number of nearest particles $= 8$

Coordination Number



Second Nearest Neighbor in BCC

- 🟡 Reference Particle
- 🟢 Nearest particle
- 🔴 Second Nearest particle



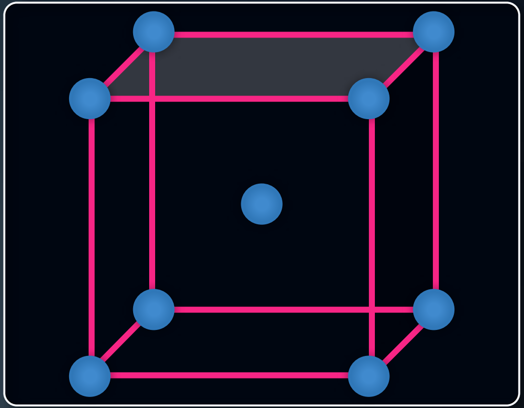
Distance of the second nearest particle (d_1) $= a = \frac{4r}{\sqrt{3}}$

Number of second nearest particles $= 6$

Body-centred Cubic Unit Cell (BCC)

(i) Contains particles at each corner

(ii) One particle at body-centre



$$Z_{eff} = \frac{1}{8} \times 8 + 1 = 2$$

Packing Efficiency in BCC

Z_{eff} for BCC $=$ 2

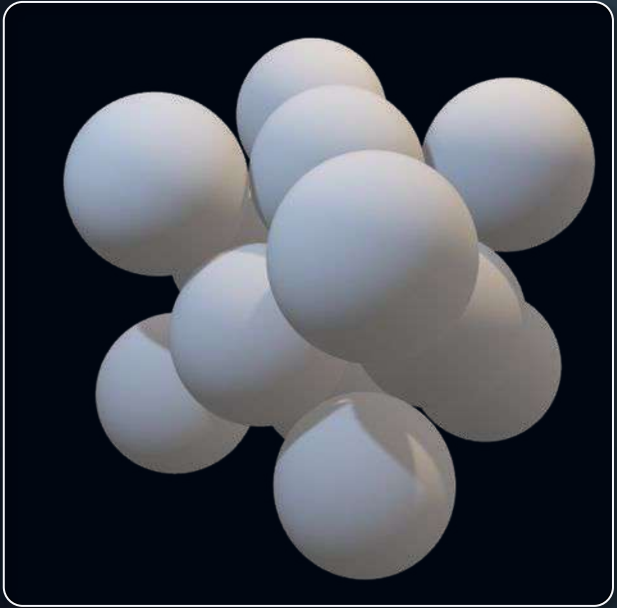
Total volume occupied by particles $=$ $2 \times \frac{4}{3} \pi r^3$

Volume of the cube/unit cell (a^3) $=$ $(4r/\sqrt{3})^3$

Packing efficiency $=$ $\frac{2 \times (4/3)\pi r^3}{(4r/\sqrt{3})^3} \times 100$

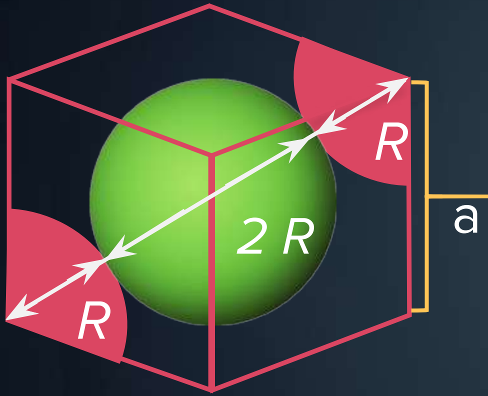
$\approx$ **68%**

Face-centred Cubic Unit Cell



Constituent particles touch each other across a face diagonal of the unit cell.

Face-centred Cubic Unit Cell



For a FCC unit cell,

$\sqrt{2}a = 4r$

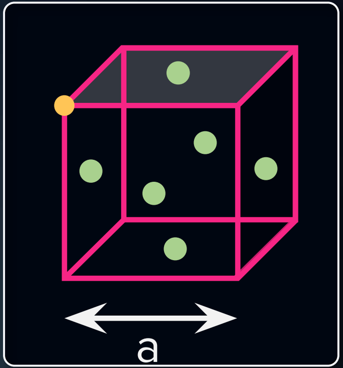
- a = Edge length of a FCC unit cell
- r = Radius of a particle present in that unit cell

Nearest Neighbor in FCC

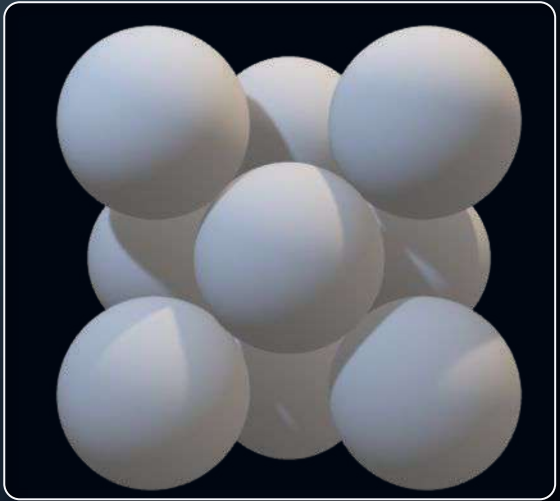
Distance of nearest particle in FCC (d) $= \dfrac{\sqrt{2}a}{2}$

$= \dfrac{a}{\sqrt{2}}$

$= 2r$



- 🟡 Reference Particle
- 🟢 Nearest particle



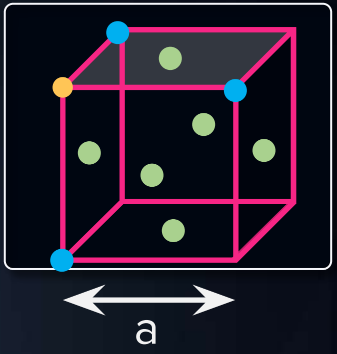
Second Nearest Neighbor in FCC

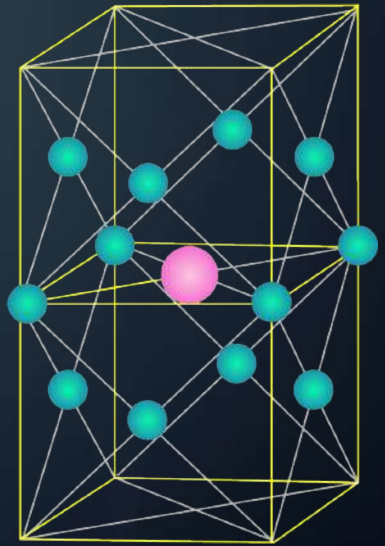
Distance of the second nearest particle (d_1) $= a$

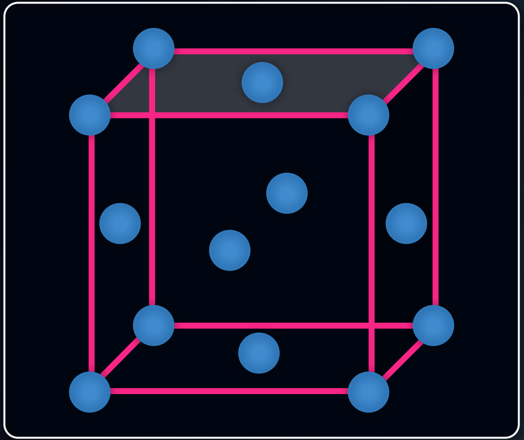
$$= \frac{4r}{\sqrt{2}}$$

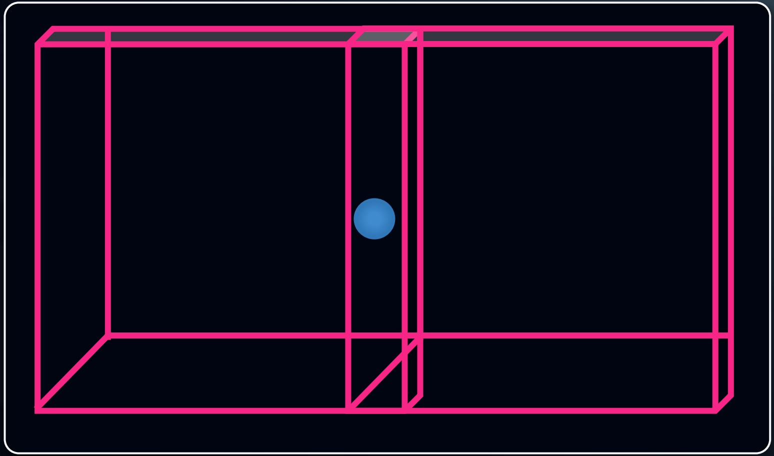
Number of second nearest particles = 6

- ● Reference Particle
- ● Nearest particle
- ● Second Nearest particle









Face-centred Cubic Unit Cell (FCC)

(i) Contains particles at each corner.

(ii) Contains particles at the centre of all the faces of the unit cell.

$$Z_{eff} = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$$

Packing Efficiency in FCC

Z_{eff} for FCC $= 4$

Total volume occupied by sphere $= 4 \times \frac{4}{3}\pi r^3$

Volume of the cube (a^3) $= (2\sqrt{2}r)^3$

Packing efficiency $= \frac{4 \times (4/3)\pi r^3}{(2\sqrt{2}r)^3} \times 100$

$\approx$ **74%**

Density of Unit Cell

$$\text{Density } (\rho) = \frac{(\text{Number of particles in a unit cell}) \times (\text{Molar mass})}{(\text{Volume of unit cell}) \times (N_A)}$$

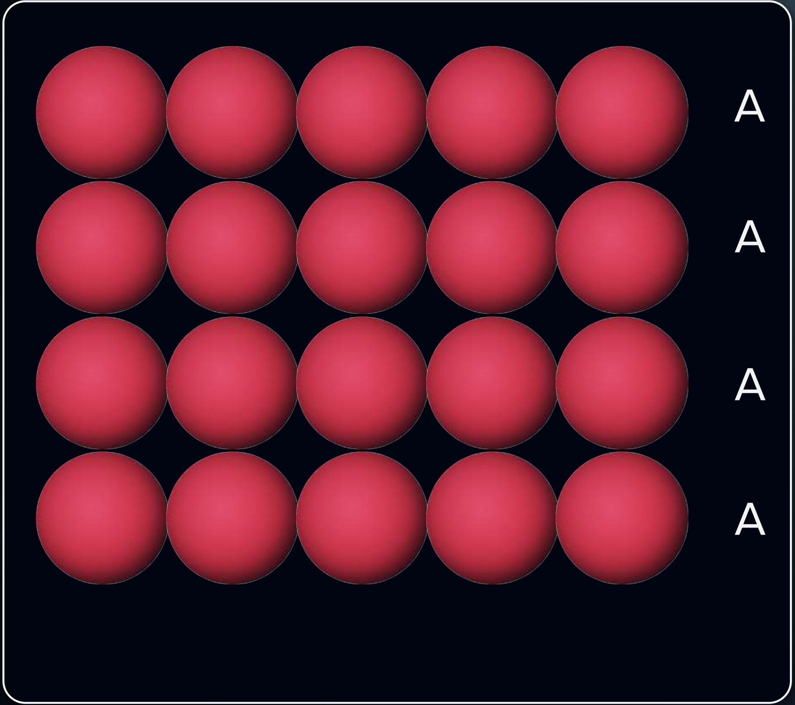
$$\text{Density } (\rho) = \frac{Z_{eff} \times M}{N_A\,(a^3 \times 10^{-30})}\ \text{g cm}^{-3}$$

a = edge length in pm

Close-packed Structure

In crystalline solids, the constituent particles are close-packed, leaving very less vacant space.

Square Close Packing



C.N. is 4

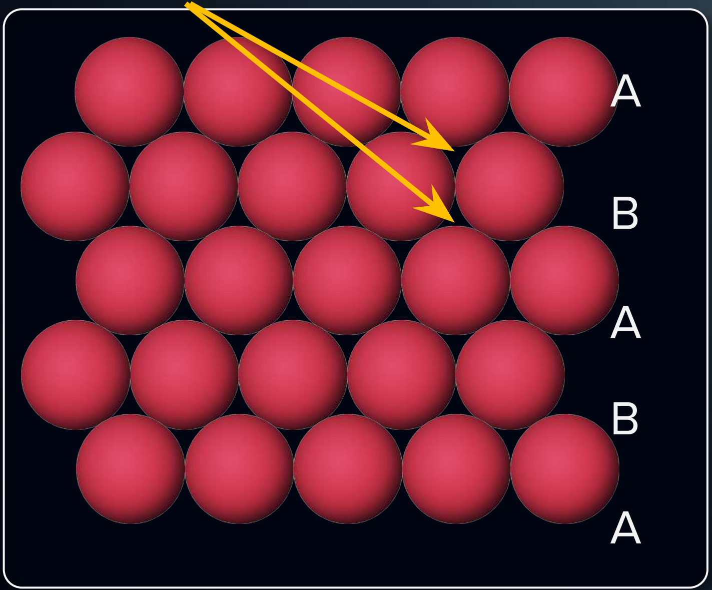
Each sphere touches 4 other neighbors.

The centres of the neighboring spheres join to form a square.

So, the packing is known as square close packing in2-D.

Hexagonal Close Packing

Triangular
Voids



C.N. is 6

Each sphere touches 6 other neighbors.

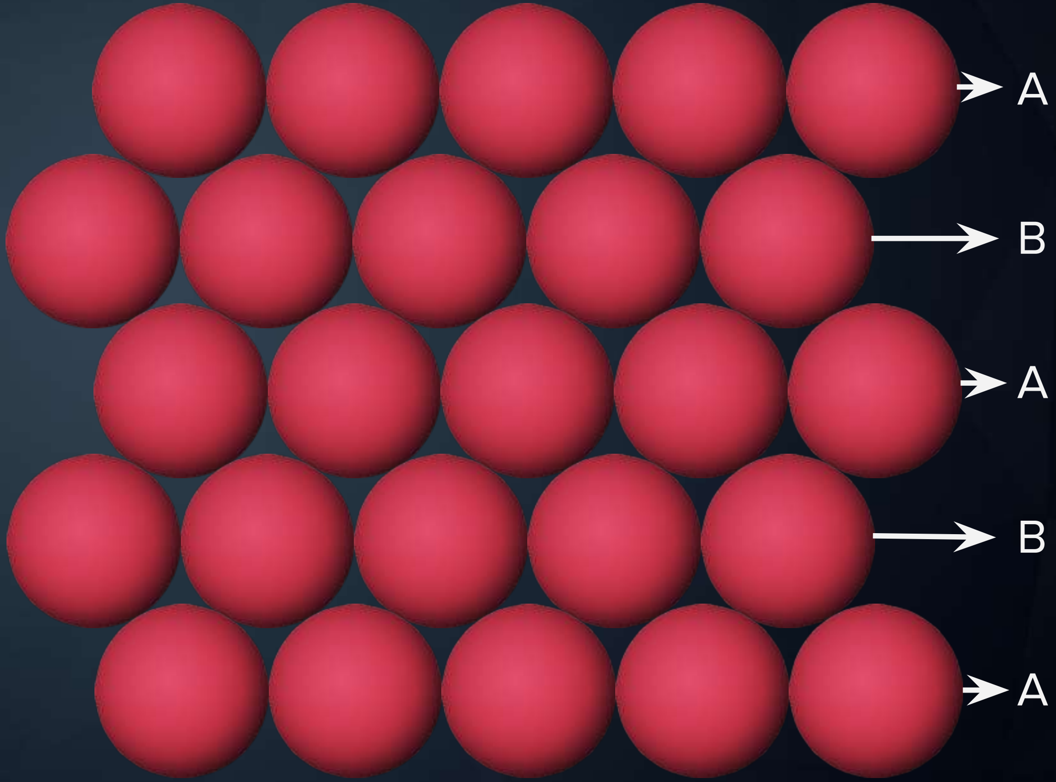
The centres of the neighboring spheres join to form a hexagon

Hence, the packing is known as hexagonal close packing (hcp) in 2-D.

