

Welcome to



Solid

Solid state has **strong** interparticle attraction and **negligible** thermal motion of particles.

Properties of Solids

1

Have a **definite mass, volume,** and shape.

2

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

3

Strong interparticle forces of **attraction.**

4

Particles **cannot flow.**

5

Constituting particles have **fixed positions.** They can oscillate only about their **mean position**, i.e., they have **vibrational motions** only.

6

Rigid and incompressible.



Classifications of Solids

Based on the Arrangement of the Particles

Crystalline Solid

Particle follow a definite regular arrangement.

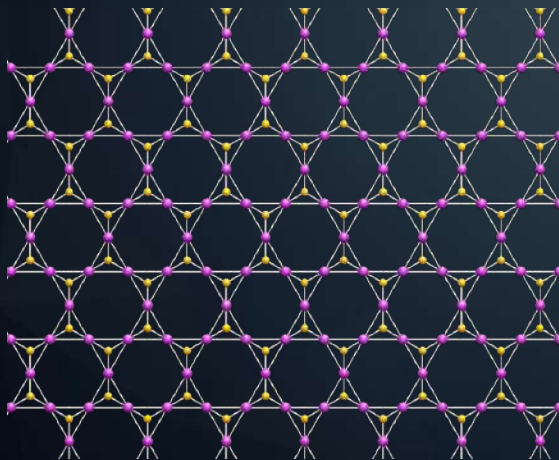
Amorphous Solid

No particular pattern is followed, and particles are randomly arranged.

Difference between Crystalline and Amorphous Solids

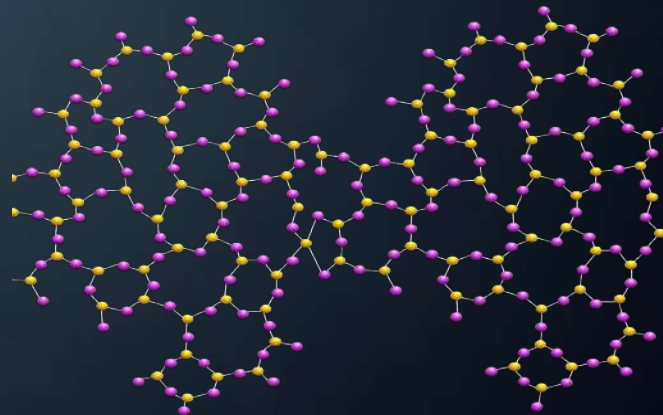
Crystalline Solid

Particle follow a definite regular arrangement.



Amorphous Solid

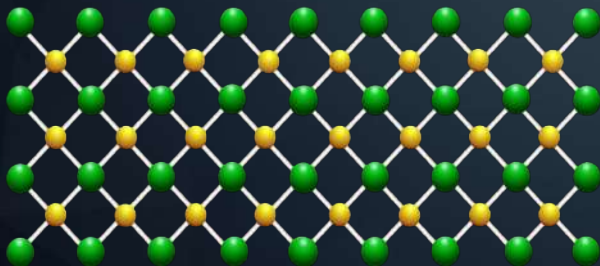
No particular pattern is followed, and particles are **randomly arranged**.



Difference between Crystalline and Amorphous Solids

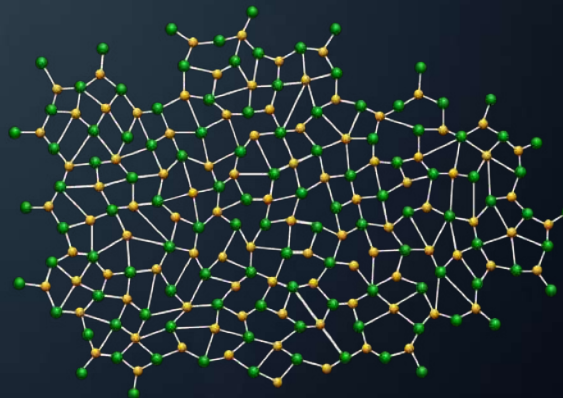
Crystalline Solid

Long-range order in the arrangement.



Amorphous Solid

Short range order in the arrangement





Difference between Crystalline and Amorphous Solids

Crystalline Solid

Produced by **slow cooling** under controlled condition of liquid. The crystalline structure is also dependent on conditions.

Amorphous Solid

Produced by **rapid cooling** of the liquid



Difference between Crystalline and Amorphous Solids

Crystalline Solid

Have a **fixed or sharp** melting point and enthalpy of fusion.

Amorphous Solid

Have a **range of temperature** in which they melts as M.P. and the enthalpy of fusion is not fixed.



Difference between Crystalline and Amorphous Solids

Crystalline Solid

Have a **fixed or sharp** melting point and enthalpy of fusion.

True solids.

Amorphous Solid

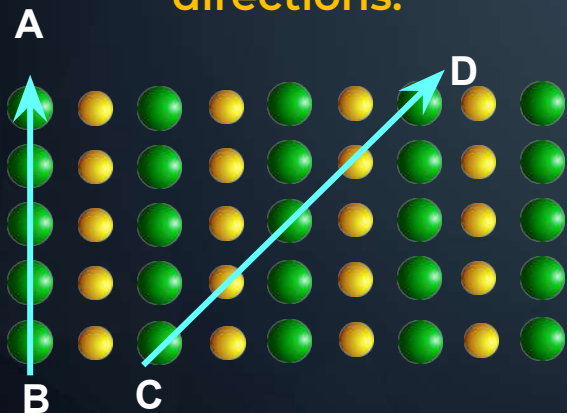
Have a **range of temperature** in which they melts as M.P. and the enthalpy of fusion is not fixed.

Pseudo solids or supercooled liquids.

Difference between Crystalline and Amorphous Solids

Crystalline Solid

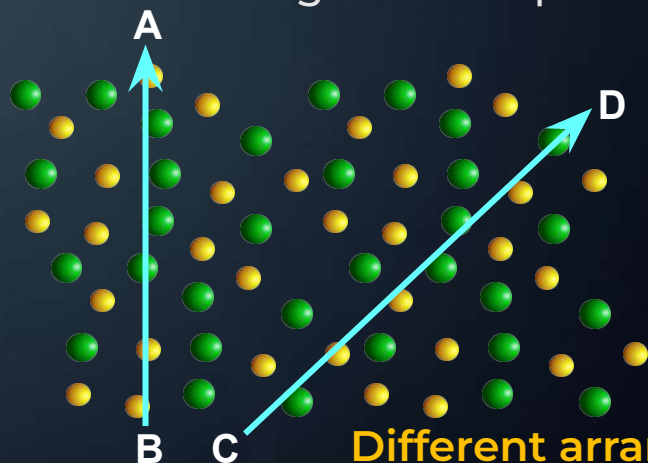
Anisotropic:
Different values of physical properties in different directions.



AB: Same arrangement
DC: Different arrangement

Amorphous Solid

Isotropic:
Same values of physical properties in all different directions due to random arrangement of particles



Different arrangement along AB and CD

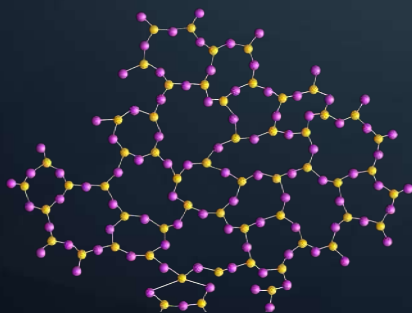
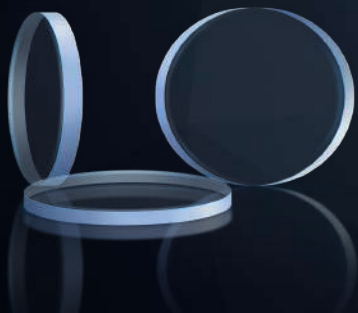
Difference between Crystalline and Amorphous Solids

Crystalline Solid

Example:

Ag, Fe, Cu, NaCl, $\text{H}_2\text{O}(\text{s})$,
diamond, quartz, sucrose
(sugar)

Quartz Glass:

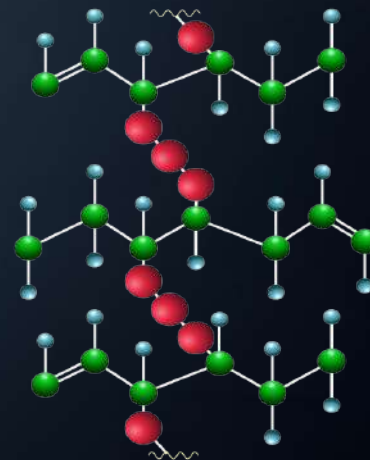


Amorphous Solid

Example:

Glass, plastic, amorphous
silica, rubber, starch

Rubber:

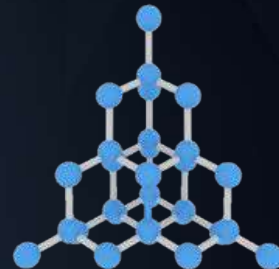


Polymorphism

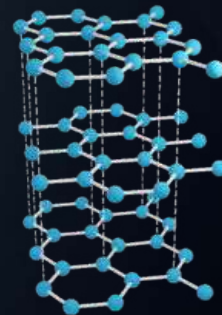
Different crystalline structure of the **same substance** are called its polymorphic forms.

Due to the difference in the arrangement of the constituent particles, two types of solids differ in their properties.

Diamond



Graphite

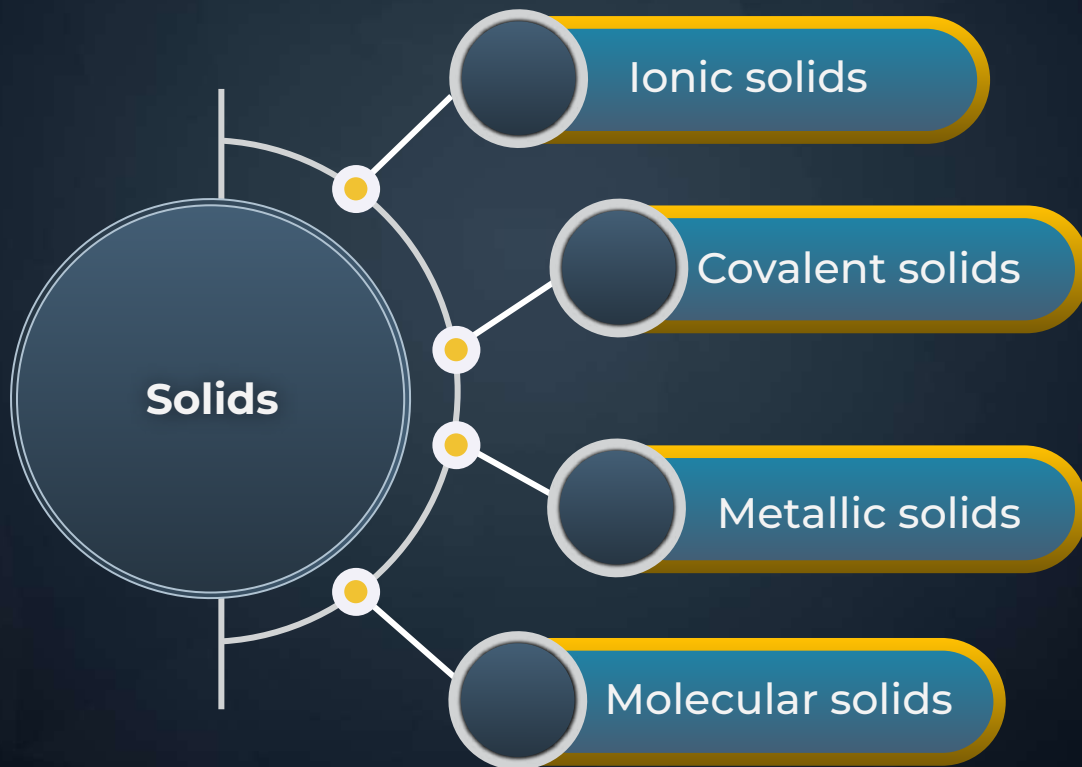


Amorphous Solids

- Amorphous solids have the same structural features as liquids are conveniently
- regarded as **extremely viscous liquids**.