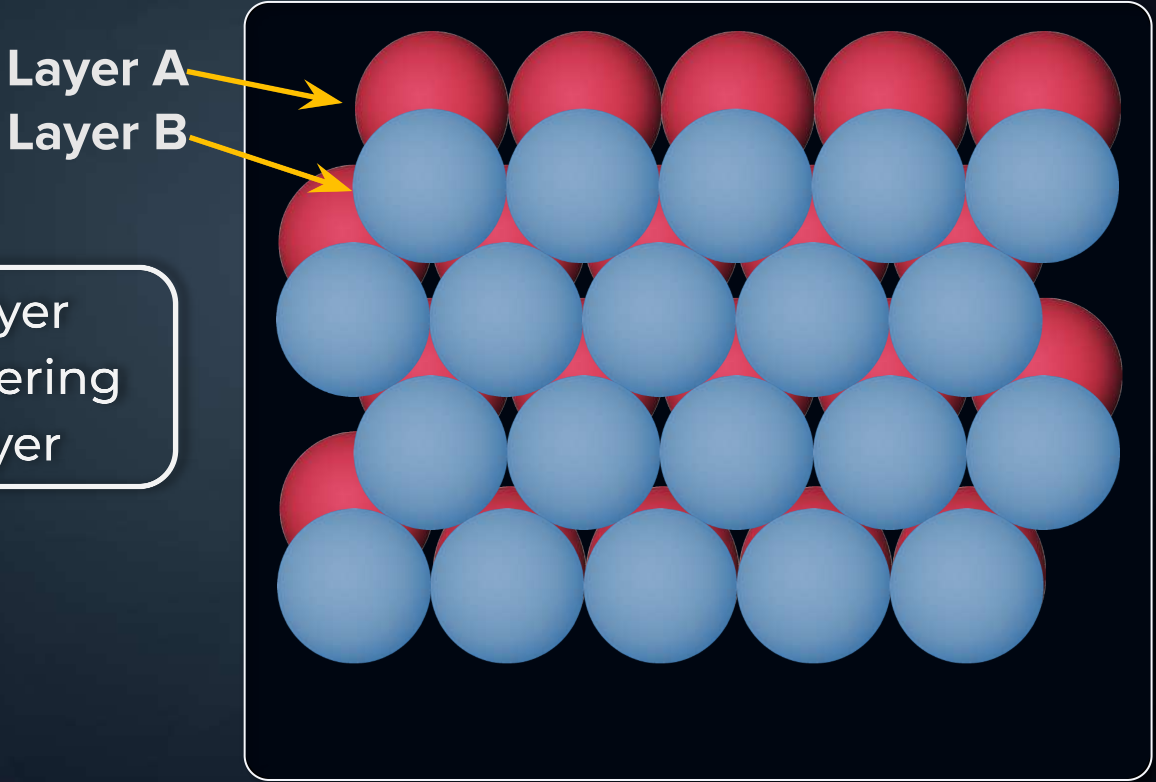
From 2-D Square Closed Packing

Square packed layers/sheets are placed exactly above one another.

Lattice thus generated is simple cubic lattice and its unit cell is simple cubic unit cell.

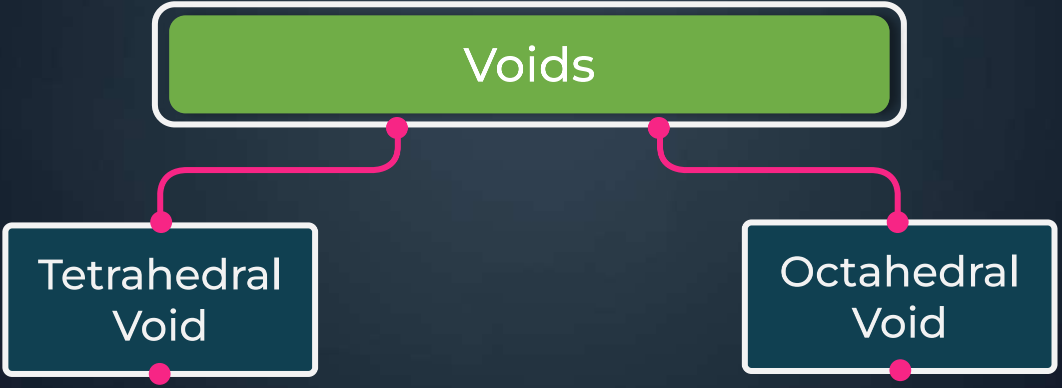


From 2-D Hexagonal Close Packing



Placing the second layer above the first layer covering the voids of the 1st layer

Types of Voids in Hexagonal Packing

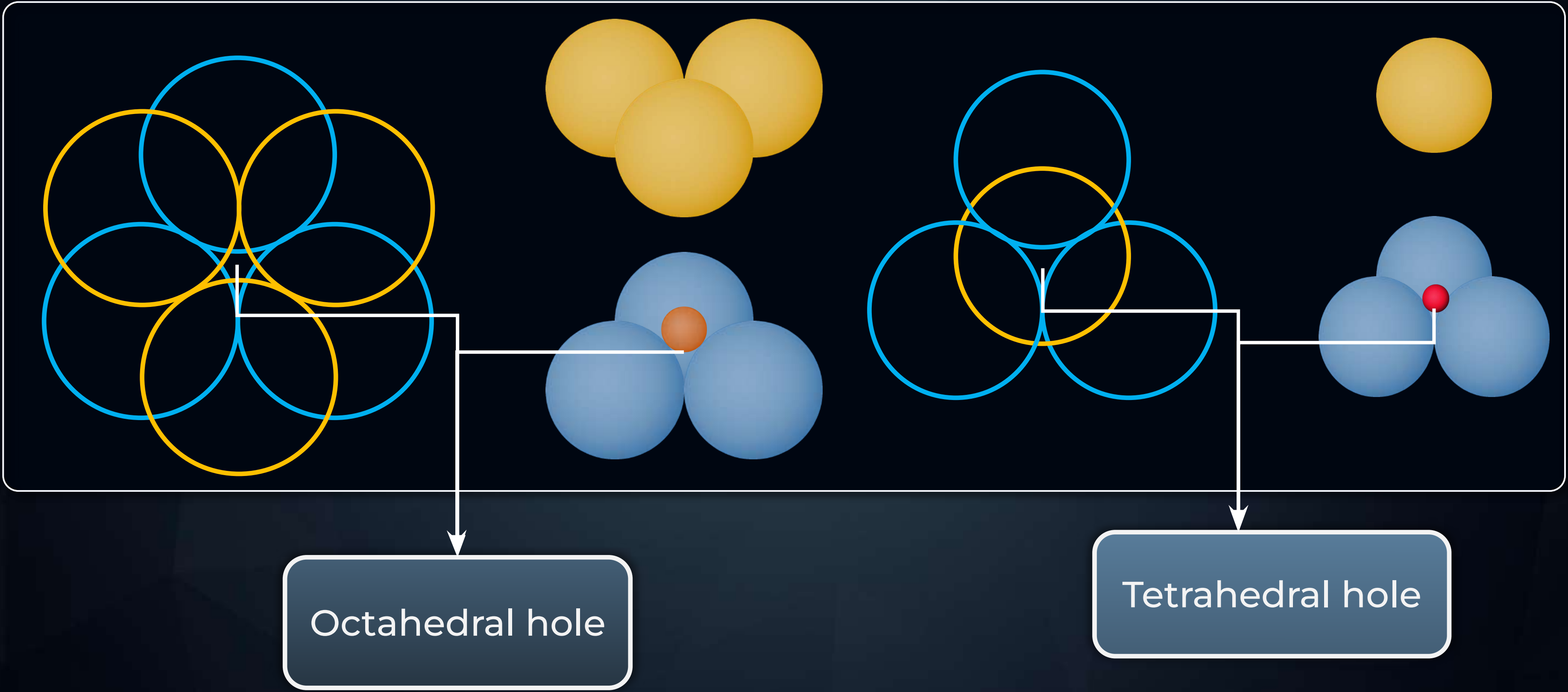


Voids

Tetrahedral Void

Octahedral Void

Types of Voids



Octahedral hole

Tetrahedral hole

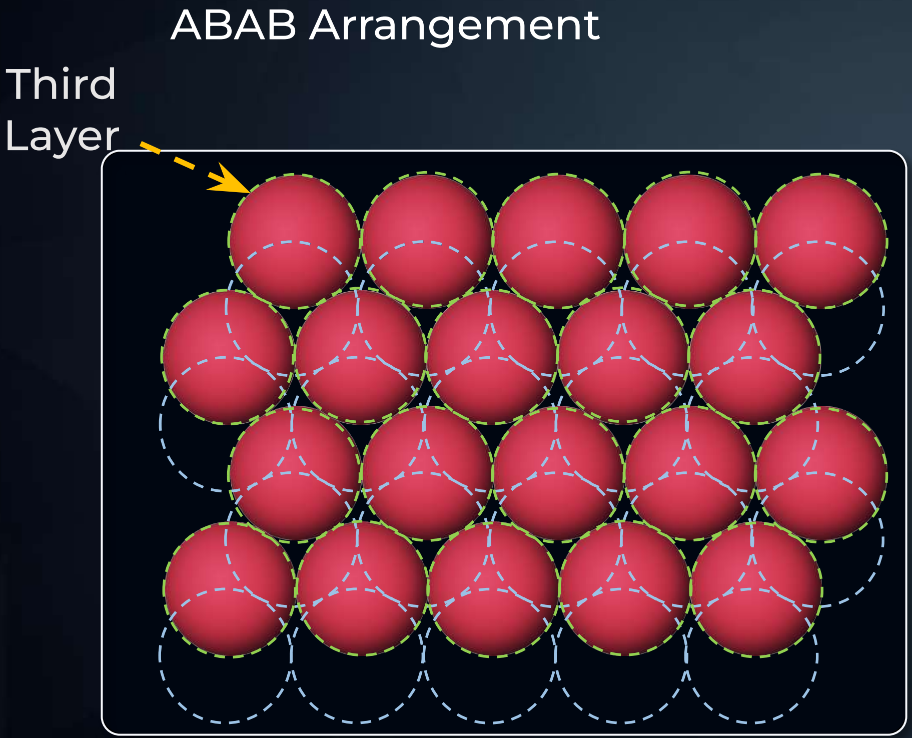
From 2-D Hexagonal Close Packing

2 possibilities for placing the third layer spheres over second layer

Covering Tetrahedral Voids

Covering Octahedral Voids

Hexagonal Close Packing

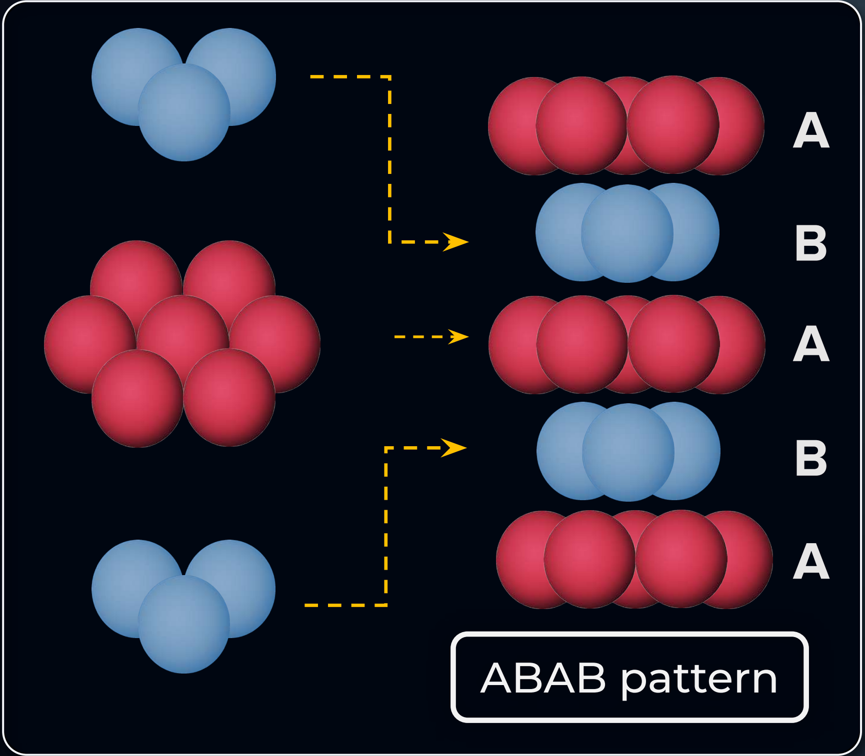


Spheres of third layer are placed over voids of second layer so that

Spheres of third layer are exactly aligned with the spheres of first layer

The pattern is repeated in alternative layers, written as ABAB Pattern.

Hexagonal Close Packing (hcp)



ABAB pattern

The structure is called hexagonal close packing (hcp) structure.

Packing in Mg, Zn, Cd etc. Follows this type of arrangement.