- Amorphous solids have a **tendency to flow** (very slowly), hence they are called
- pseudo solids** or **supercooled liquids**.

Classification of Solids based on the Nature of Intermolecular Force



Ionic Solids

Constituent particles

Ions

Electrical
conductivity

Force of interaction

Coulombic
(electrostatic)

Solid form → Insulator
Molten & aqueous form →
Conducting

Physical state

Very hard (brittle)

Examples

Melting point

Very high

NaCl, ZnS, CsCl

Covalent Solids

Constituent particles

Atoms
(Nonmetals)

Electrical
conductivity

Force of interaction

Covalent bond

Insulator except graphite

Physical state

Very **hard**
(Graphite → soft)

Examples

Melting point

Very high

Diamond, SiC,
SiO₂, graphite

Covalent Solids

They are also called **giant molecules**

Electrical
conductivity

Insulator except
graphite

Examples

Diamond, SiC,
SiO₂, graphite

Diamond



Covalent Solids

Graphite

Graphite belongs to covalent solids, but it is **soft** and a **good conductor** of electricity.



Its exceptional properties are due to its **typical structure**.

Covalent Solids

In graphite, carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighboring atoms in the same layer.

The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity.

Carbon atoms are **arranged in different layers**



Different layers can slide over the other making it a soft solid and a good solid lubricant.



Metallic Solids

Constituent particles

Metal ion at fixed locations in the sea of delocalised electrons.

Melting point

Low to high (depending on metallic bond)

Force of interaction

Metallic bond

Electrical conductivity

Good conductor in solid and molten state

Physical state

Soft & hard (depending on metallic bond)

Thermal conductivity

Good conductor in solid and molten state

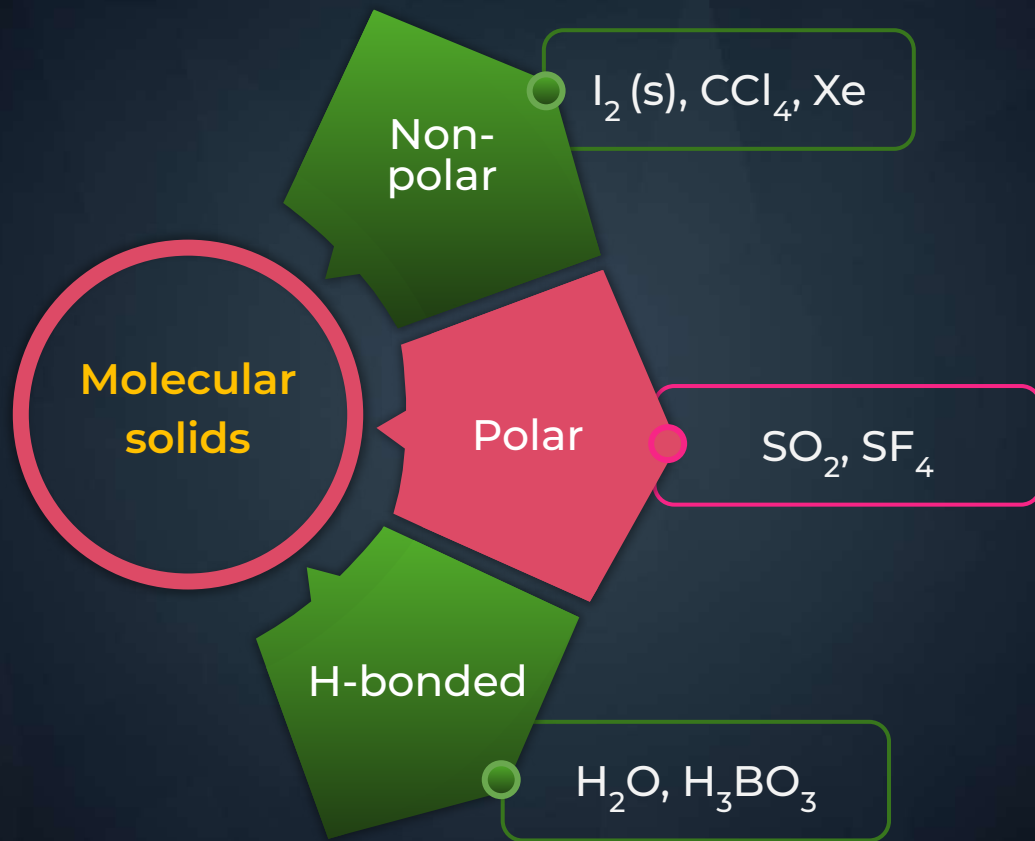
Example: Cu, Al, Zn, Ag

Molecular Solids

Constituent particles

Molecules

Type of molecules	Force of interaction
Non-polar	Dispersion force or london forces
Polar	Dipole-dipole
	H-bonding





Molecular Solids

Type	Physical state	M.P.
Non-polar	Very soft	Very low
Polar	Soft	Low
H-bonded	Hard	Low

Electrical
conductivity

Non-conducting

Examples

I_2 , Xe(s), C_6H_6 , CCl_4 , HCl,
 $H_2O(s)$, $H_3BO_3(s)$



Internal Arrangement of Particles in a Crystal

Lattice Point

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

Each dot is called a **lattice point**.

Lattice or Space or Crystal Lattice

The **3-D regular and repeating arrangement** of constituent particle represented by dots in a solid.

2-D Lattice

In **2-D**

Space
lattice

Lattice
points

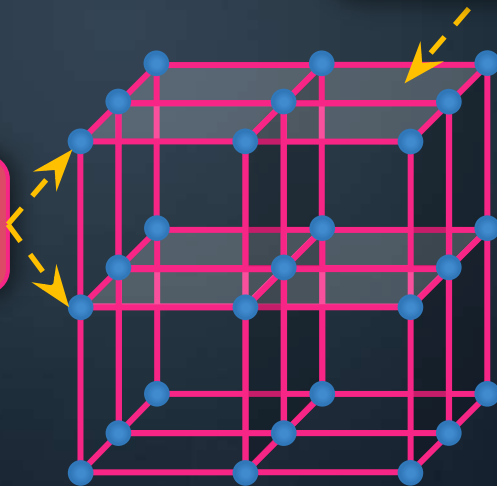


3-D Lattice

In 3-D

Space
lattice

Lattice
points



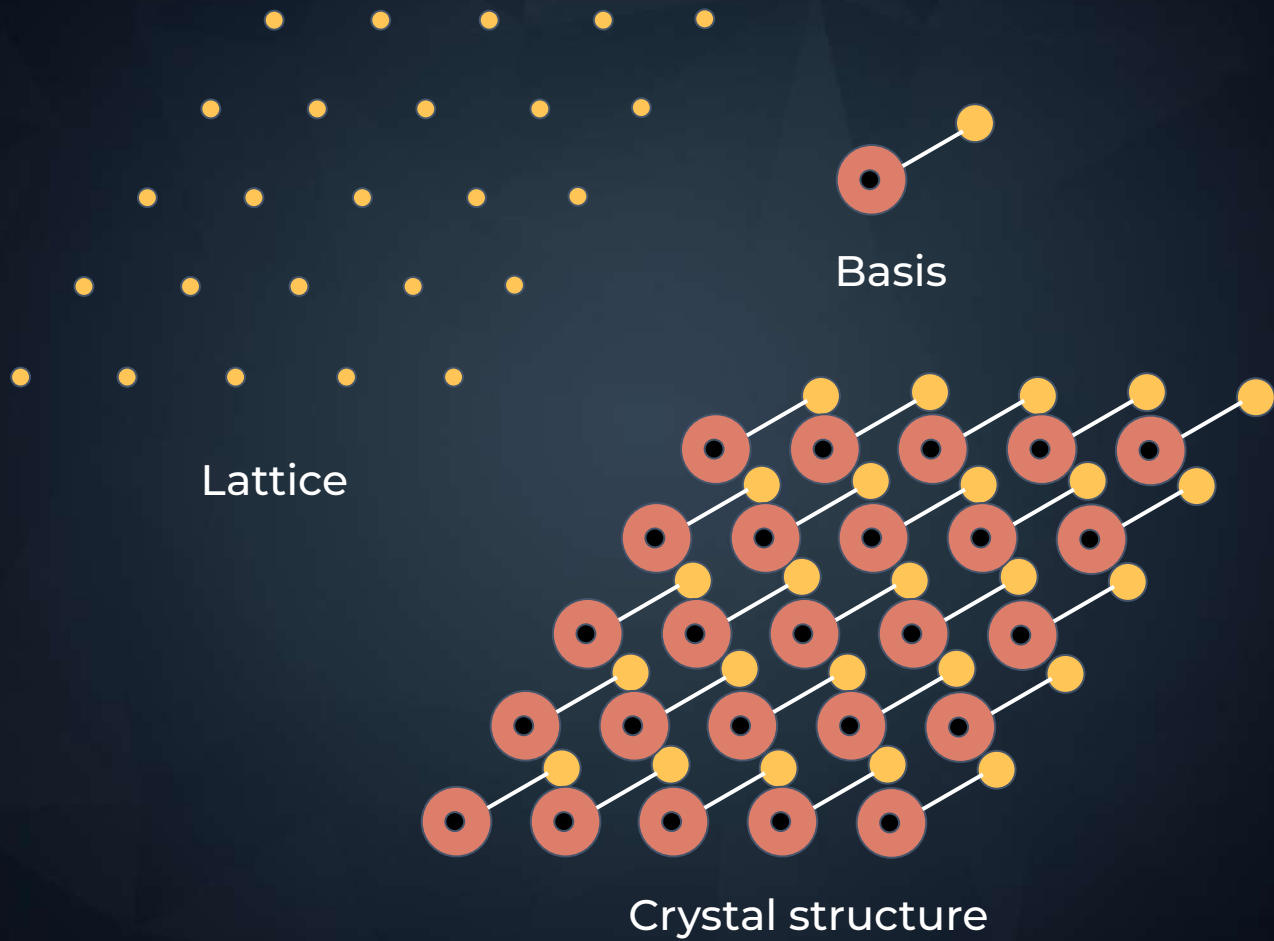


Points to Remember!!

Each lattice point specifies the location of a **structural motif** (or basis), which may be atoms, molecules, or groups of atoms, molecules, or ions.



Crystal structure is the **collection of structural motifs** arranged according to the lattice.



Unit Cell

The space lattice of a crystal can be divided into **identical parallelepipeds** (a **six-sided** geometric solid whose faces are all **parallelograms**) by joining the lattice points with straight lines.

Each such parallelepiped is called **a unit cell**.

Unit Cell

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

Generally, the **most symmetrical** and **smallest volume** unit cell is selected.

2-D Unit Cell

In 2-D

Space
lattice



Unit cell

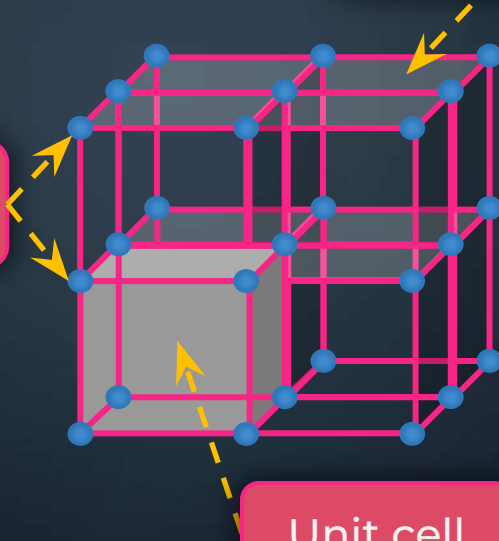
3-D Unit Cell

In 3-D

Space
lattice

Lattice
points

Unit cell



Characteristics of Unit Cell

(1)

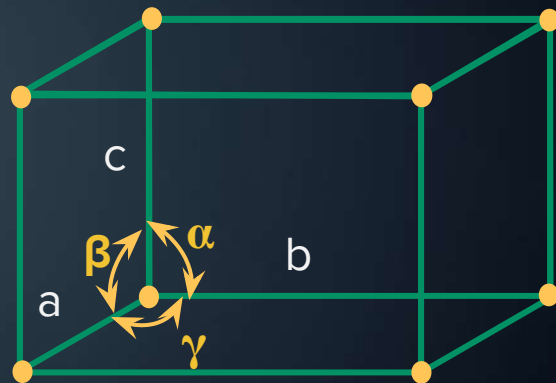
Its dimensions along the **three edges**, a , b , and c may or may not be mutually perpendicular.

(2)

Angles between the edges, **α** (between b and c), (between a and c), and **γ** (between a and b).

(3)

Each unit cell has characteristic relation between **a , b , and c** or **α , β , and γ** that gives rise to **different types** of unit cell.



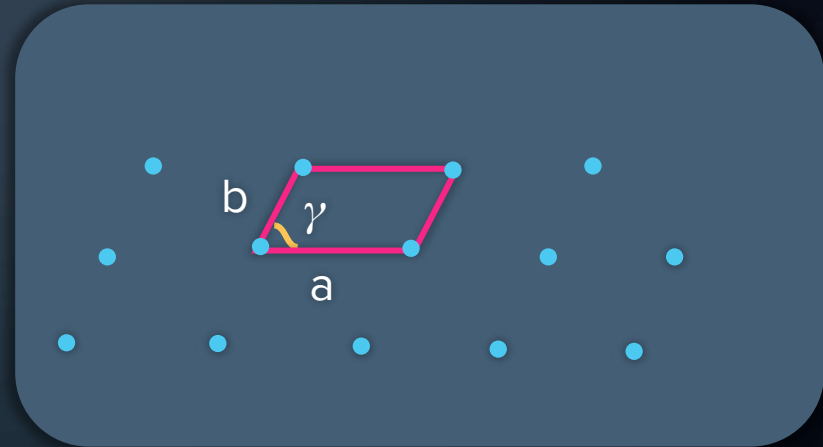
Unit Cells in 2-D

There are **5 types** of unit cells possible in **2-D lattice**.



Unit cells in 2-D is **parallelogram** which is described by **three parameters i.e., a , b , γ** .

Parallelogram



Unit Cells in 2-D

Unit Cell	a, b	γ
Square	$a = b$	$\gamma = 90^\circ$
Rectangle	$a \neq b$	$\gamma = 90^\circ$
Hexagonal	$a = b$	$\gamma = 120^\circ$
Rhombic	$a = b$	$\gamma \neq 90^\circ,$ $\gamma \neq 60^\circ \&$ $\gamma \neq 120^\circ$
Parallelogram	$a \neq b$	$\gamma \neq 90^\circ$

3-D Unit Cell

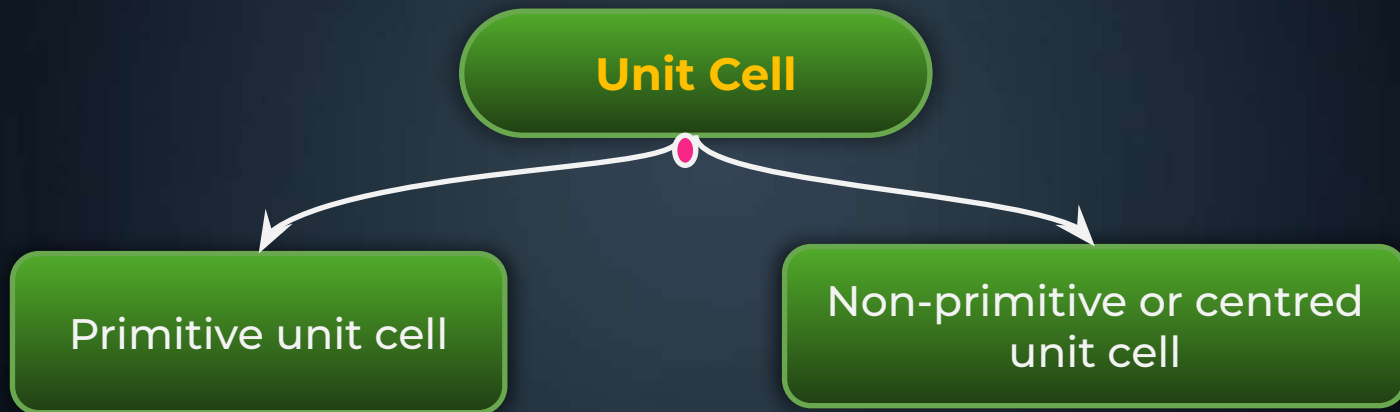
In 3-D lattice to specify any unit cell **6 parameters** are required.

3-edge length (**a, b, c**) and 3-angle between these i.e., **α , β , and γ** .

In 3-D lattice, 14 different types of unit cells are found and these are also known as Bravais lattice.

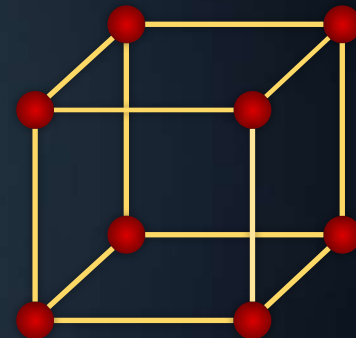
These 14 unit cells are grouped in 7 crystal systems depending upon **7 types** of primitive unit cells.

Unit Cell



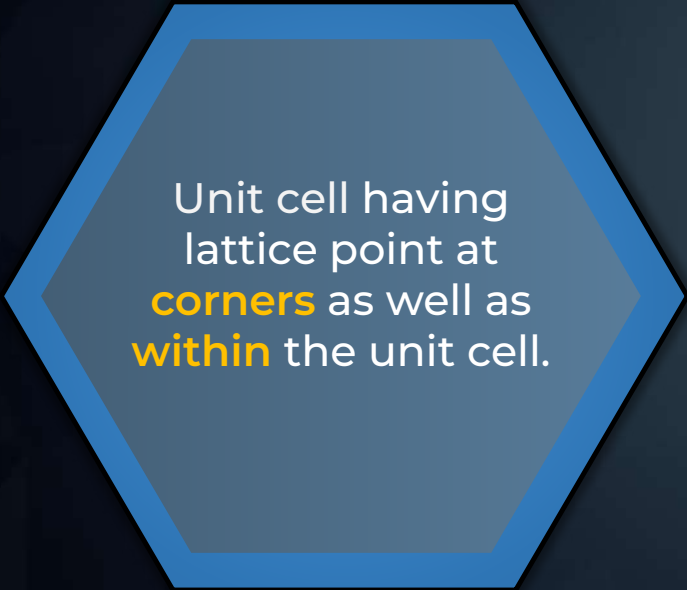
Primitive Unit Cell

Unit cell having lattice point only
at the **corners**.



Primitive/Simple
unit cell

Non-Primitive or Centred Unit Cell



Unit cell having
lattice point at
corners as well as
within the unit cell.

Non-primitive or Centred Unit Cell



Body-centred (B.C.)

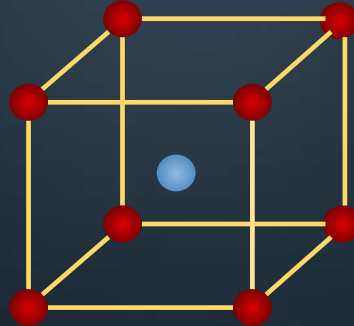
Face-centred (F.C.)

End-centred (E.C.)

Non-Primitive or Centred Unit Cell

Body-centred unit cell

It contains one constituent particle (atom, molecule, or ion) at its body centre besides the particles at its corners. In body centred unit cell, the constituent particles are present at the eight corners of the unit cell and also at the centre of the unit cell as shown below.

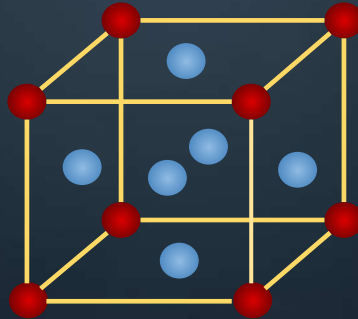


Body-centred
unit cell

Non-Primitive or Centred Unit Cell

Face-centred unit cell

Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that at its corners. In face centred unit cell, constituent particles are present at the eight corners of the unit cell and also at the centre of six faces of the unit cell as shown below.