Coordination Number in hcp

Each sphere touches

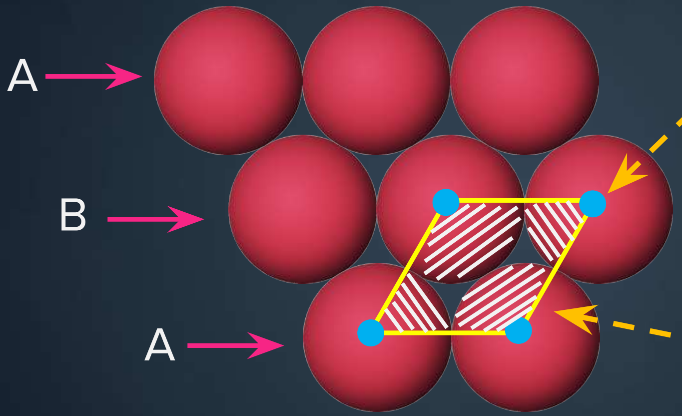
6 spheres in its layer + 3 spheres, below the layer + 3 spheres, above the layer

For hcp structure, the number of nearest neighbors of a particle is - 12

C.N. is 12

e.g.: Mg, Cd, Zn, Ti and Be

Z_{eff} in HCP



Two such spheres are Shared by six unit cells

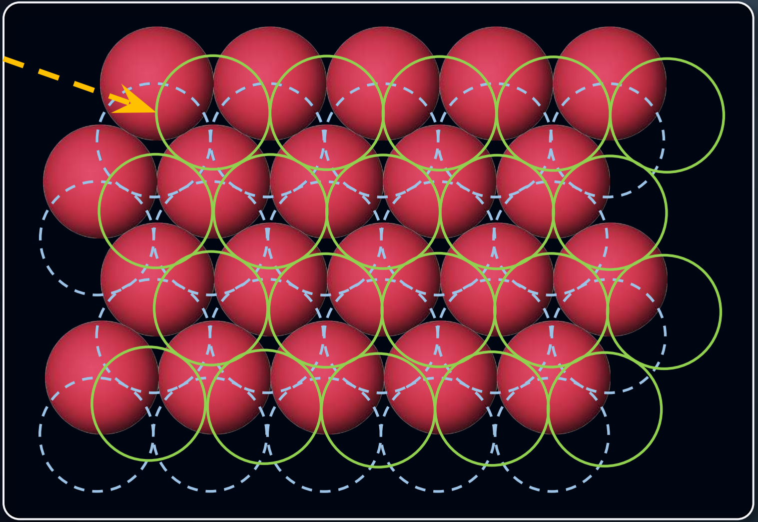
Two such spheres are Shared by three unit cells.

$$Z_{eff} = 2 \times \frac{1}{6} + 2 \times \frac{1}{3} = 1$$

Packing Efficiency in HCP

Packing efficiency in HCP packing (f) $\approx$ 74%

Covering Octahedral Voids

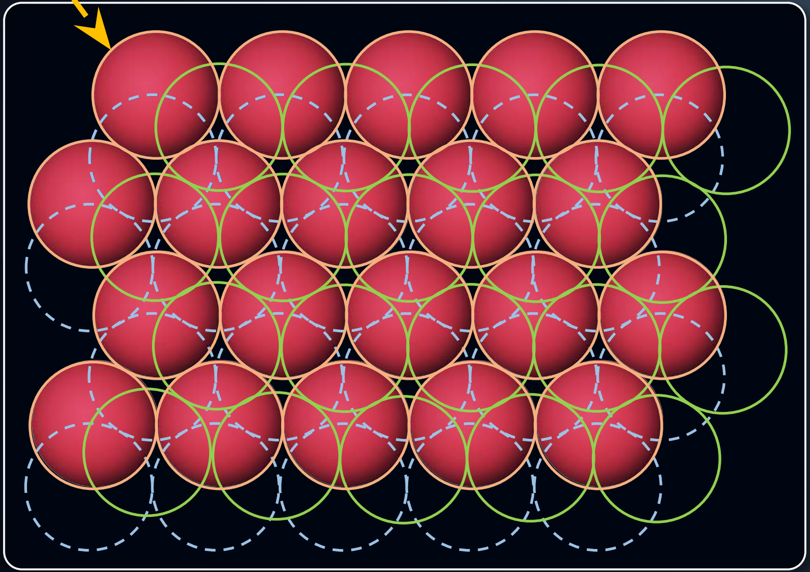


Third
Layer

Third layer spheres are placed over second layer such that,

Its spheres cover the octahedral voids (which aren’t covered by spheres of second layer).

Covering Octahedral Voids



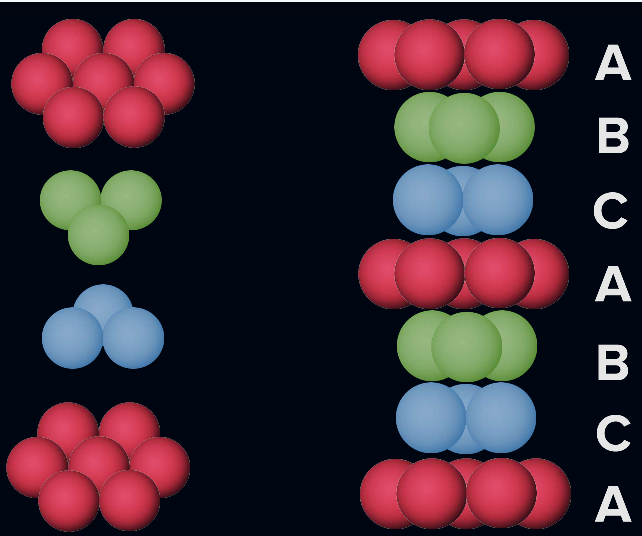
The third layer isn't aligned with either first or second layer.

Fourth layer, above third layer, repeats layer A orientation.

The pattern of layers is known as ABC–ABC pattern

Covering Octahedral Voids

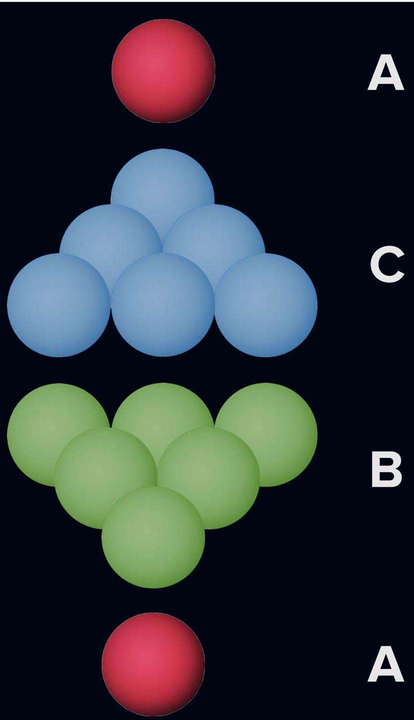
ABCABC pattern

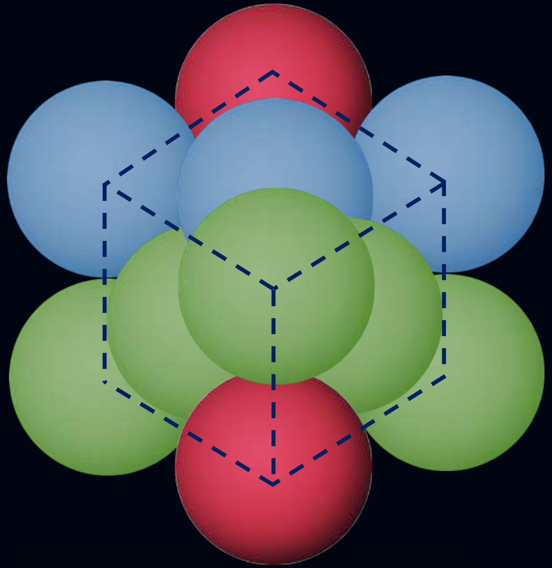


Such structure is called cubic close packing(ccp) or face-centred cubic (fcc) structure.

Packing in Ca, Sr, Cu, Ag, Au etc. follows this type of arrangement.

Cubic Close Packing (ccp)



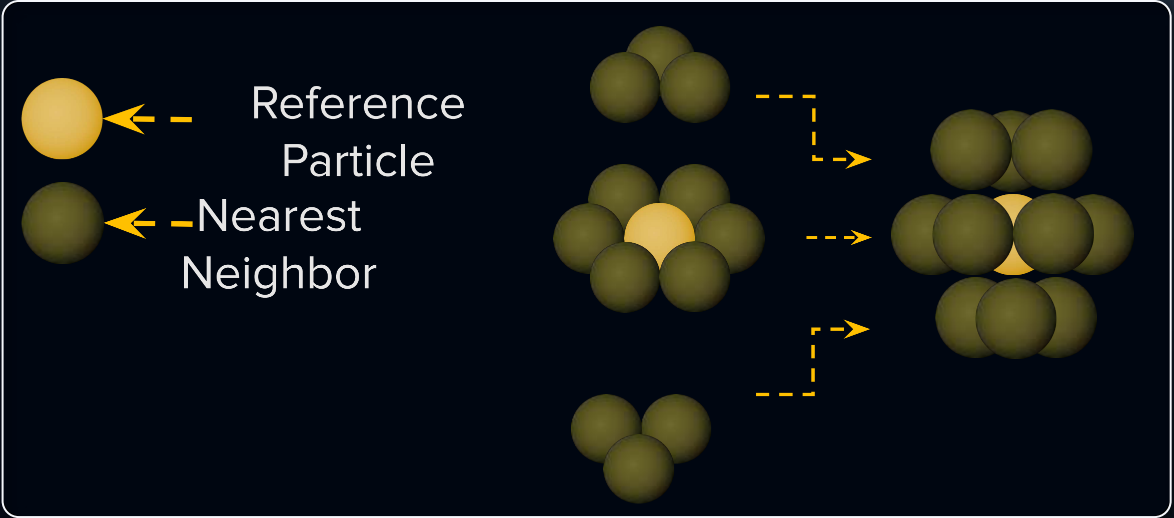


FCC structure

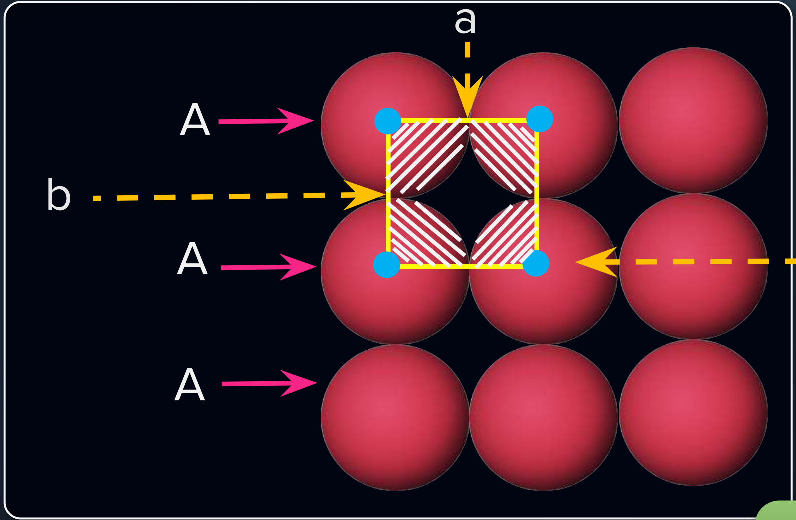
Coordination Number of Particles in fcc

C.N. is 12

For ccp/fcc structure, the number of nearest neighbors of a particle is - 12



CCP



a = b = 2R

Shared by
four unit cells

$$Z_{eff} = 4 \times \frac{1}{4} = 1$$

Packing Efficiency in CCP

Packing efficiency in CCP packing (f) $\approx$ **74%**

Voids (Interstitial Voids)

The close packed structures have maximum packing efficiency

But there are some empty spaces left in the arrangement

Voids/Interstitial Voids

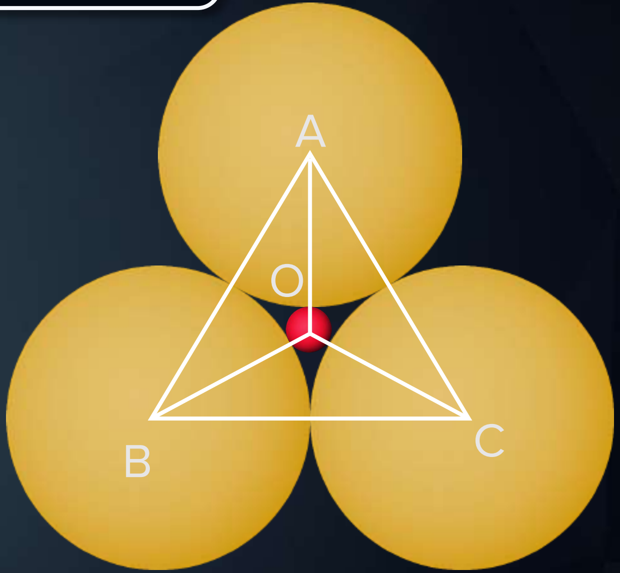
Triangular Void

Radius ratio

$$\frac{r}{R} = 0.155$$

R = atomic radius
r = radius of the triangular void

Maximum radius of a triangular Void = 0.155 × Radius of the sphere (Bigger atom/ion)



Coordination Number = 3

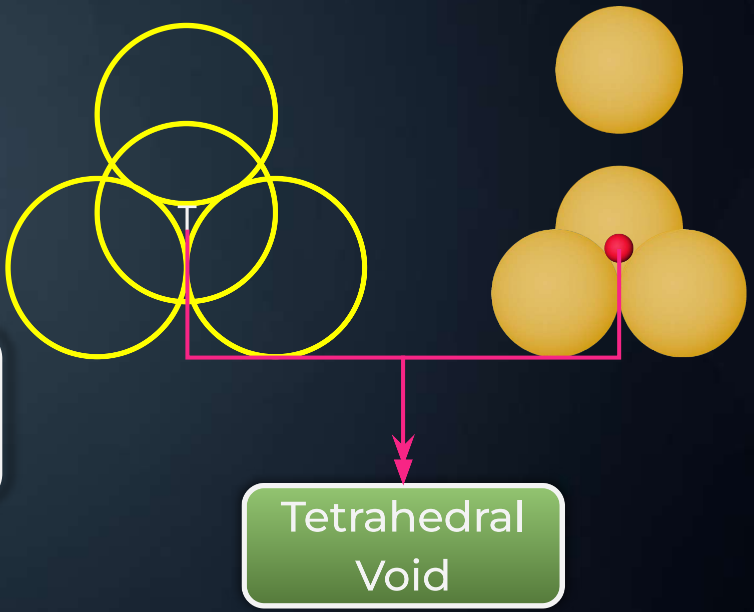
Tetrahedral Void

Radius ratio

$$\frac{r}{R} = 0.225$$

R = atomic radius
r = radius of the tetrahedral void

Coordination Number = 4



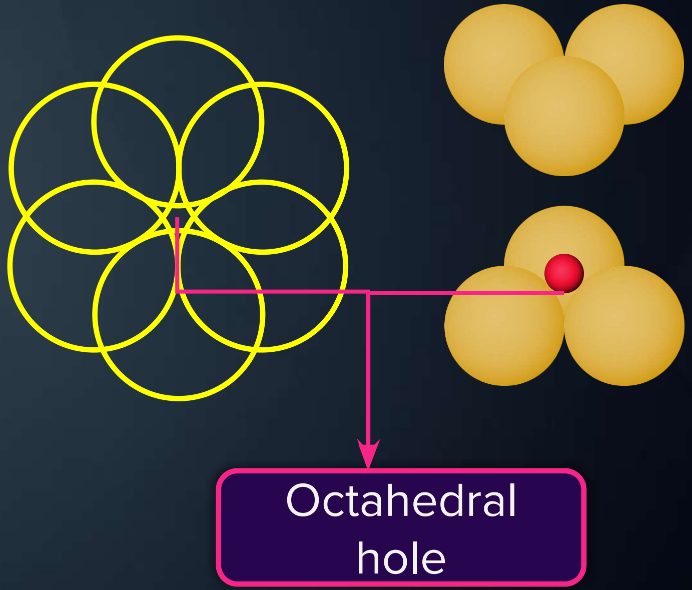
Octahedral Void

Radius ratio

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

R = atomic radius
r = radius of the octahedral void

Coordination Number = 6



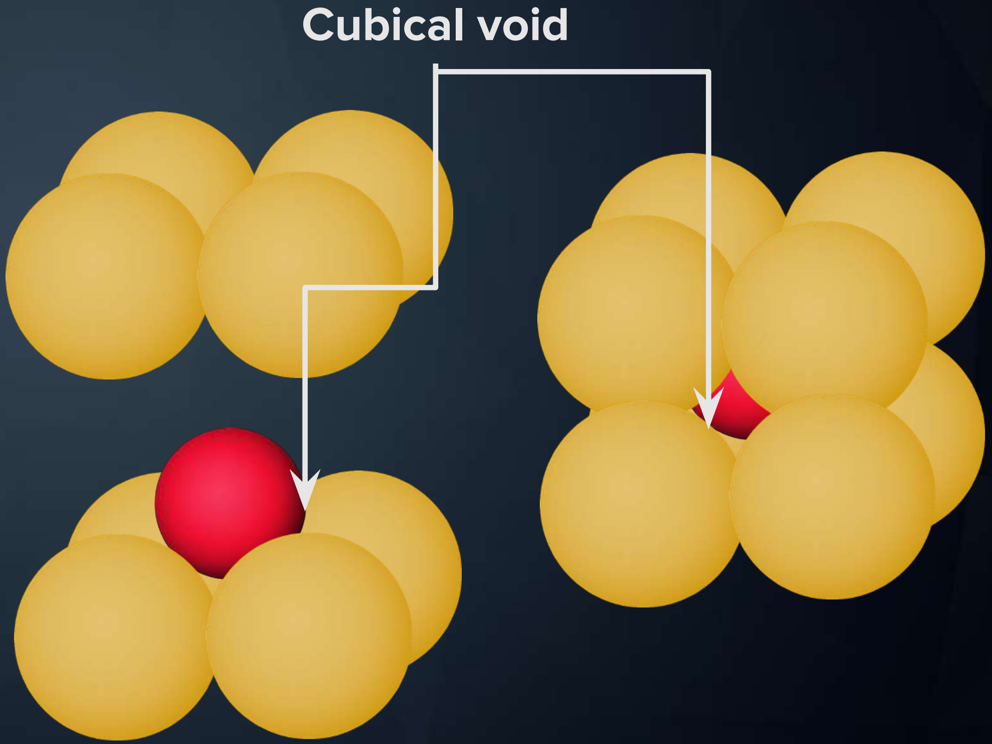
Cubical Void

Radius ratio

$$\frac{r}{R} = 0.732$$

R = atomic radius
r = radius of the cubical void

Coordination number = 8



Points to Remember!!

Let the number of close packed spheres in a unit cell be N

(1) The number of Tetrahedral Voids generated = 2N

(2) The number of Octahedral Voids generated = N

Tetrahedral Voids in fcc or ccp

Each fcc unit cell has 4 body diagonals.

Each body diagonals contains 2 tetrahedral voids.

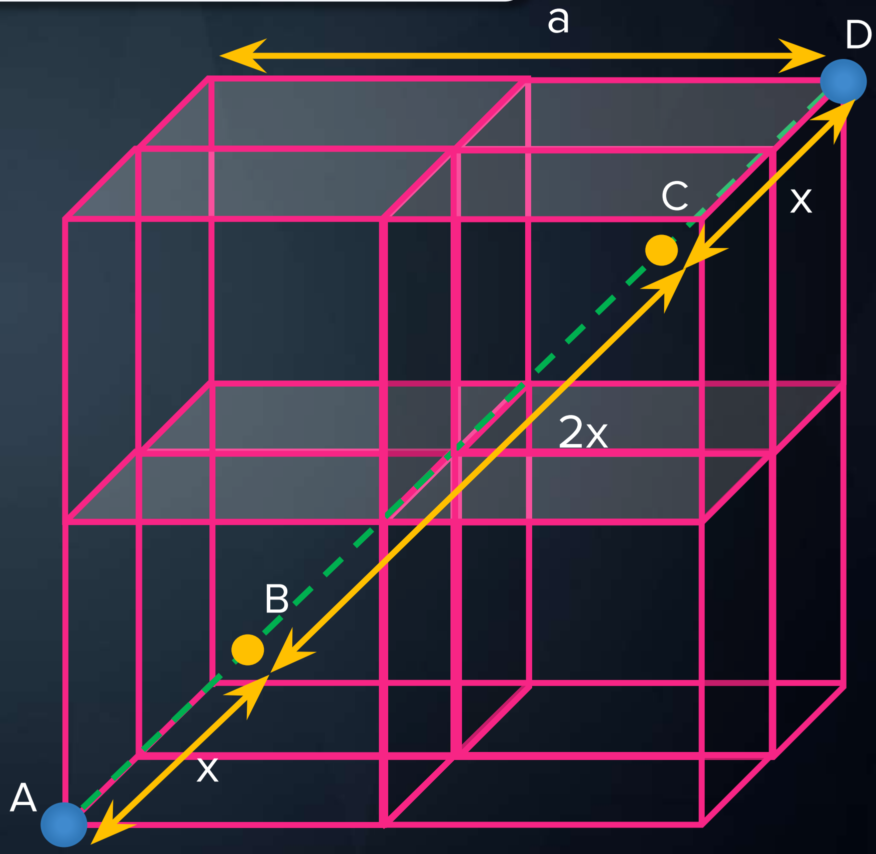
FCC unit cell has
8 tetrahedral voids

Tetrahedral Voids in fcc or ccp

$\sqrt{3}a$ = $4x$

Distance of a tetrahedral void from corner (x) = $\frac{\sqrt{3}a}{4}$

Distance between two tetrahedral voids (2x) = $\frac{\sqrt{3}a}{2}$



Number of Octahedral Voids in fcc or ccp

Number of octahedral voids per unit cell $= 1 + 12 \times \frac{1}{4} = 4$

Void at body centre

Voids at edge centres

Number of octahedral voids =
No. of particles in an unit cell

Voids in HCP

01

Tetrahedral Voids

12 per unit cell

02

Octahedral Voids

6 per unit cell

Remember

Unit cell	Z_{eff}	Tetrahedral Void (Z_{eff} × 2)	Octahedral Void (Z_{eff})
CCP (FCC)	4	8	4
HCP	6	12	6

Packing in Ionic Compounds

Larger ions
(Generally anion)

Form the close-packed structure

Smaller ions
(Generally cation)

Inserted in the voids

Radius-Ratio Rule

Size and type of void occupied by an ion

Is determined by knowing relative size of cations and anions

$$\text{Radius Ratio} = \frac{\text{Radius of Cation}}{\text{Radius of Anion}} = \frac{r_+}{r_-}$$

Summary – Radius Ratio

Radius Ratio	Type of Void Occupied	Coordination Number	Examples
< 0.155	Liner void	2	
0.155 to 0.225	Planar Triangular Void	3	Boron oxide
0.225 to 0.414	Tetrahedral Void	4	Zinc sulphide
0.414 to 0.732	Octahedral Void	6	Sodium Chloride
0.732 to 1.000	Body Centered Cubic Void	8	Calcium chloride

Rock Salt (NaCl)

Experimental ratio,

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.51$$

$$0.414 \leq \frac{r_{Na^+}}{r_{Cl^-}} < 0.732$$

Cl^- ions form the FCC lattice

While Na^+ ions occupy all the octahedral voids

Rock Salt (NaCl)

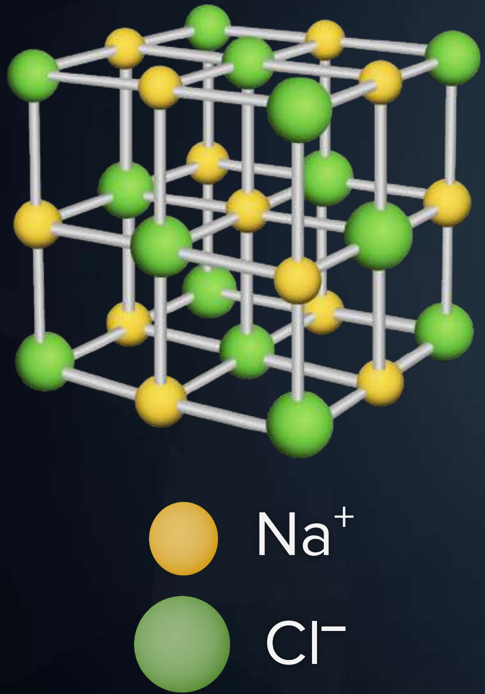
Ratio of Coordination number

4 : 4

1 : 1

So, General formula = AB

Rock Salt (NaCl)



For anion Cl^-,

(i) Distance of nearest cation = $\frac{a}{2}$

Na^+ at edge Center

Number of nearest cations = 6

(ii) Distance of nearest anion = $\frac{a}{\sqrt{2}}$

Number of nearest anions = 12

Rock Salt (NaCl)

Na^+ at Body Center

(iii) Distance of second nearest cation = $\frac{\sqrt{3}a}{2}$

Number of second nearest cations = 8

(iv) Distance of second nearest anion = a

Number of second nearest anions = 6

Rock Salt (NaCl)

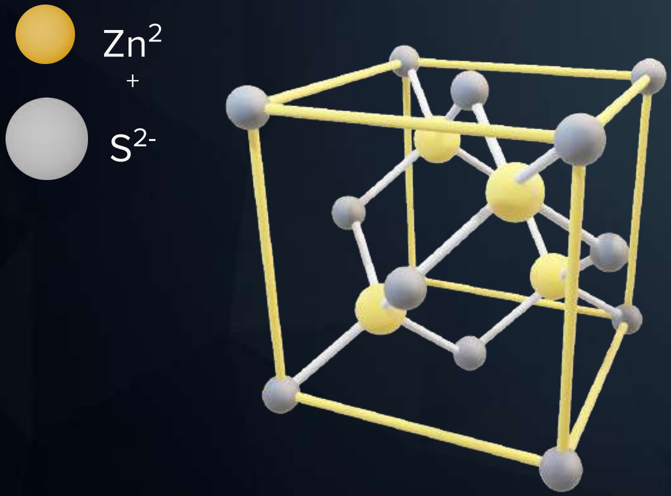
Examples

1. Alkali metal halides — Except CsCl
2. Ammonium halides, silver halides — Except AgI
3. Oxides and sulphides of alkaline earth metals — Except BeS

Zinc Blende (ZnS)

S^{2-} ions form the FCC lattice

Occupy 8 corners and 6 face centres.



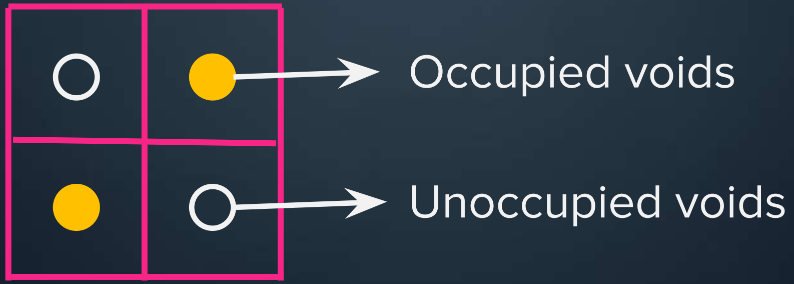
Number of S^{2-} ions in each unit cell $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

$= 1 + 3 = 4$

Zinc Blende (ZnS)

Zn^{2+} ions occupy alternate (nonadjacent) tetrahedral voids

Half of the tetrahedral voids are filled with Zn^{2+}



Occupied voids

Unoccupied voids

Zinc Blende (ZnS)

Zn^{2+} ions occupy alternate (nonadjacent) tetrahedral voids = 8

So, Number of Zn^{2+} ions = 4

Total ZnS units in one unit cell = 4

Ratio of Coordination number

4 : 4

1 : 1

So, General formula = AB

Zinc Blende (ZnS)

Experimental ratio,

$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.3$$

$$0.225 \leq \frac{r_{Zn^{2+}}}{r_{S^{2-}}} < 0.414$$

Zinc Blende (ZnS)

For S^{2-} anion
(placed at the corner)

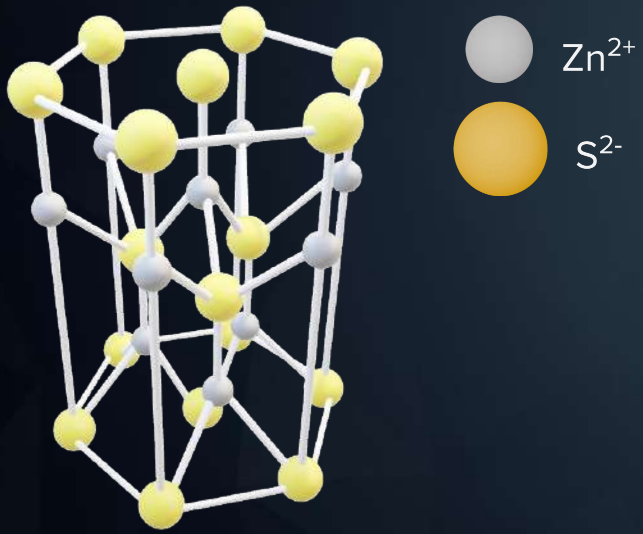
(i) Distance of nearest cation = $\frac{\sqrt{3}a}{4}$

Number of nearest cations = 4

(ii) Distance of nearest anion = $\frac{a}{\sqrt{2}}$

Number of nearest anions = 12

Zinc Blende (ZnS)



S^{2-} ions form the hcp lattice

Number of S^{2-} ions = 6

Zn^{2+} ions occupy alternate (non-adjacent) tetrahedral voids.

Number of S^{2-} ions = 6

As total tetrahedral voids = 12

Rock Salt (NaCl)

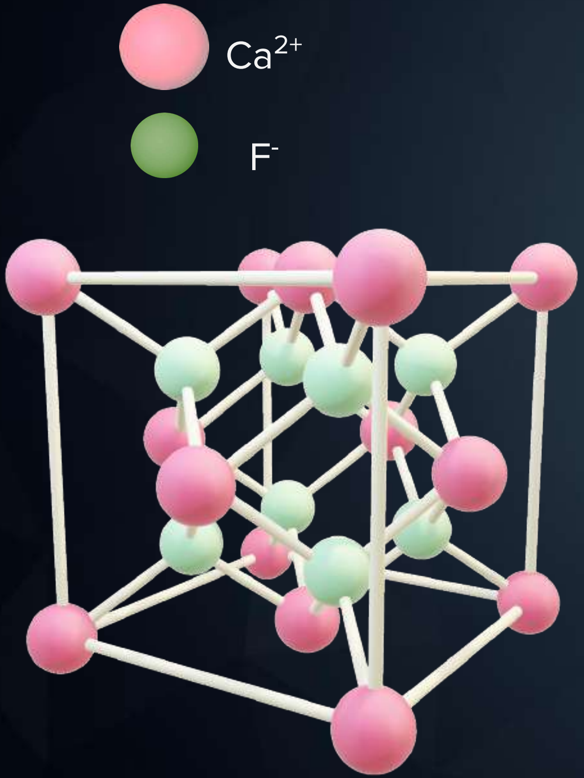
4 : 4

Coordination number of cations

Coordination number of anions

So, General formula = AB

Fluorite Structure (CaF_2)



Ca^{2+} ions form the FCC lattice ❯ Ca^{2+} ions in each unit cell = 4

F^- ions occupies all the tetrahedral voids ❯ Number of F^- ions = 8

As total tetrahedral voids = 8

Total CaF_2 units in one unit cell = 4

Fluorite Structure (CaF_2)

Ratio of Coordination number

8 : 4

2 : 1

So, General formula = AB_2

Other examples of fluorite structure

BaF_2, $BaCl_2$, SrF_2, $SrCl_2$ etc.