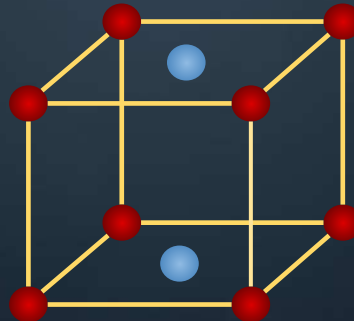


Face-centred
unit cell

Non-Primitive or Centred Unit Cell

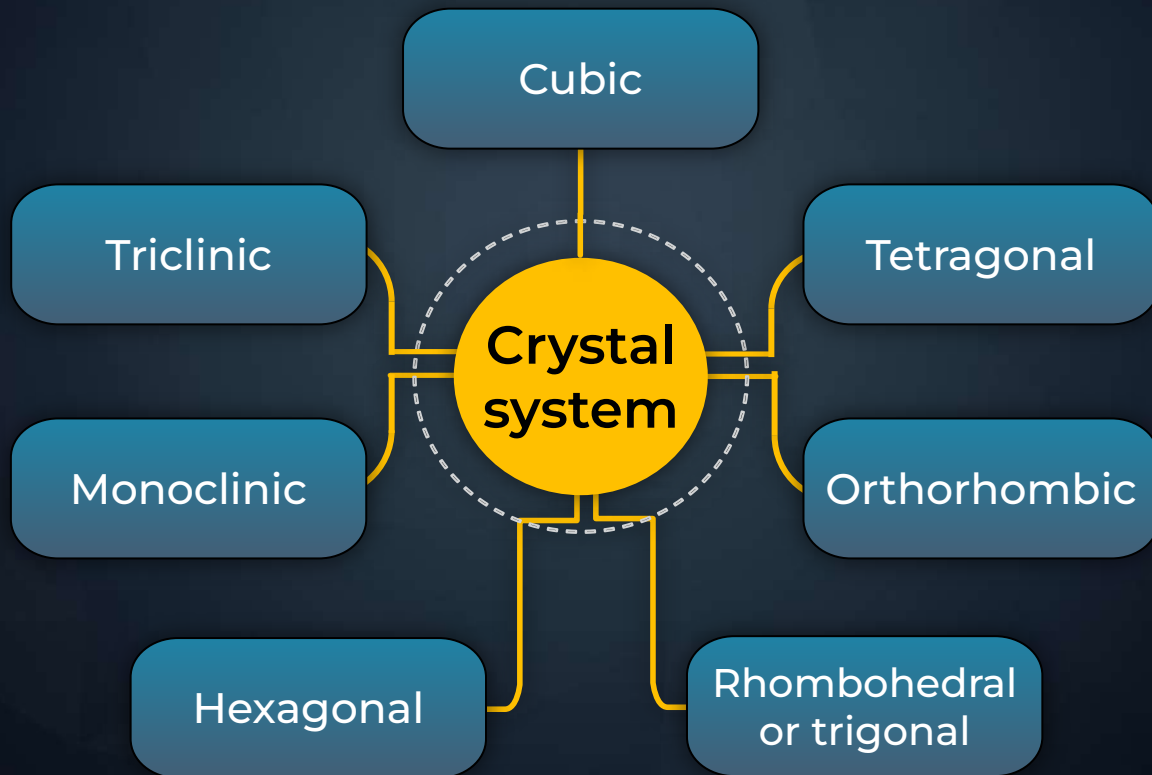
End-centred unit cell

In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners. In end centred unit cell, constituent particles are present at the eight corners of the unit cell and also at the centre of any two opposite faces of the unit cell as shown below.



End-centred
unit cell

Crystal systems



Crystal systems



Cubic Crystal Lattice

Edge length

$$a = b = c$$

Angle

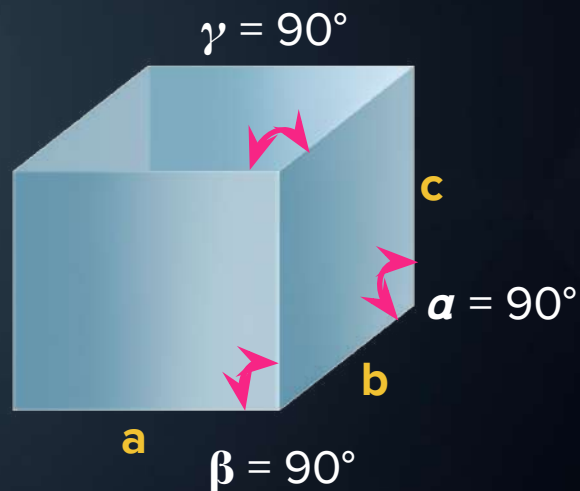
$$\alpha = \beta = \gamma = 90^\circ$$

Unit cell found

Primitive, BC, FC

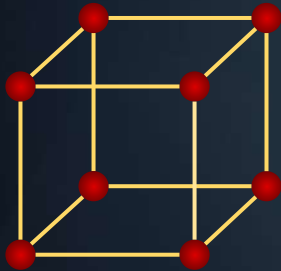
Examples

NaCl, ZnS, Cu

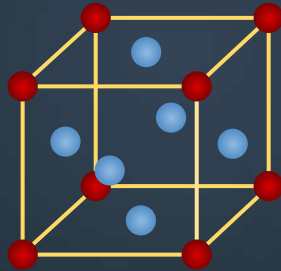


Crystal systems

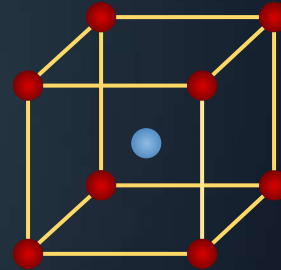
Cubic



Simple cubic

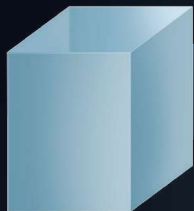


Face-centred
cubic



Body-centred
cubic

Crystal systems



Tetragonal Crystal Lattice

Edge length

$$a = b \neq c$$

Angle

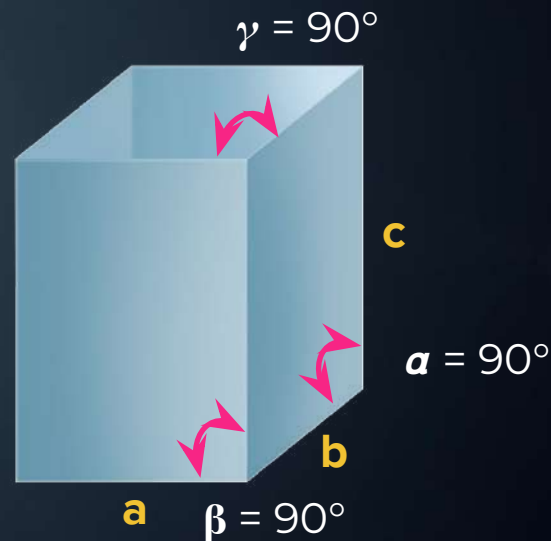
$$\alpha = \beta = \gamma = 90^\circ$$

Unit cell found

Primitive, BC

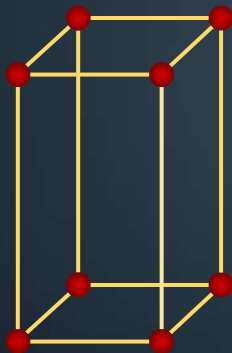
Examples

White tin,
 SnO_2 , TiO_2

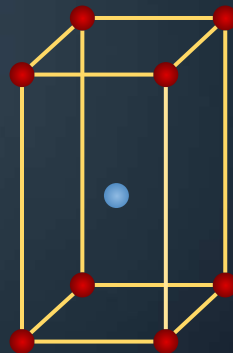


Crystal systems

Tetragonal

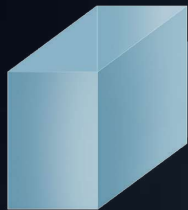


Primitive



Body-centred

Crystal systems



Orthorhombic crystal lattice

Edge length

$$a \neq b \neq c$$

Angle

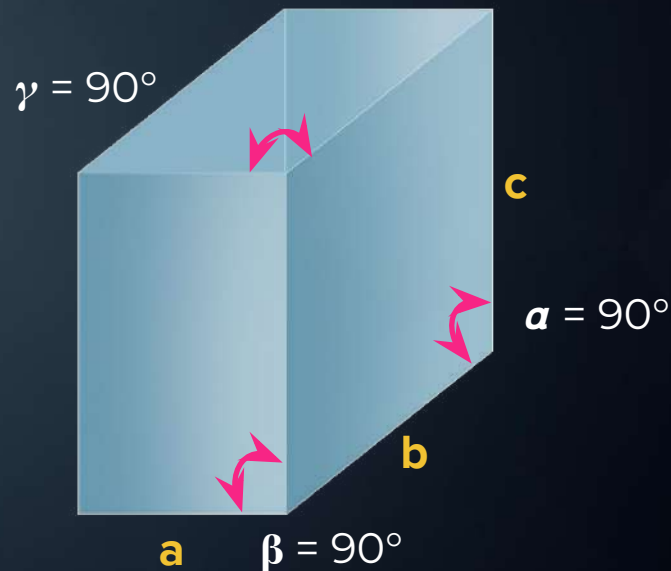
$$\alpha = \beta = \gamma = 90^\circ$$

Unit cell found

Primitive, BC,
FC, EC

Examples

Rhombic sulphur,
 KNO_3 , BaSO_4



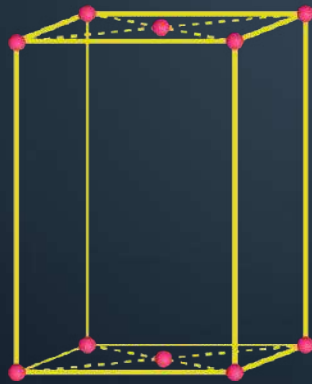
Crystal systems

Orthorhombic system

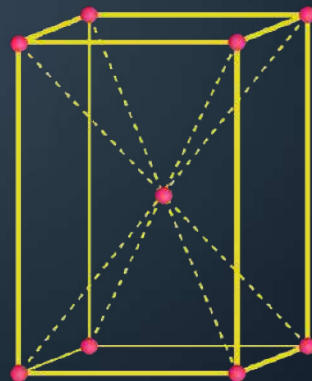
Simple (primitive), end-centred, body-centred, and face-centred unit cells are possible in an orthorhombic crystal system.