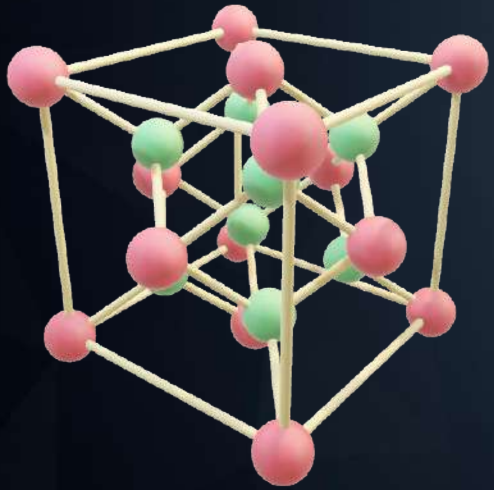
Fluorite Structure (CaF_2)

$$0.225 \le \frac{r_{F^-}}{r_{Ca^{2+}}} < 0.414$$

$$r_{F^-} + r_{Ca^{2+}} = \frac{\sqrt{3}a}{4}$$

Fluorite Structure (CaF_2)

For cation, Ca^{2+}
(placed at the corner)



(i) Distance of nearest anion = $\frac{\sqrt{3}a}{4}$

Number of nearest anion = 8

(ii) Distance of nearest cation = $\frac{a}{\sqrt{2}}$

Number of nearest cation = 12

Fluorite Structure (CaF_2)

For F^- anion,

(i) Distance of nearest cation = $\frac{\sqrt{3}a}{4}$

Number of nearest cations = 4

(ii) Distance of nearest anion = $\frac{a}{2}$

Number of nearest anions = 2

Anti-Fluorite Structure (Na_2O)

Total Na_2O units in one unit cell = 4

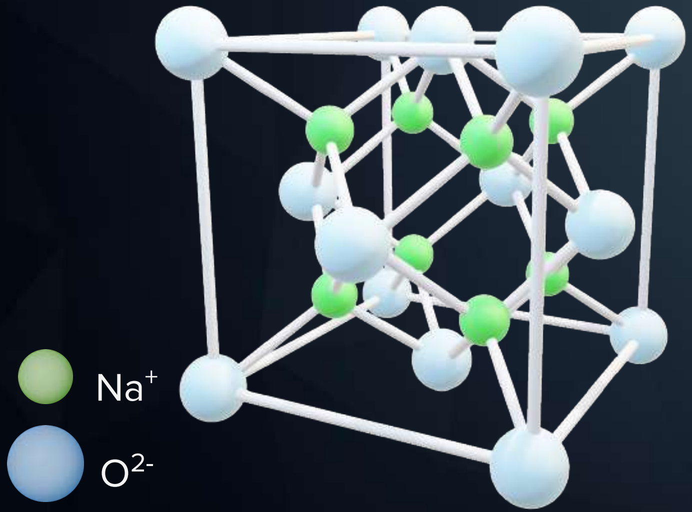
O^{2-} ions form the FCC lattice

Number of O^{2-} ions in each unit cell = 4

Na^+ ions occupy all tetrahedral voids

Number of Na^+ ions = 8

As total tetrahedral voids = 8



Anti-Fluorite Structure (Na_2O)

Ratio of Coordination number

4 : 8

1 : 2

So, General formula = A_2B

Examples

Alkali metal oxides M_2O (M = Li, Na, K, Rb) crystallize in the anti-fluorite structure.

Caesium Chloride (CsCl)

Cl^- ions form simple cubic lattice

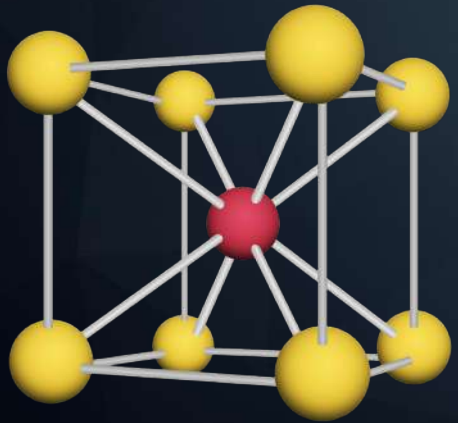
Number of Cl^- ions per unit cell = 1

Cs^+ ions occupy cubical void

Number of Cs^+ ions = 1

● Cs^+

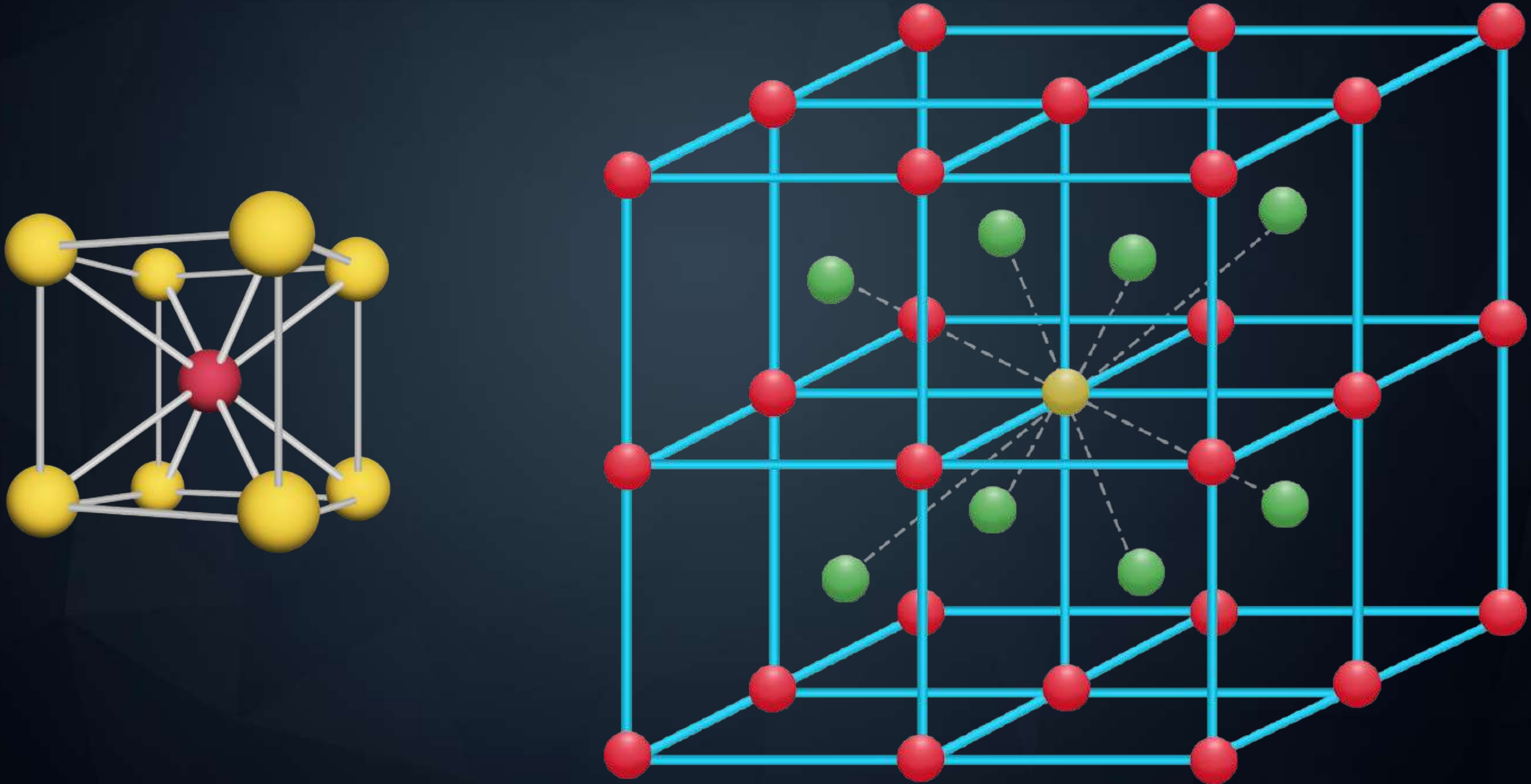
● Cl^-



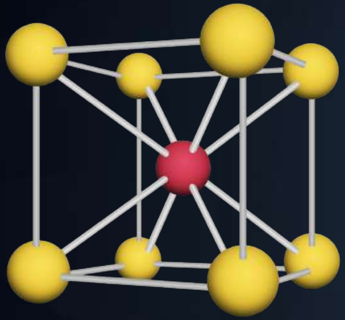
As total cubical voids = 1

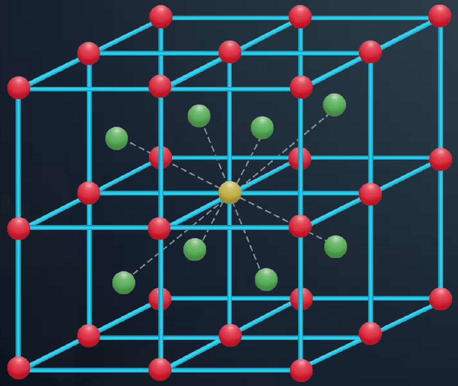
Total CsCl units per unit cell = 1

Caesium Chloride (CsCl)



Caesium Chloride (CsCl)





Coordination number ratio 8 : 8

1 : 1

So, General formula = AB

Fluorite Structure (CaF_2)

Experimental ratio, $\frac{r_{Cs^+}}{r_{Cl^-}} \simeq 0.93$

$\frac{r_{Cs^+}}{r_{Cl^-}} > 0.732$

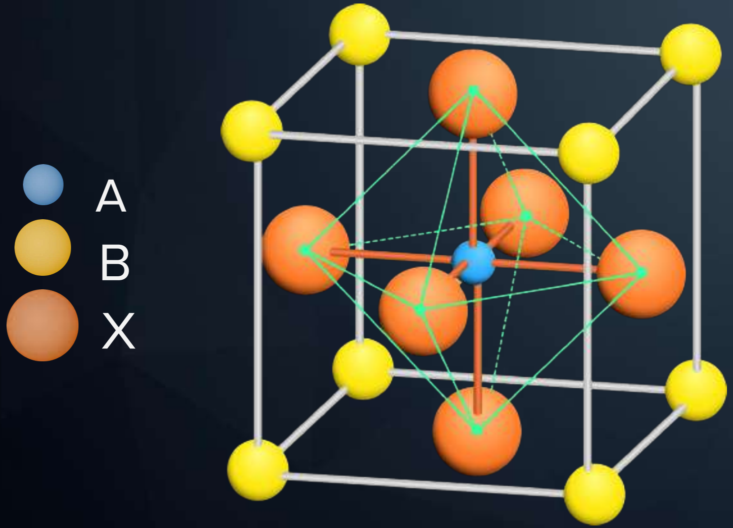
Other examples of CsCl like structures

CsBr, CsI, CsCN, TiCl, TiBr, TiCN etc.

Perovskite Structure

General Formula : ABX_3

e.g.: $CaTiO_3$, $BaTiO_3$



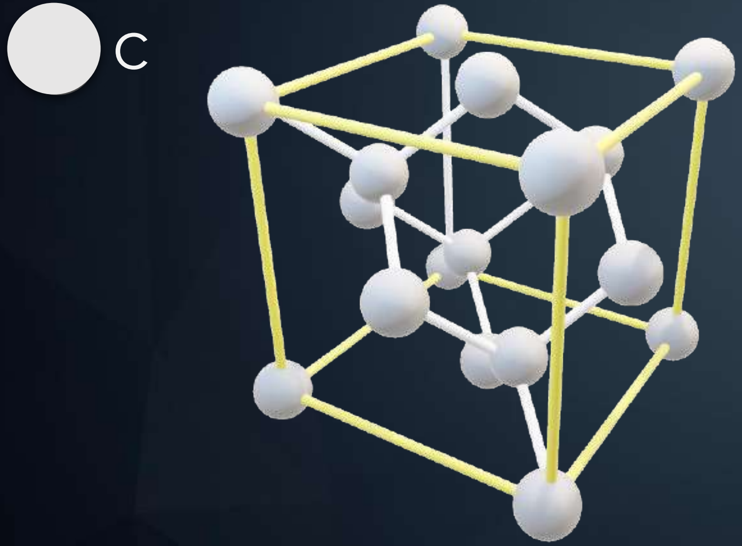
Central atom A (Ca) located → At the body centre

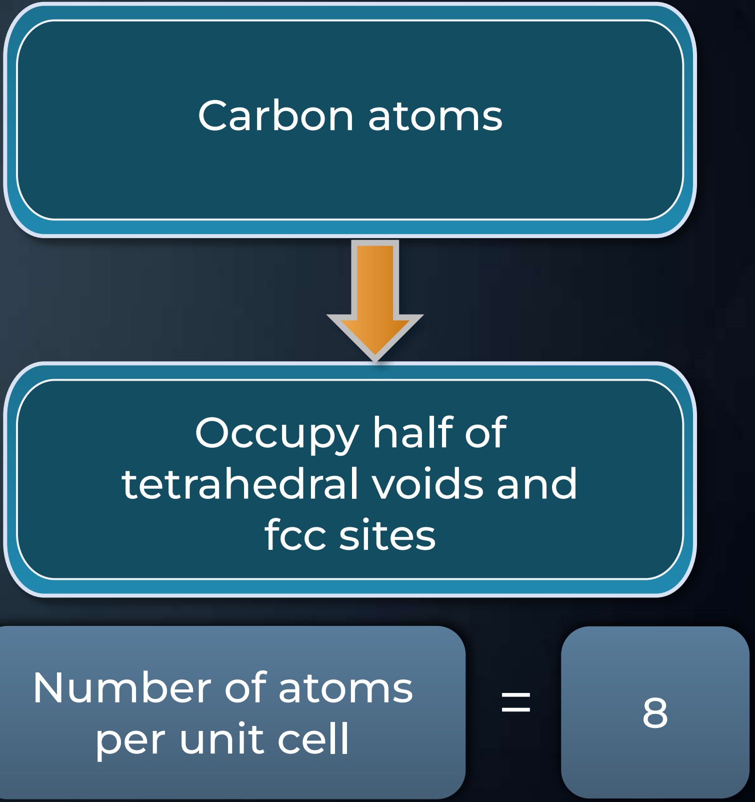
B atoms (Ti) → Form simple cubic arrangement

X atoms (O) → At the face centres

$$12 \times \frac{1}{4} = 3$$

Diamond Structure





Carbon atoms

Occupy half of tetrahedral voids and fcc sites

Number of atoms per unit cell = 8

Spinel Structure AB_2O_4

Number of O^{2-} ions $= 4$

Number of A^{2+} ions $= \frac{1}{8} \times$ (tetrahedral voids)

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

O^{2-} ions → Form ccp lattice

A^{2+} ions → $\frac{1}{8}$ of tetrahedral voids

B^{3+} ions → $\frac{1}{2}$ of octahedral voids

Spinel Structure AB_2O_4

Number of B^{3+} ions $= \frac{1}{2} \times$ (octahedral voids)

$= \frac{1}{2} \times 4 = 2$

Examples

$MgAl_2O_4$, $ZnFe_2O_4$ etc.

Summary

S.N.	Crystal	C.N.		Z	Structural arrangement
		Cation	Anion	Total formula unit	
1.	NaCl	6	6	$Na^+ = 4$ $Cl^- = 4$	$Na^+ \longrightarrow$ All O.V.s $Cl^- \longrightarrow$ FCC
2.	ZnS (Zinc Blende)	4	4	$Zn^{2+} = 4$ $S^{2-} = 4$	$Zn^{2+} \longrightarrow$ At ½ T.V.s $S^{2-} \longrightarrow$ FCC
3.	ZnS (wurtzite)	4	4	$Zn^{2+} = 6$ $S^{2-} = 6$	$Zn^{2+} \longrightarrow$ ½ T.V.s $S^{2-} \longrightarrow$ HCP
4.	CaF2 (Fluorite)	8	4	$Ca^{2+} = 4$ $F^- = 8$	$Ca^{2+} \longrightarrow$ FCC $F^- \longrightarrow$ All T.V.s

Summary

S.N.	Crystal	C.N.		Z	Structural arrangement
		Cation	Anion	Total formula unit	
5.	Na_2O (Antifluorite)	4	8	$Na^+ = 8$ $O^{2-} = 4$	$Na^+ \longrightarrow$ All T.V.s $O^{2-} \longrightarrow$ FCC
6.	CsCl	8	8	$Cs^{2+} = 1$ $Cl^- = 1$	$Cs^+ \longrightarrow$ cubit void $Cl^- \longrightarrow$ Corners

Effect of Temperature & Pressure on Crystal Structure

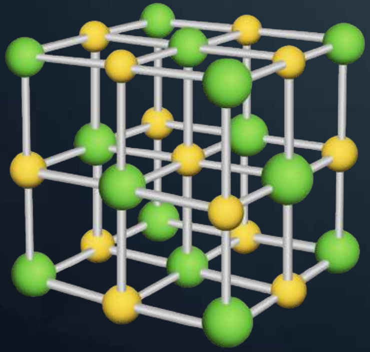
NaCl Type

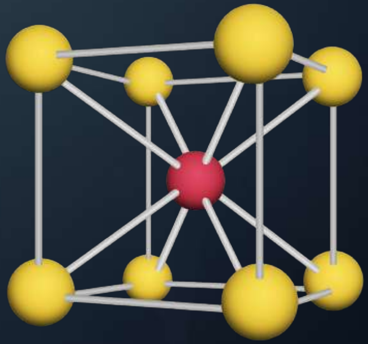
$$\underset{\text{High Temperature (750 K)}}{\overset{\text{High Pressure}}{\rightleftharpoons}}$$

CsCl Type

Coordination (6:6)

Coordination (8:8)

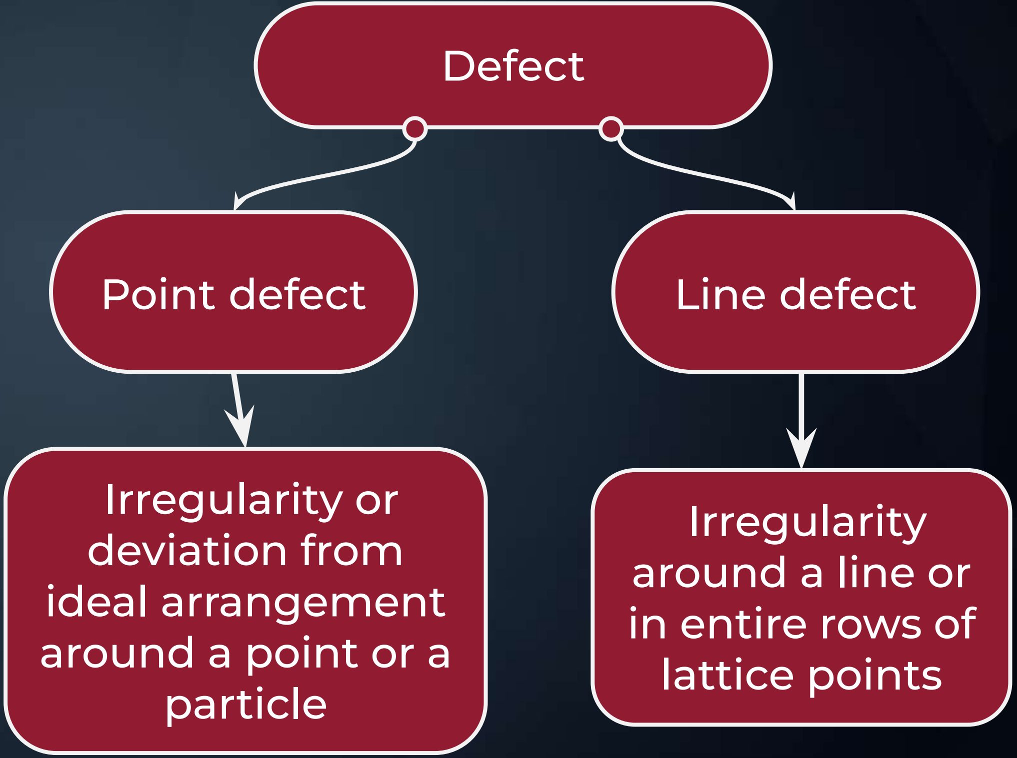




Defects in Crystals

Defect is a disruption in the periodic order of a crystalline material.

Occurs in crystals to lower their energy and increase thermodynamic stability.



Defect

Point defect

Line defect

Irregularity or deviation from ideal arrangement around a point or a particle

Irregularity around a line or in entire rows of lattice points

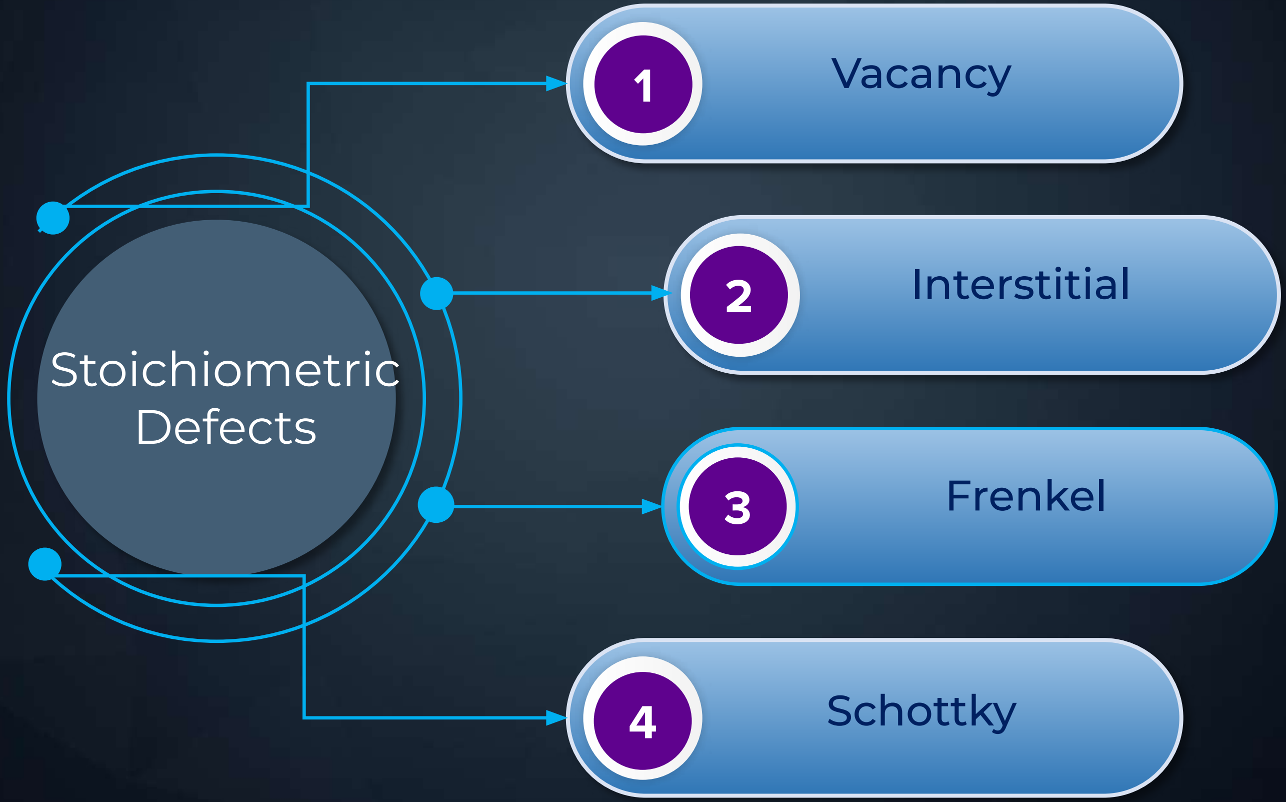
Stoichiometric Defects

Point defects that do not disturb the stoichiometry of the solid.

The tendency to show defects depends on the temperature

Also called thermodynamic or intrinsic defects.

Stoichiometric Defects



Stoichiometric Defects

1 Vacancy

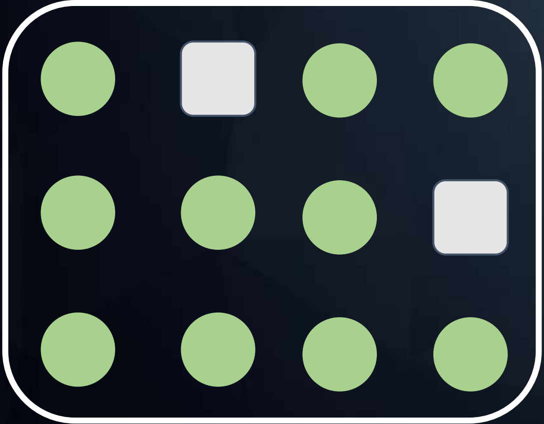
2 Interstitial

3 Frenkel

4 Schottky

Vacancy Defect

Such defect arises when some of the lattice sites in the crystal are vacant.



Develop during crystal formation or when a substance is heated

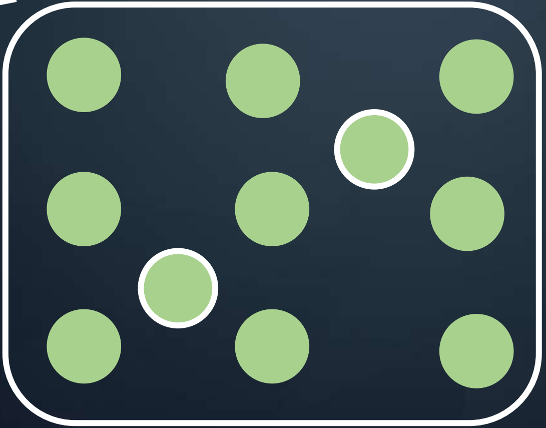
Since the number of particles per unit volume is reduced

↓

The density of the solid decreases.

Interstitial Defect

Arises when some constituent particles occupy interstitial sites in the crystal.



Interstitial sites

Since the number of particles per unit volume is more than in a regular crystal.

↓

The density of the solid increases

Stoichiometric Defects

Ionic solids must maintain electrical neutrality.

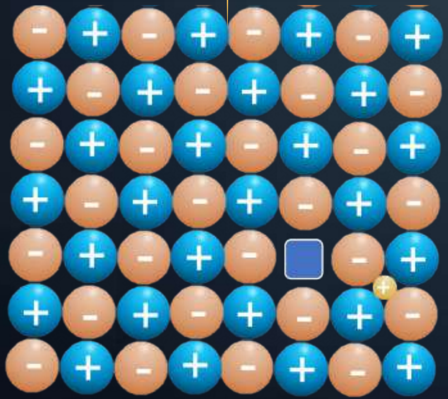
Rather than showing simple vacancy or interstitial defects, such solids show frenkel and schottky defects

Frenkel Defect

When an ion is displaced from its regular position to an interstitial position

It creates a vacancy

Frenkel Defect



Smaller ion, usually cation, is dislocated from normal site to interstitial site

Creates vacancy defect at its original site and interstitial defect at its new site

Characteristics

(i) Shown by ionic solids having large difference in size between the positive & negative ions

Ex: ZnS, AgCl, AgBr & AgI

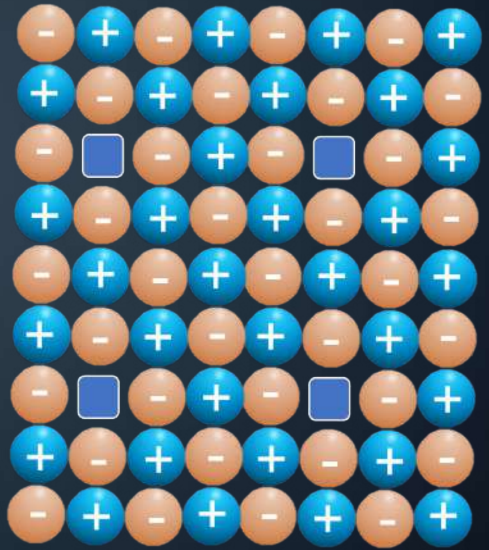
Comparatively smaller size of Zn^{2+} and Ag^{+} ions

(ii) Density of a solid does not change

Schottky Defect

Arises when a pair of cation and anion of equal valency is missing from an ionic crystal

A vacancy defect in ionic solids



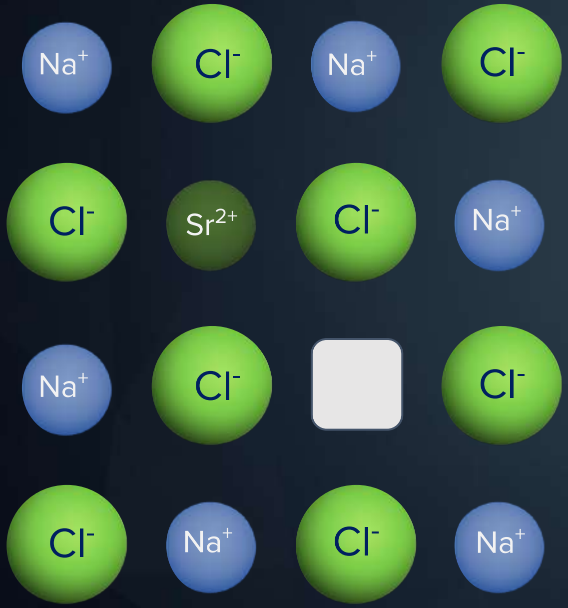
Schottky Defect

These ion–pair vacancies decrease density of the solid

Shown by solids having small difference in the sizes of cations and anions

Ex : NaCl, KCl, KBr, AgBr and CsCl

Impurity Defects



Defects in ionic crystals, can be introduced by adding impurities

In which the ions are in different valence state than the constituent ions of the crystal.