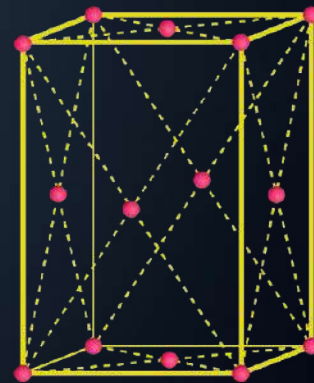
Primitive



End centered

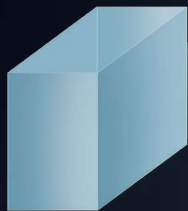


Body centered



Face centered

Crystal systems



Orthorhombic Crystal Lattice

Edge length

$$a \neq b \neq c$$

Angle

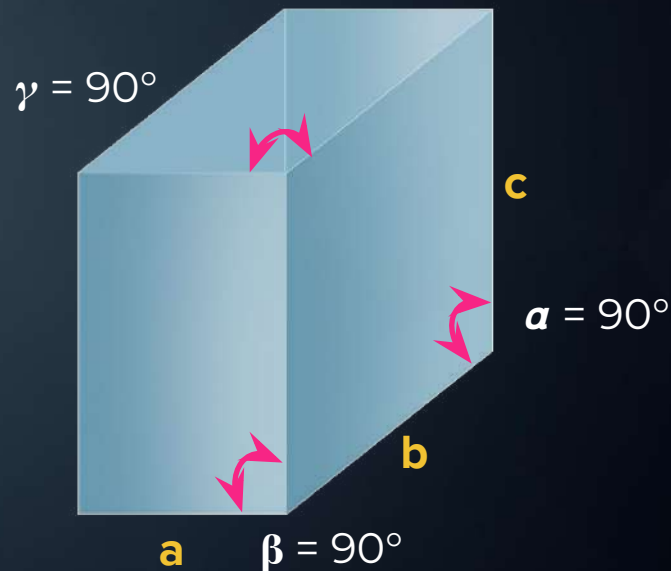
$$\alpha = \beta = \gamma = 90^\circ$$

Unit cell found

Primitive, BC,
FC, EC

Examples

Rhombic sulphur,
 KNO_3 , BaSO_4



Crystal systems



**Rhombohedral or Trigonal
crystal system**

Edge length

$$a = b = c$$

Angle

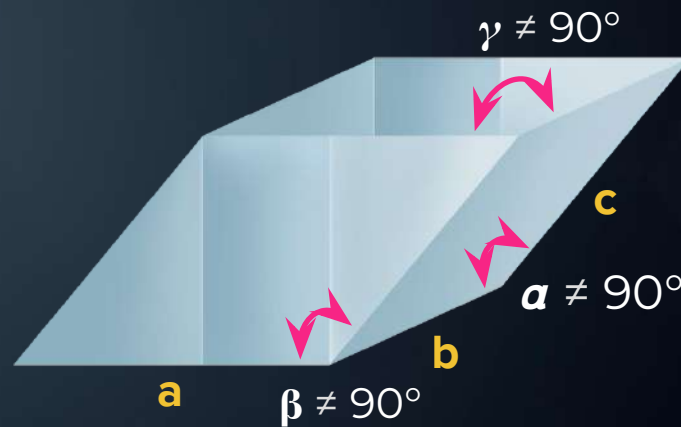
$$\alpha = \beta = \gamma \neq 90^\circ$$

Unit cell found

Primitive

Examples

Calcite (CaCO_3),
cinnabar (HgS)



Hexagonal

Edge length

$$a = b \neq c$$

Angle

$$\alpha = \beta = 90^\circ$$

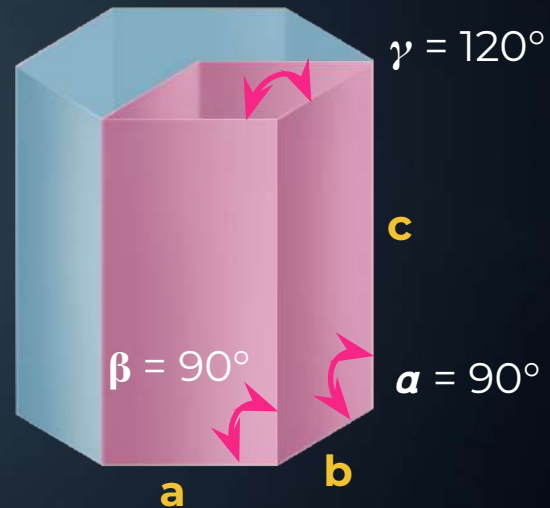
$$\gamma = 120^\circ$$

Unit cell found

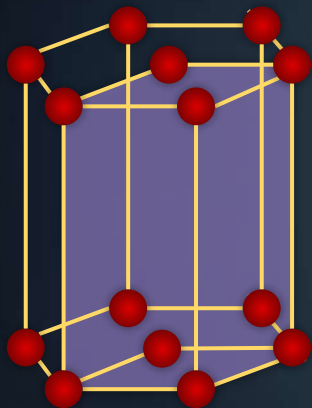
Primitive

Examples

Graphite,
ZnO, CdS

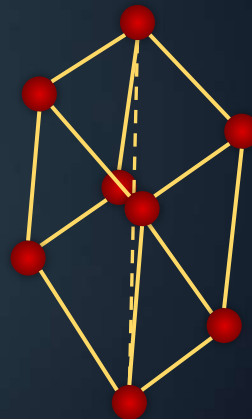


Hexagonal



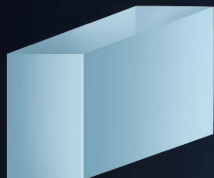
Primitive

Rhombohedral
or trigonal



Primitive

Crystal systems



Monoclinic crystal system

Edge length

$$a \neq b \neq c$$

Angle

$$\alpha = \gamma = 90^\circ$$
$$\beta \neq 120^\circ, 90^\circ, 60^\circ$$

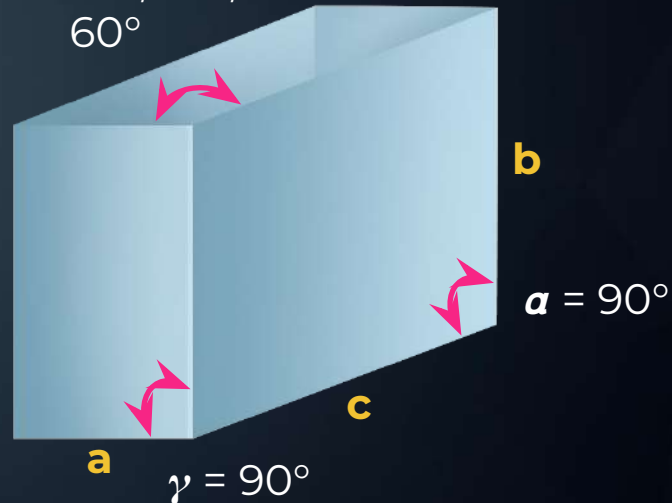
Unit cell found

Primitive, EC

Examples

Monoclinic, sulphur,
 $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

$$\beta \neq 120^\circ, 90^\circ, 60^\circ$$



Crystal systems



Triclinic crystal system

Edge length

$$a \neq b \neq c$$

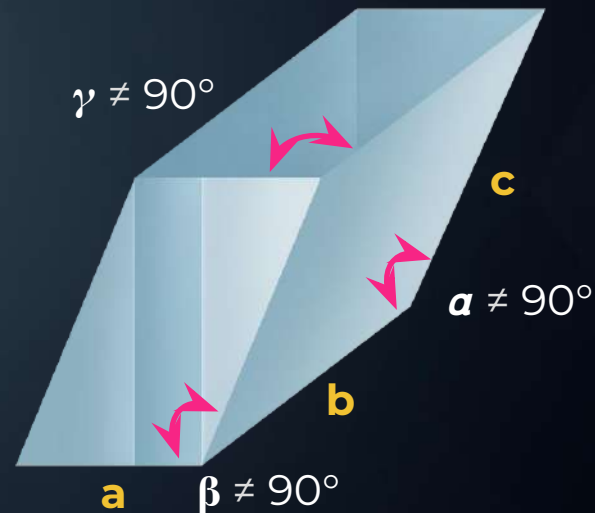
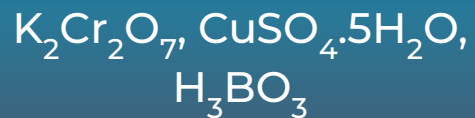
Angle

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

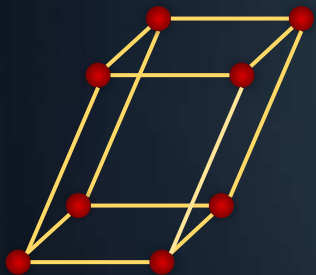
Unit cell found

Primitive

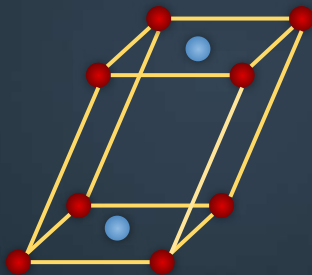
Examples



Monoclinic

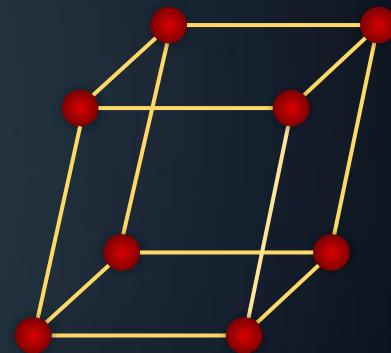


Primitive



End-centred

Triclinic



Primitive

Crystal systems

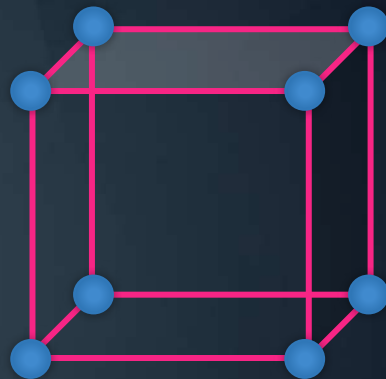
Crystal system	Edge length	Angles	Unit cell(s) found
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BCC, FCC
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BC
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, BC, FC, EC

Crystal systems

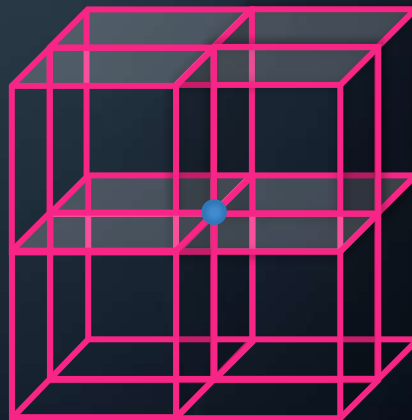
Crystal system	Edge length	Angles	Unit cell(s) found
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ,$ $\beta \neq 90^\circ$	Primitive, EC
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ,$ $\gamma = 120^\circ$	Primitive

Contribution of Corner Particles

A particle at the corner of a unit cell is shared by **eight unit cells**.

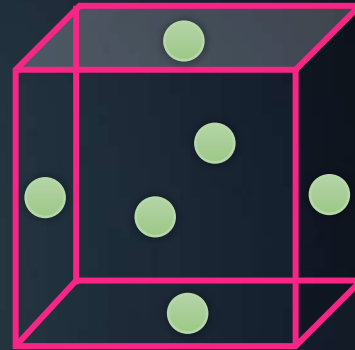


Contributes $\frac{1}{8}$ part
to the unit cell.

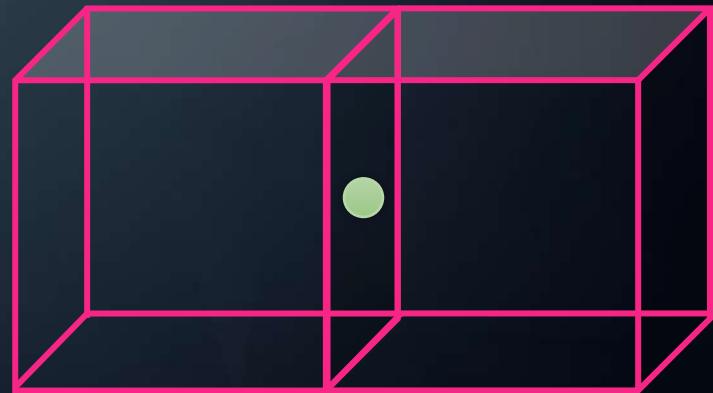


Contribution of Face-Centred Particles

A particle at the face-centre is shared by **two unit cells**.