Impurity Defects

For example:

Small amounts of strontium chloride ($SrCl_2$) are added to molten sodium chloride (NaCl)

↓

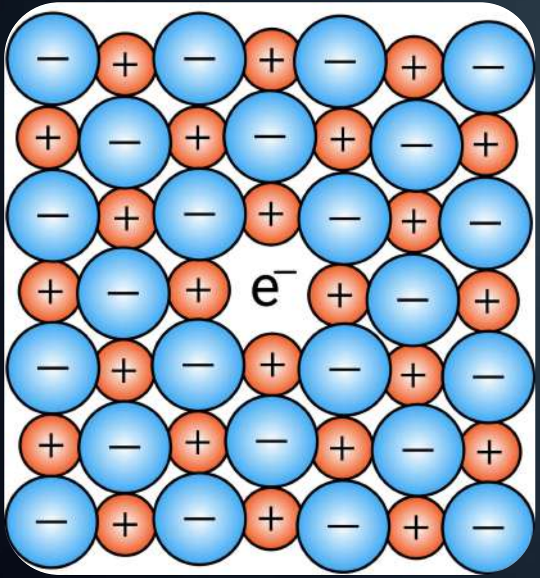
Some Sr^{2+} ions replace Na^+ ions and occupy the sites earlier occupied by the Na+ ions

↓

Each Sr^{2+} replaces two Na^+ ions by occupying a site and other site remaining vacant

Other example:
solid solution of AgCl and $CdCl_2$

Due to Anionic Vacancies



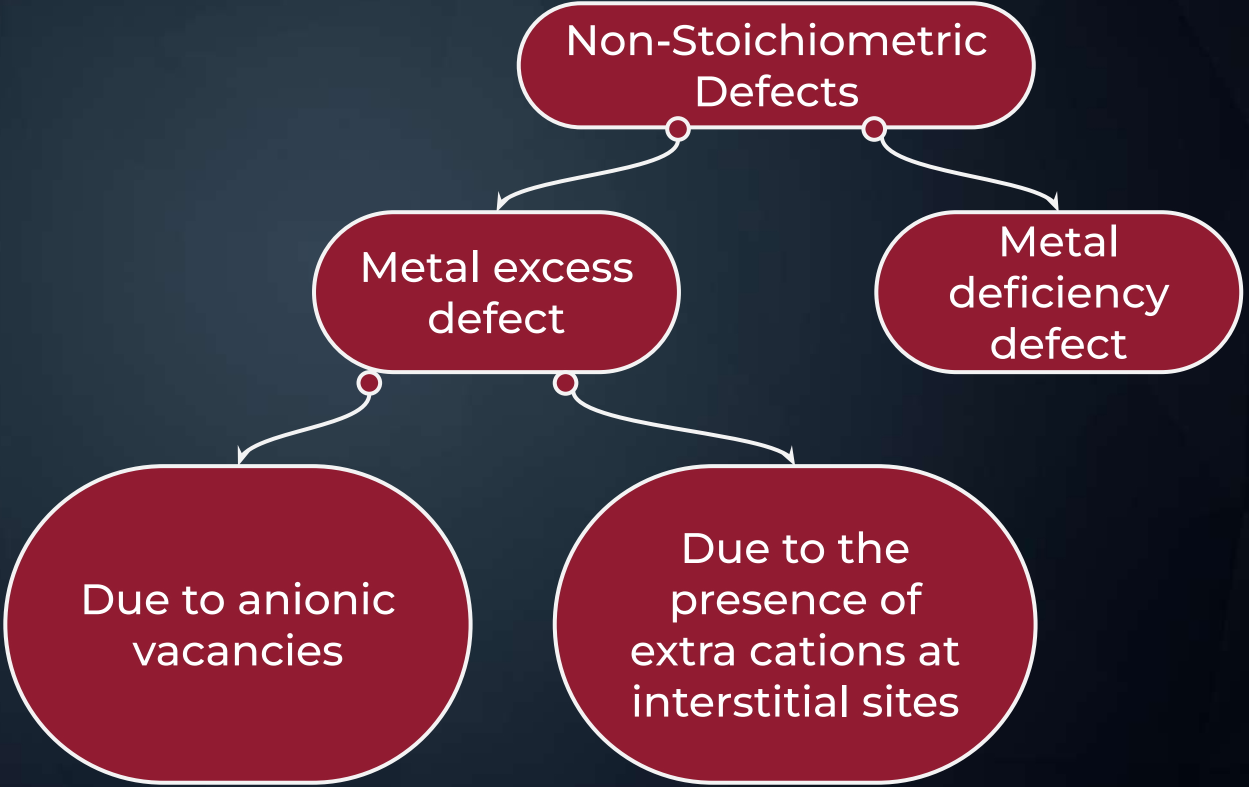
A negative ion may be absent from its lattice site, leaving a “hole”

Which is occupied by an electron, thereby maintaining the electrical neutrality.

Alkali halides like NaCl and KCl show such defects

Non-Stoichiometric Defects

Occur in solids which contain constituent elements in non-stoichiometric ratio due to defects in their crystal structures .



Non-Stoichiometric Defects

Metal excess defect

Metal deficiency defect

Due to anionic vacancies

Due to the presence of extra cations at interstitial sites

Heating of NaCl

When crystals of NaCl are heated in an atmosphere of sodium vapour

Cl- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.

This happens by loss of electron by sodium atoms to form Na+ ions.

The released electrons diffuse into the crystal and occupy anionic sites

These anionic sites occupied by unpaired electrons are called **F-centres**

Now, the crystal has an excess of sodium ions

Metal Excess Defect

These free electrons may be excited to higher energy levels

↓

Giving rise to absorption spectra

↓

So the compounds are often colored

Ex: Crystal of NaCl is yellow, KCl is violet or lilac and LiCl is pink

General formula = $AX_{1-\delta}$

Anionic deficiency in a solid

Ex: NaCl, KCl, LiH etc.

Due to the Presence of Extra Cations

General formula = $A_{1+\delta}X$

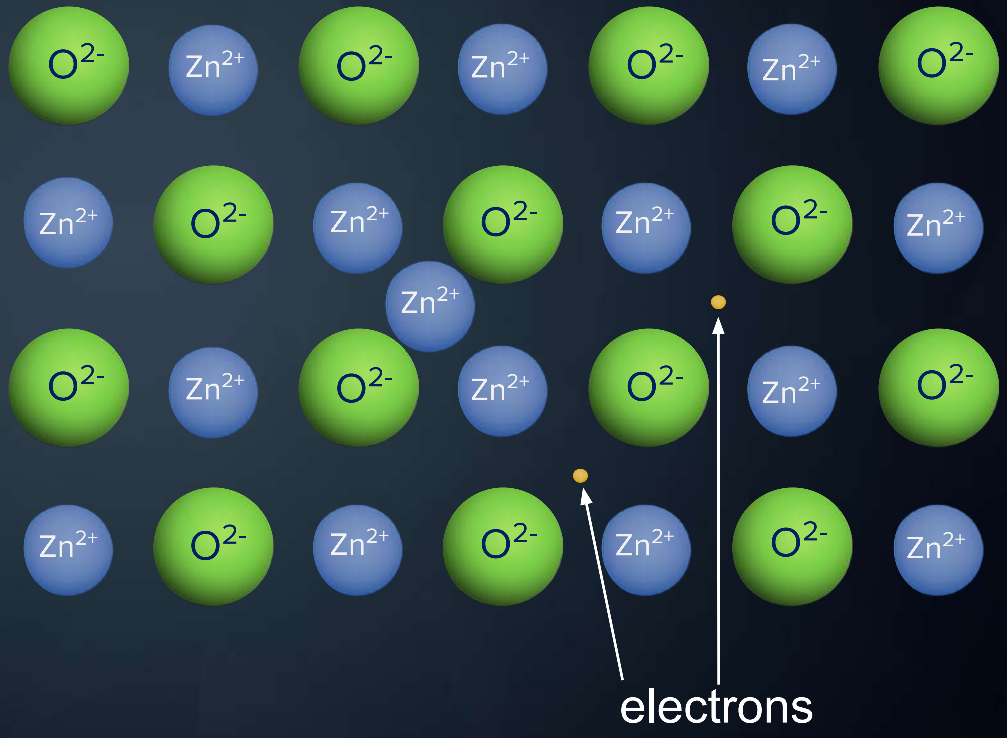
Ex: , ZnO, CdO, Fe_2O_3 and Cr_2O_3.

When an extra positive ion occupies an interstitial position in the lattice

And electrical neutrality is maintained by the inclusion of an interstitial electron

Due to the Presence of Extra Cations

ZnO



Due to the Presence of Extra Cations

Example,

Zinc oxide is white in colour at room temperature

On heating, it loses oxygen and turns yellow.

Heating of ZnO,

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

Excess of zinc in the crystal, so the formula becomes

$Zn_{(1+\delta)}O$

Metal Deficiency Defect

Example,

Some solids contain less amount of metal as compared to the stoichiometric proportion

↓

oxidation number of metal ion/cation changes to maintain electrical neutrality.

FeO is found, mostly, with a composition of $Fe_{0.95}O$.

↓

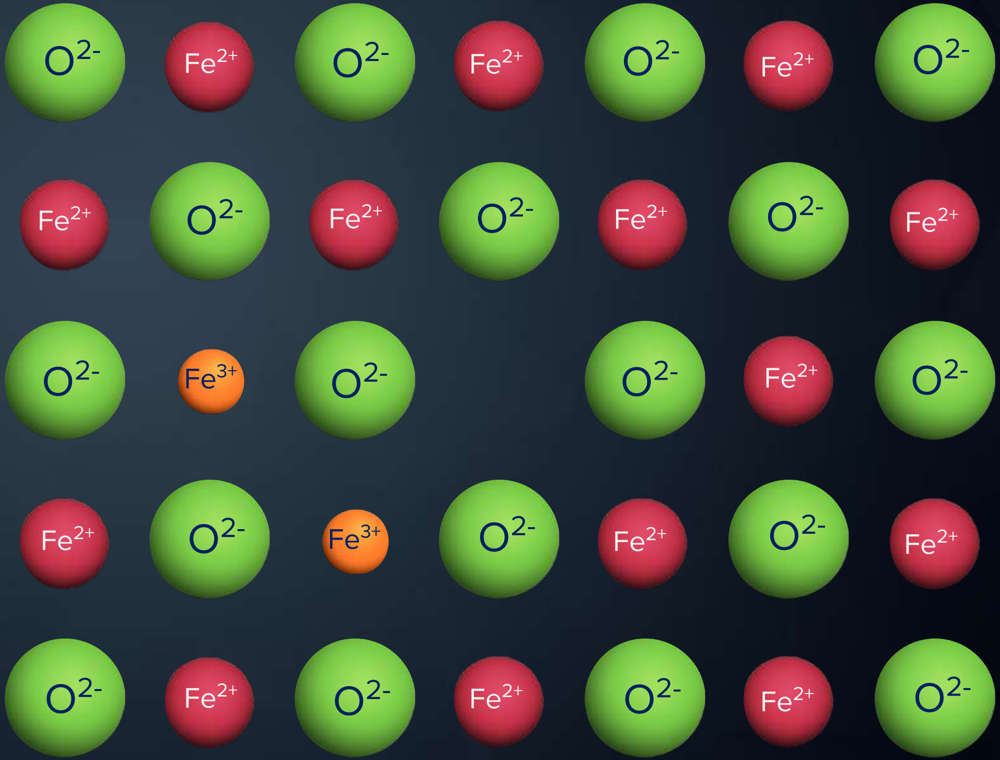
loss of some Fe^{2+} ions is compensated by presence of required number of Fe^{3+} ions

Metal Deficiency Defect

FeO

General formula = $A_{1-\delta}X$

Ex: FeO, NiO, FeS, CuI etc.



Electrical Properties of Solids

Solids exhibit an amazing range of electrical conductivities.

The range of electrical conductivities varies from 10^{-20} to 10^{7} ohm^{-1}m^{-1}.

Electrical Properties of Solids

Conductors

- Solids with conductivities ranging between 10^4 to 10^7 ohm^{-1} m^{-1}.
- Metals are good conductors and have conductivity in the range 10^7 ohm^{-1} m^{-1} .

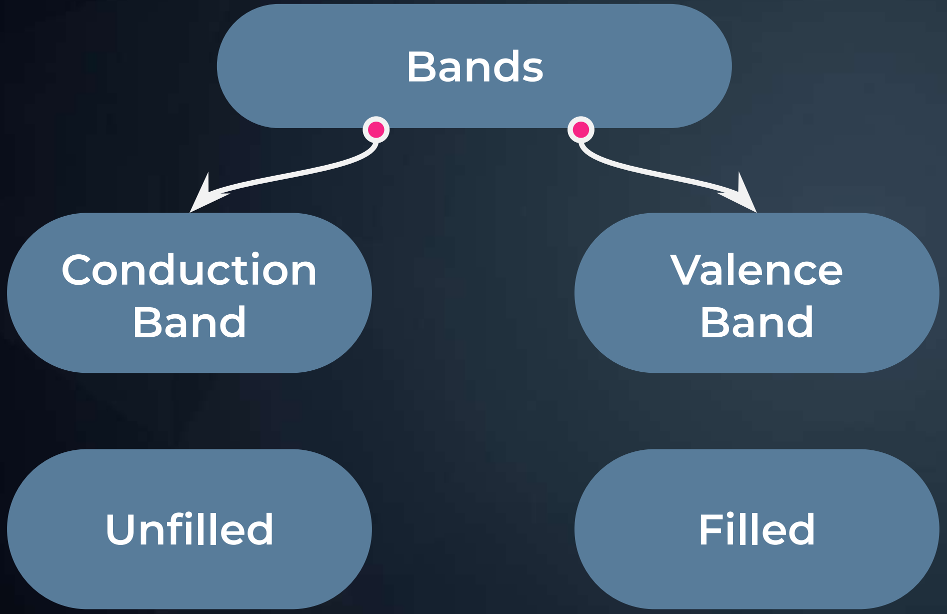
Insulators

- Solids with very low conductivity, generally in the range 10^{-20} to 10^{-10} ohm^{-1} m^{-1}.
- Examples - non-metals, rubber, wood etc.

Semiconductors

- Solids with conductivity that is intermediate between conductors and insulators and lies in the range 10^{-6} To 10^4 ohm^{-1} m-1.
- Example - Germanium (Ge), Silicon (Si) etc.

Aspects of Band Theory



Bands

Conduction Band

Valence Band

Unfilled

Filled

Band Gap

Energy difference between valence band and conduction band

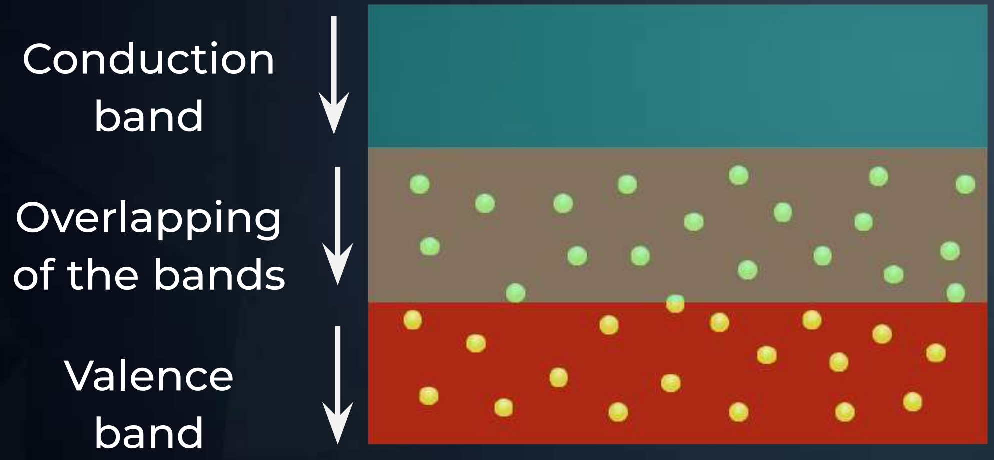
Aspects of Band Theory

The essential criterias for any solid to conduct electricity are:

(1) Presence of electrons in conduction band

(2) Small gap between the valence and conduction band.

Conduction of Electricity in Metals

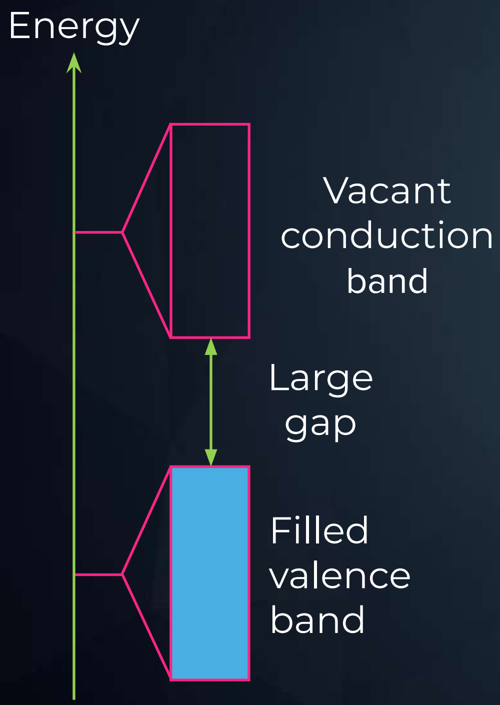


The mobile electrons account for the high electrical conduction of metals.

Electrical conduction takes place through a minor disturbance in energy

Promoting an electron to an unfilled level, where it can move readily

Insulators (Non-Conducting)

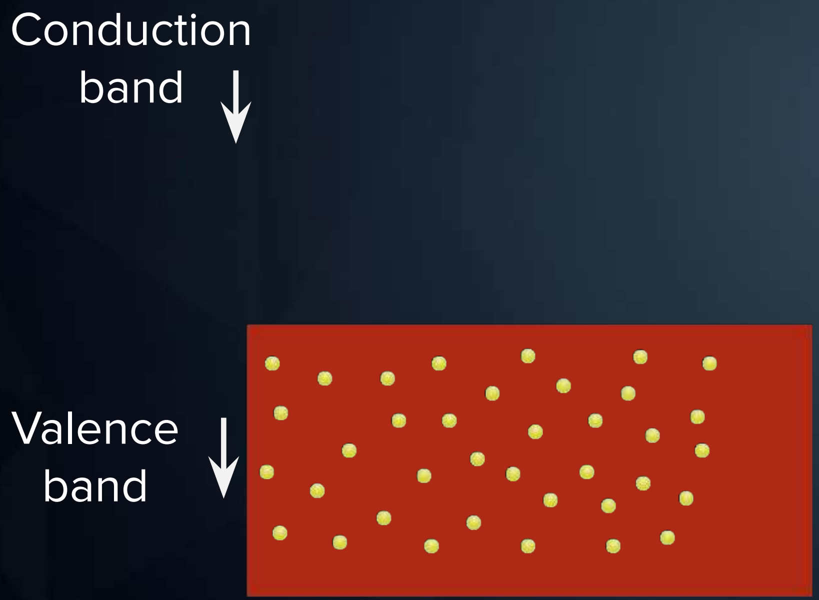


Insulator

(a) The valence band is full, so perturbation within the band is impossible,

(b) The electrons in the valence band are separated by a large energy gap from the conduction band

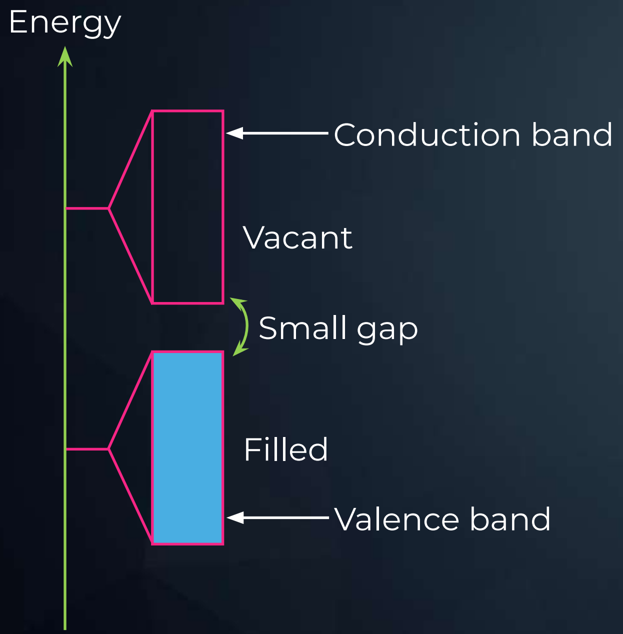
Insulators (Non-Conducting)



(c) Electrons cannot, therefore, be promoted to an empty level where they could move freely

(d) And very small or negligible conductivity is observed.

Conduction of Electricity in Semiconductors



A small difference in energy is seen

Between the filled valence band and conduction band of electrons

Conduction of Electricity in Semiconductors

If cooled to absolute zero

The electrons occupy their lowest possible energy levels. The conduction band is empty

The material is a perfect insulator.

At normal temperatures

Some electrons are thermally excited from the valence band to the conduction band

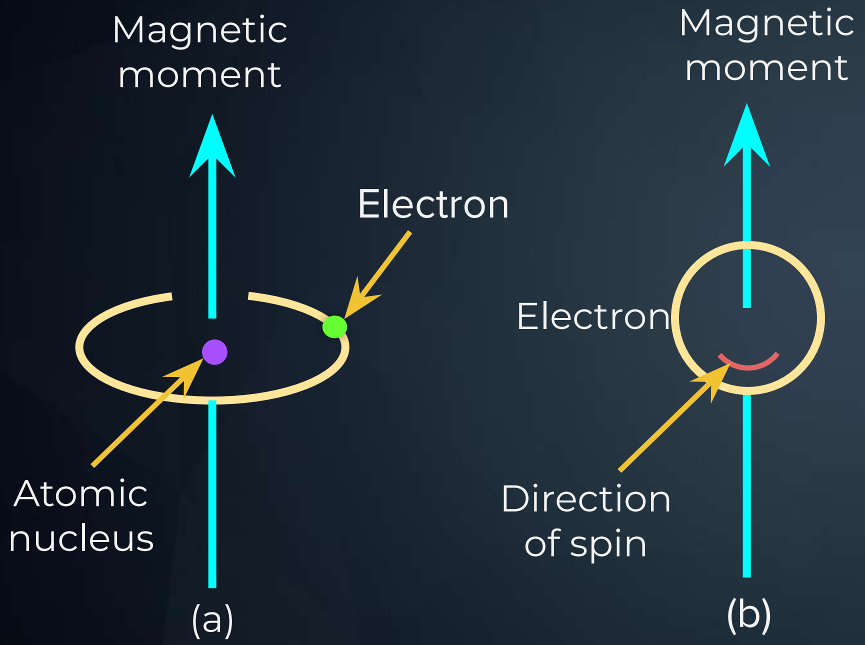
So, they can conduct electricity

Magnetic Properties

Every substance has some magnetic properties associated with it. The origin of these properties lies in electrons.

Each electron in an atom behaves like a tiny magnet.

Magnetic Properties



Demonstration of the magnetic moment associated
with (a) an orbiting electron and (b) a spinning electron.

Magnetic moment of an electron originates from two types of motion.

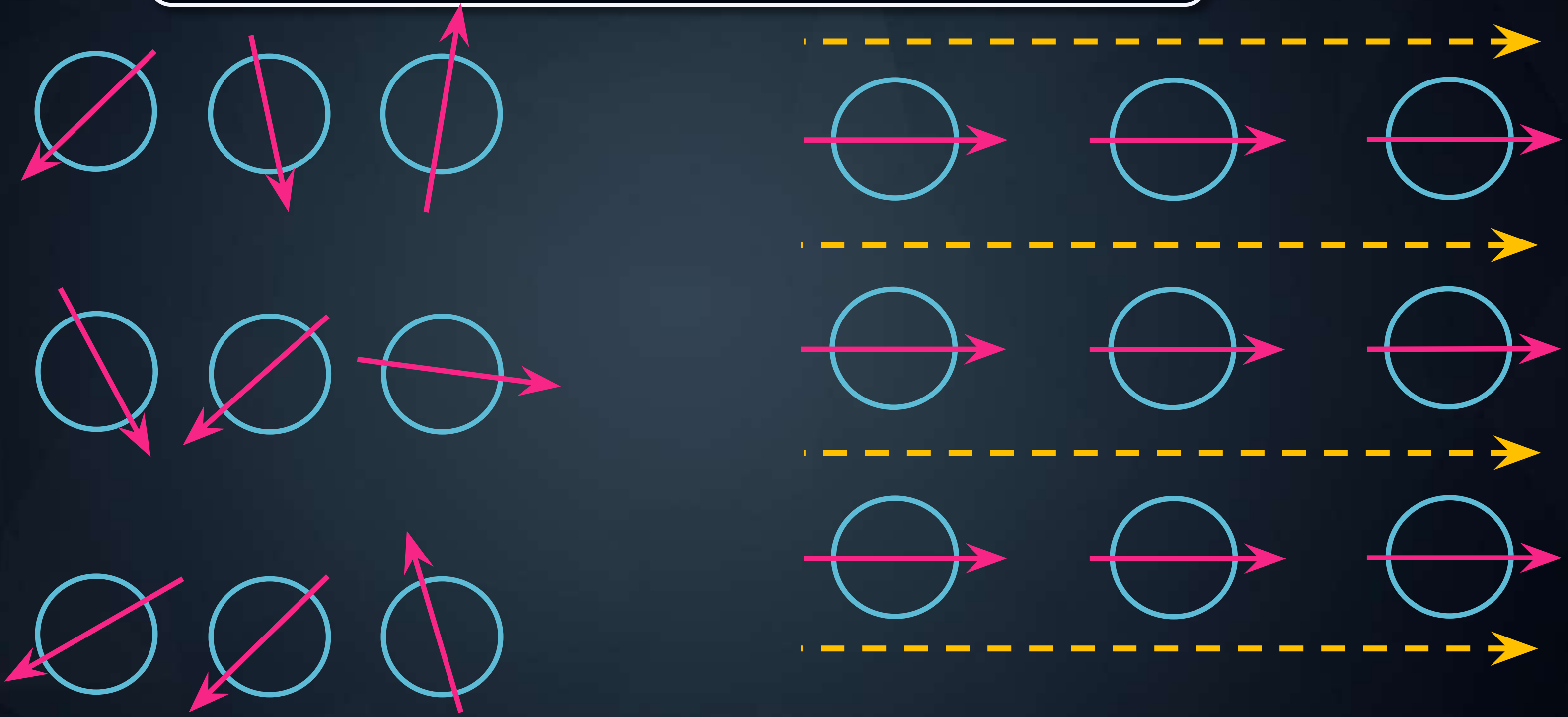
(1) Its **orbital** motion around the nucleus.

(2) Its **spin** around its own axis.

On the basis of their magnetic properties, substances are

- Paramagnetic
- Diamagnetic
- Ferromagnetic
- Antiferromagnetic
- Ferrimagnetic

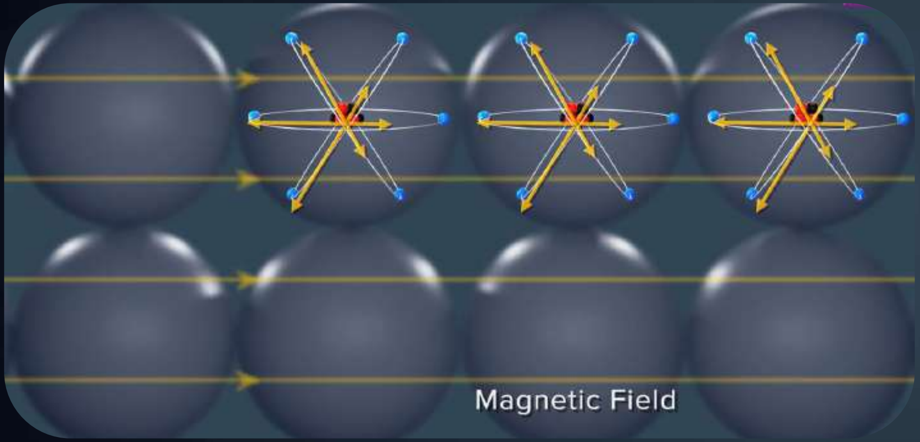
Paramagnetic Substances



Case A: In the absence of external magnetic field

Case B: In the presence of external magnetic field

Diamagnetic Substances



Substances that are repelled by magnetic field

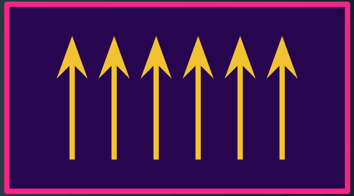
They do not have unpaired electrons.

Examples: Cu^{2+},TiO_2, NaCl and C_6H_6.

Ferromagnetic Substances

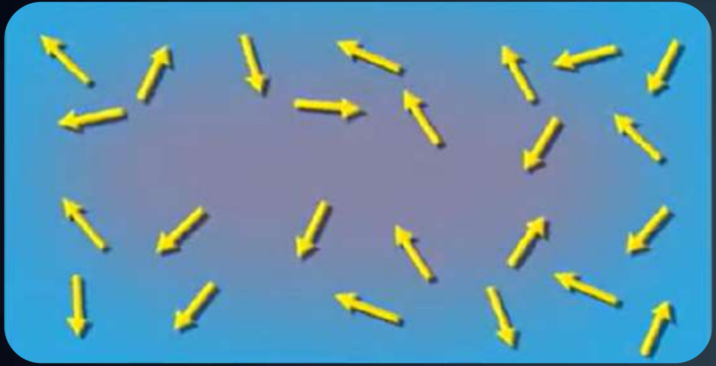
Substances that are attracted very strongly by a magnetic field

Substances that show permanent magnetism even in the absence of the magnetic field.



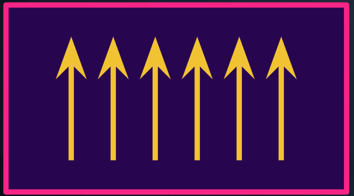
Examples: Fe, Ni, Co and CrO_2.

Ferromagnetic Substances



In an unmagnetised piece of a ferromagnetic substances, domains are randomly oriented and their magnetic moments get cancelled.

When the substance is placed in a magnetic field, all domains get oriented in the direction of the magnetic field and a strong magnetic field is produced.



On applying magnetic field

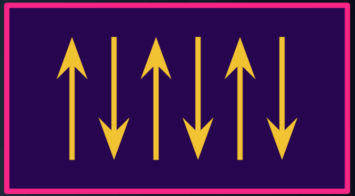
Ferromagnetic Substances

This ordering of domains persist even when the magnetic field is removed & the substance become a permanent magnetic.

In a solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains.

Antiferromagnetic Substances

Substances showing anti- ferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment.

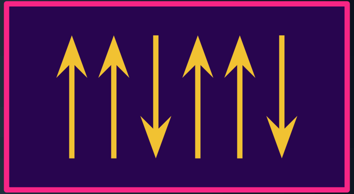


Examples: MnO.

Ferrimagnetic Substances

Substance in which the magnetic moments of the domains are aligned in parallel and antiparallel directions in unequal numbers.

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



Examples: Fe_3O_4, ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$

Ferrimagnetic Substances

On heating, ferrimagnetic substance convert into paramagnetic substances.