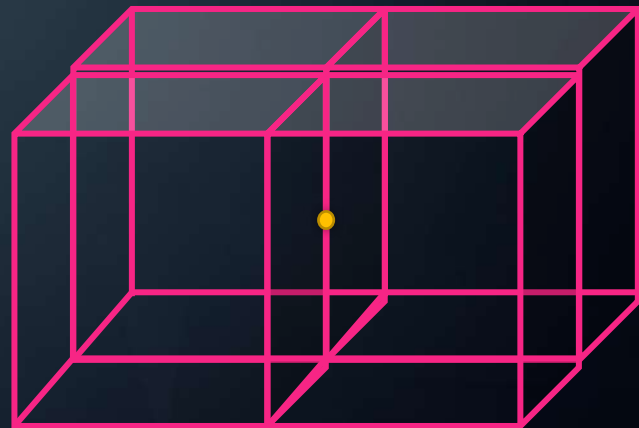
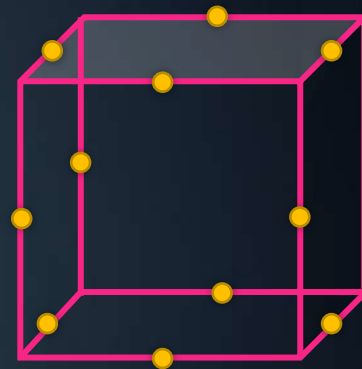
Contributes $\frac{1}{2}$ part
to the unit cell.



Contribution of Edge-Centred Particles

A particle present at the edge-centre is shared by **four unit cells**.

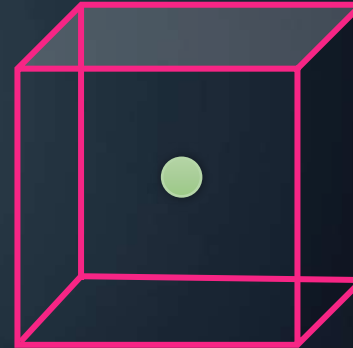
Contributes $\frac{1}{4}$ part
to the unit cell.



Contribution of Body-Centred Particles

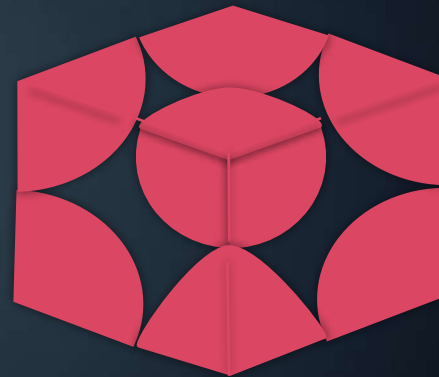
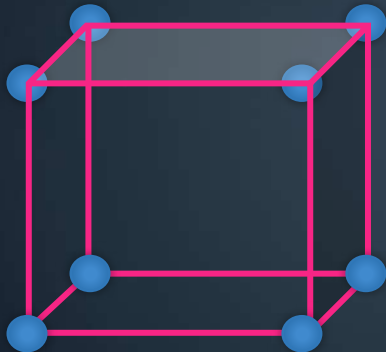
A particle present at the body-centre wholly belongs to the **unit cell** in which it is present.

Contributes **1 part**
(fully) to the unit cell.



Effective number of particles

Primitive Cubic Unit Cell



Effective number of
particles in a unit cell

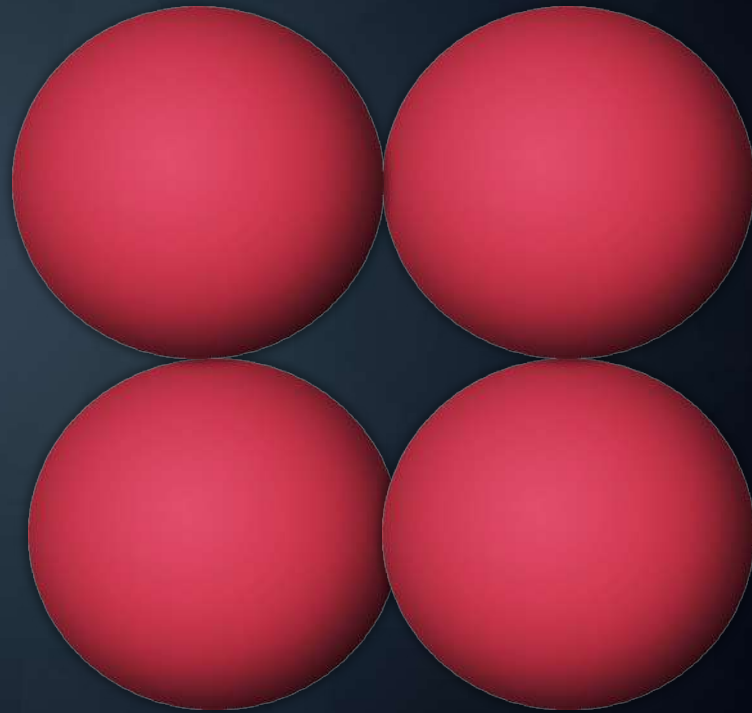
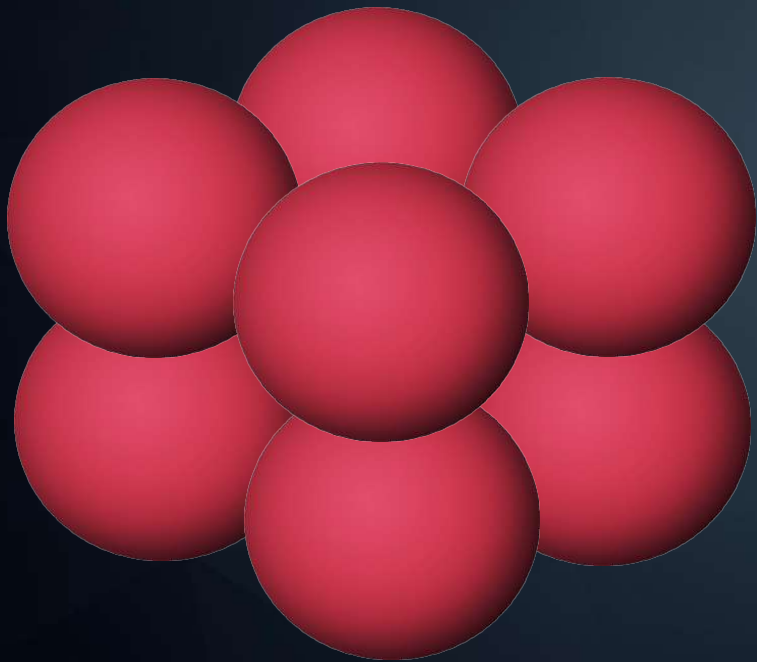
=

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

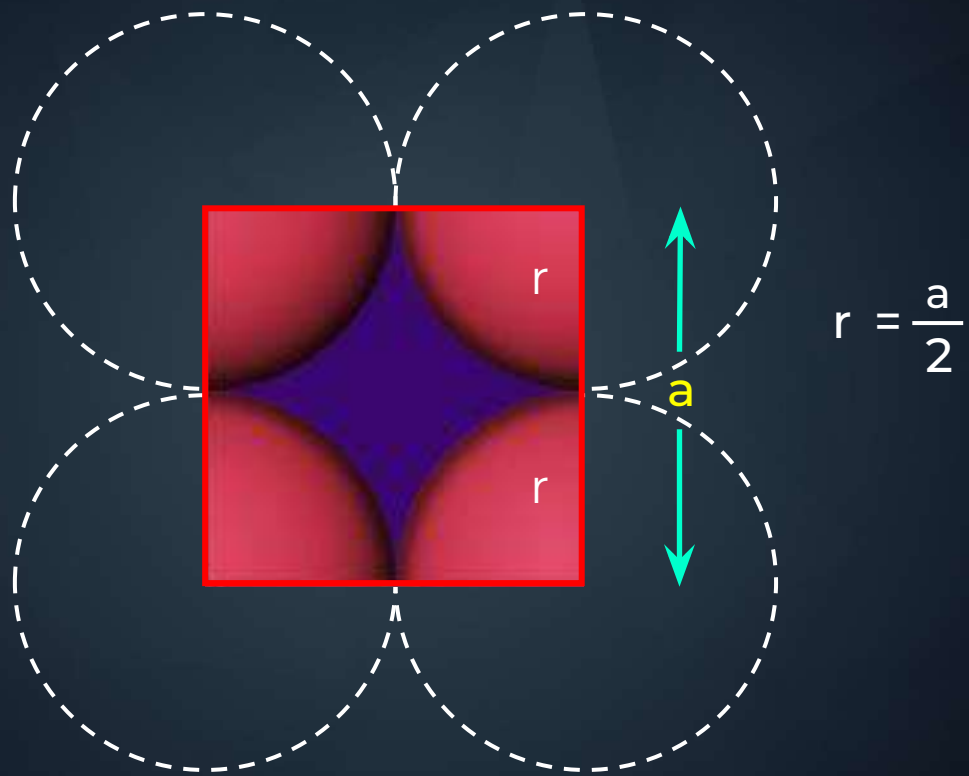
=

1

Simple Cubic Unit Cell



Face of a simple cubic unit cell



Relation between a & r

Corner atoms are touching each other.

a

=

2r

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

Packing Efficiency

The percentage of the total space **filled** by the particles



Packing Efficiency (P.E)

For **3-D** arrangement

P.E.

=

$$\frac{\text{Volume occupied by particles in a unit cell}}{\text{Total volume of the unit cell}} \times 100$$

=

$$\frac{Z \times \text{Volume of one particle}}{\text{Total volume of the unit cell}} \times 100$$

- Z = Effective number of atoms in the unit cell



Packing Efficiency (P.E)

Total volume
occupied by
particles

=

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

P.E.

=

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

Volume of
the unit cell

=

$$a^3$$

=

$$(2r)^3$$

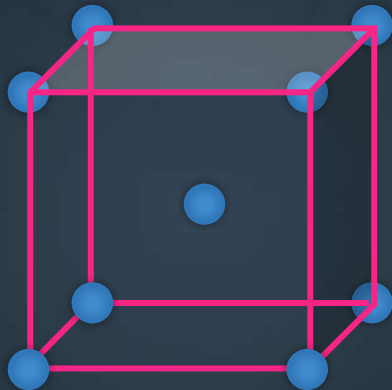
=

$$\frac{\pi \times 100}{6}$$

≈

52.33%

Body-Centred Cubic Unit Cell



Effective number of
particles in a unit
cell

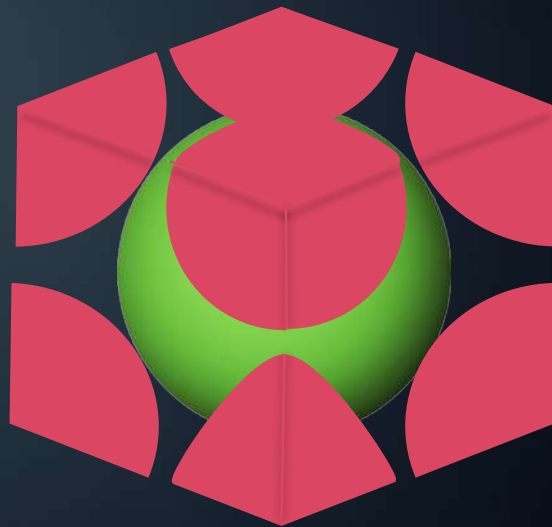
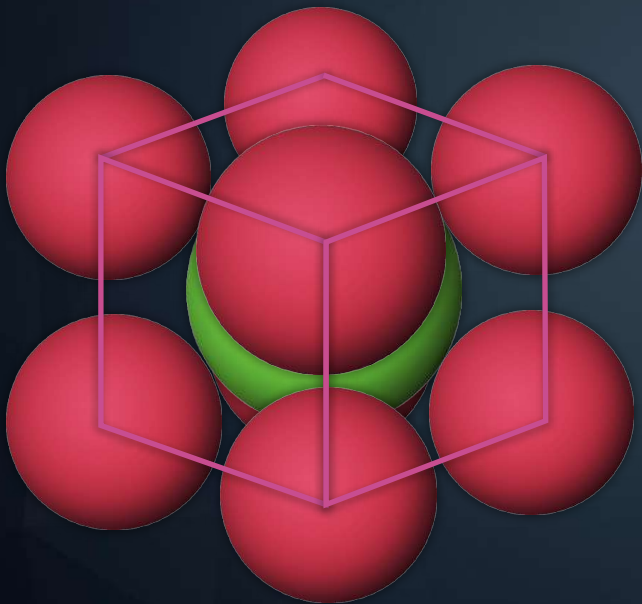
=

$$8 \times \frac{1}{8} + (1 \times 1)$$

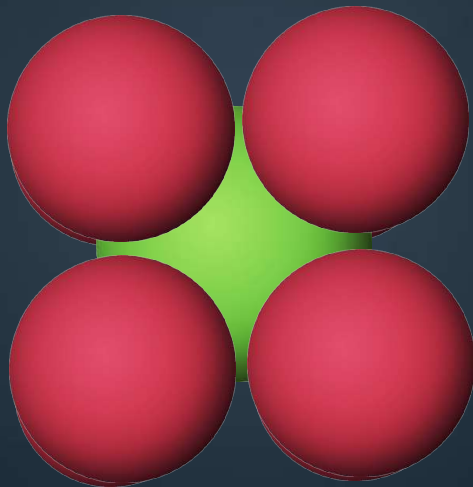
=

2

Body-Centred Cubic Unit Cell



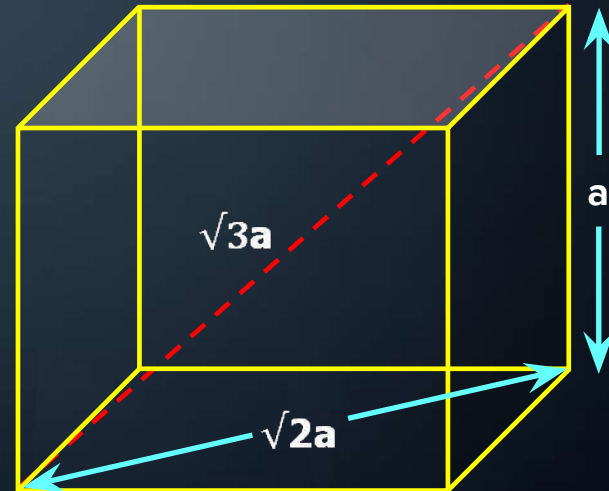
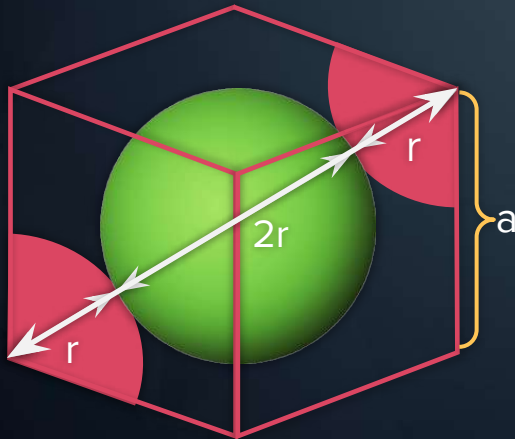
Body-Centred Cubic Unit Cell



Face of a body-centred cubic unit cell

Body-Centred Cubic Unit Cell

Spheres are **not touching** along the **edge**.
They are **touching** along the **body diagonal**.





Body-Centred Cubic Unit Cell

Relation between a & r

Along the **body diagonal**

$$\sqrt{3}a$$

=

$$4r$$

$$a$$

=

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

Packing efficiency (P.E)

Total volume
occupied by
particles

=

$$2 \times \frac{4}{3} \pi r^3$$

Packing
efficiency

=

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

Volume of
the unit cell

=

$$a^3$$

=

$$\frac{(4r/\sqrt{3})^3}{3}$$

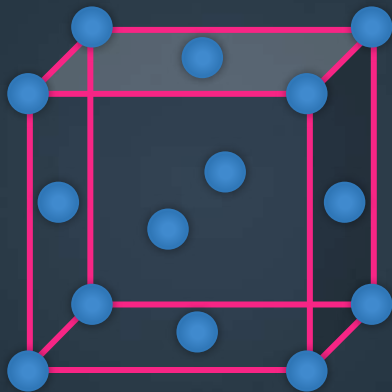
=

$$\frac{\sqrt{3} \pi \times 100}{8}$$

≈

68%

Face-Centred Cubic Unit Cell



Effective number of
particles in a unit cell

=

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

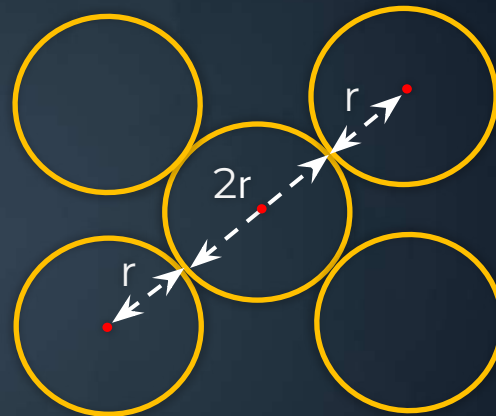
=

4

Face-Centred Cubic Unit Cell

Relation between a and r

Face of unit cell



Spheres are touching
along the face diagonal

a

$>$

$2r$

$\sqrt{2}a$

$=$

$4r$

Packing Efficiency in FCC

P.E.

=

$$\frac{4 \times (4/3) \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \times 100$$

=

$$\frac{\pi \times 100}{3\sqrt{2}}$$

≈

74%

Density of a unit cell

It is the **ratio** of **mass** of the spheres present in unit cell and **total volume** of unit cell.

Density of a unit cell

Density of
the unit cell

=

Total mass of particles in the unit cell
Volume of the unit cell

Density of
the unit cell

=

Total number of particles in the
unit cell \times mass of single particle
Volume of the unit cell

Density of a unit cell

Mass of a
single particle

=

$$\frac{\text{Molar mass}}{N_A}$$

Density (ρ)

=

$$\frac{\text{Total number of particles in unit cell} \times (\text{Molar mass})}{(\text{Volume of unit cell}) \times (N_A)}$$

Density of
unit cell

=

Density of
crystal

Density (ρ)

=

$$\frac{Z \times M}{N_A \times a^3}$$

Coordination Number (C.N.)

Number of nearest neighbour particles in a packing is called **coordination number**.

Coordination number



Simple cubic



Body-centred cubic

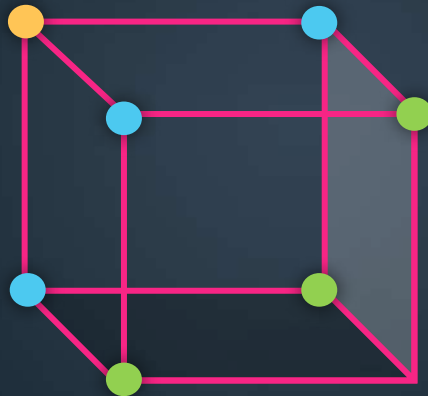


Face-centred cubic

Coordination Number (C.N.)

Simple cubic unit cell

- Reference particle
- Nearest particle
- Next nearest particle



C.N.

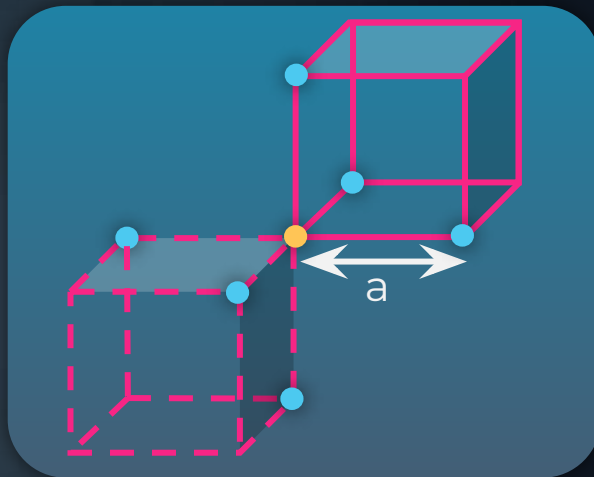
=

6

Nearest Neighbour

Simple cubic unit cell

Number of nearest neighbour is **same** as coordination number.



Distance of the **nearest** particle

=

a

=

2r

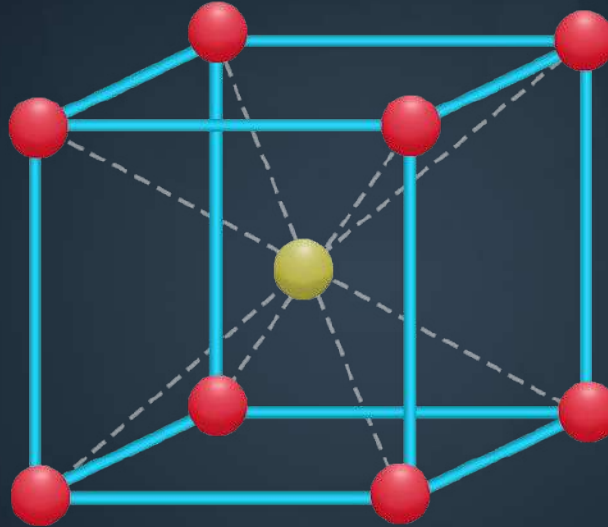
Number of nearest particles

=

6

Nearest Neighbour in BCC

- Reference particle
- Nearest particle



Number of nearest
particles

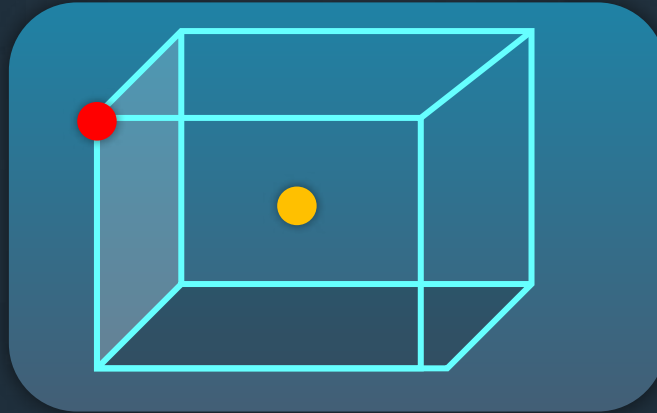
=

8

C.N.

Nearest Neighbour in BCC

- Reference particle
- Nearest particle



Distance of **nearest**
particle in BCC

=

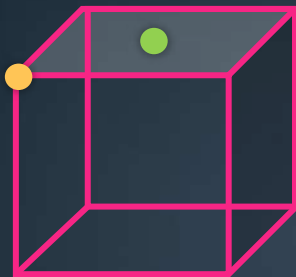
$$\frac{\sqrt{3}a}{2}$$

=

$$2r$$

Nearest Neighbour in FCC

- Reference particle
- Nearest particle



Distance of **nearest**
particle in FCC

=

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

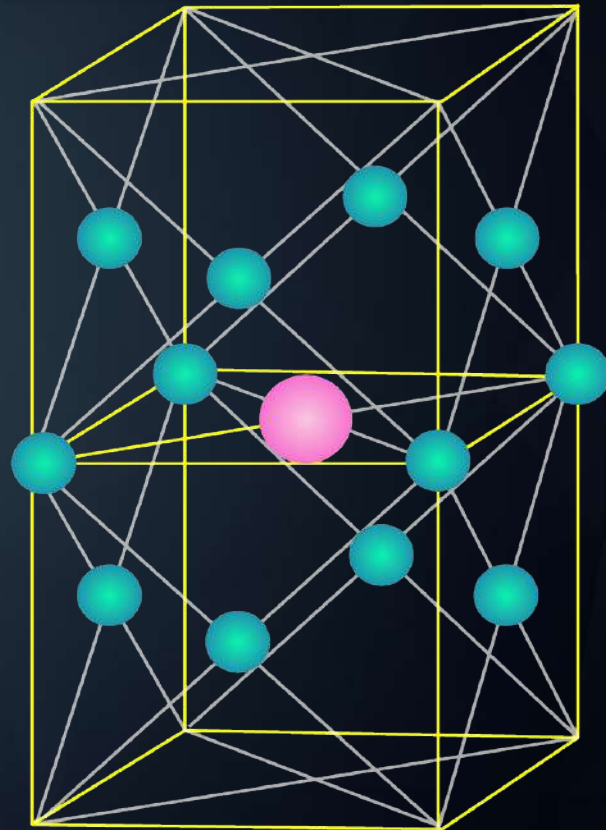
=

$$2r$$

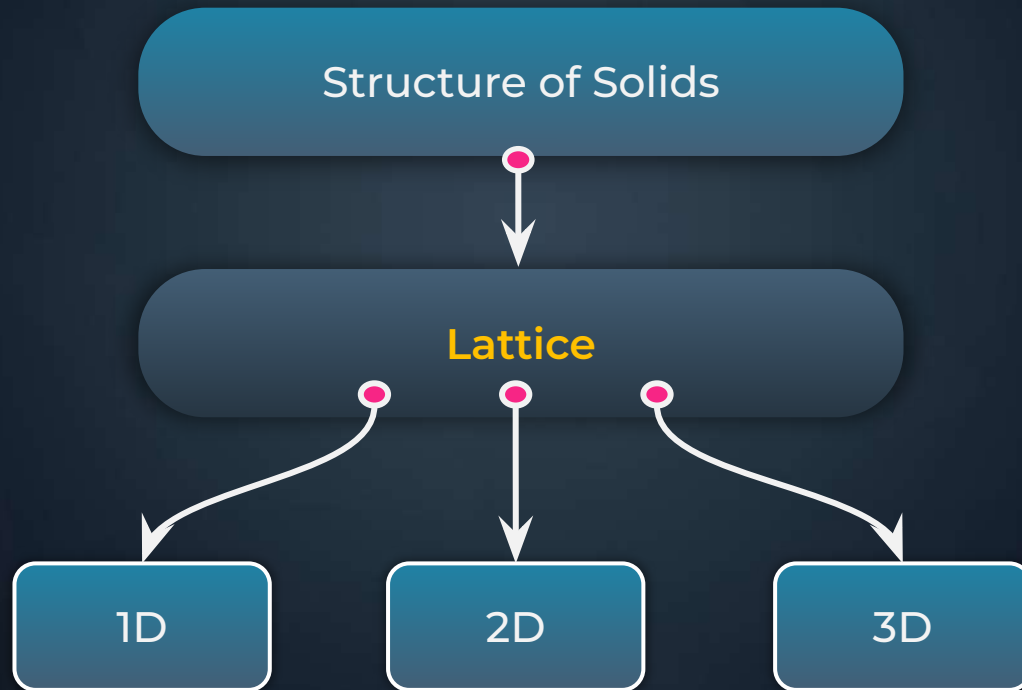
Number of
nearest particles

=

12



Structure in Solids



Structure in Solids

In 1-D, for **efficient packing**, spheres are arranged in a row and touch each other.



Structure in Solids

Coordination number (C.N.)

Number of nearest neighbour particles in a packing is called **coordination number**.



C.N. = 2

Structure in Solids

Packing in 2-D Lattice

2-D lattice can be considered to be made of 1-D array

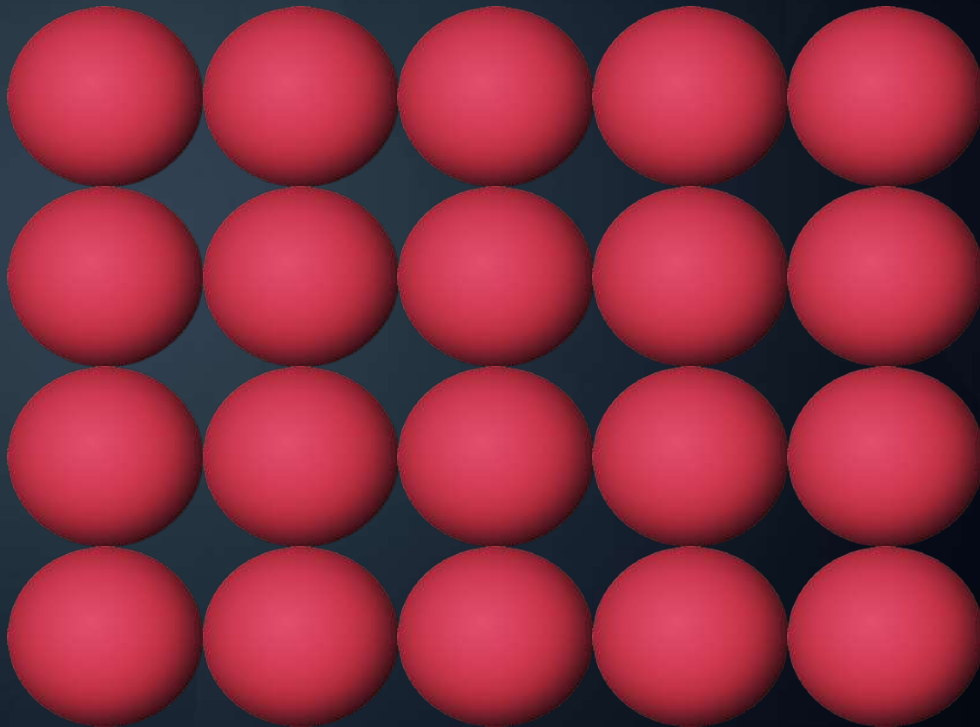
Square
arrangement

Hexagonal
arrangement

Structure in Solids

Square arrangement in
2-D lattice

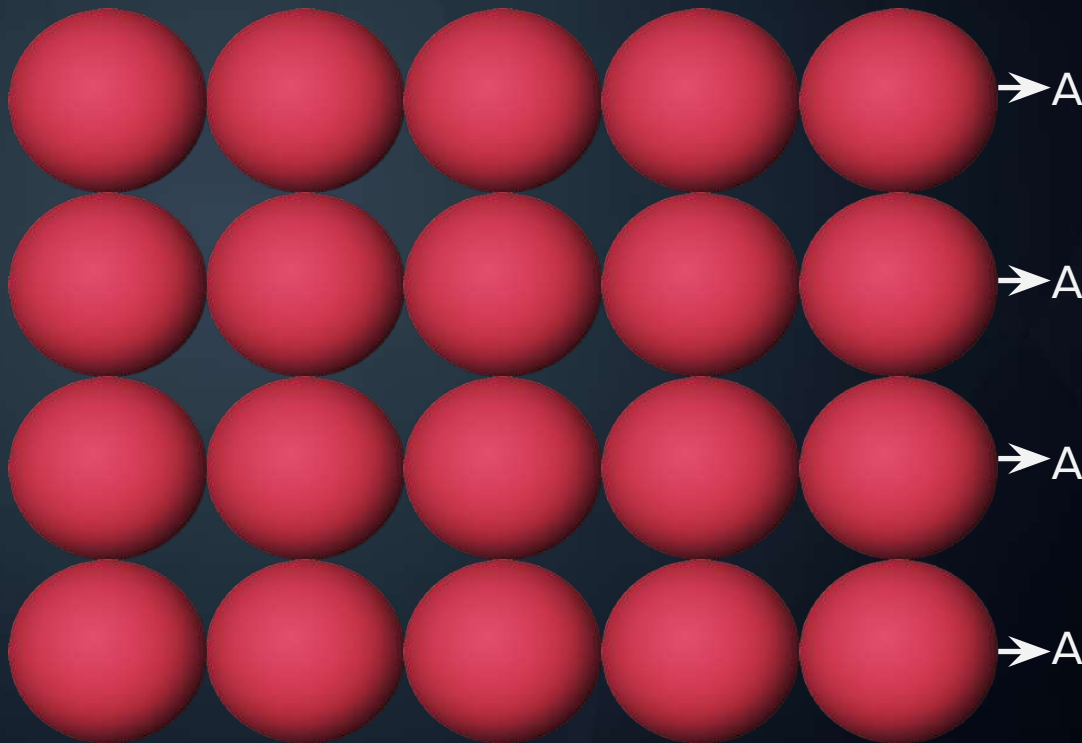
Array are arranged such that
spheres of one array are **exactly**
above the sphere of another
array.



Structure in Solids

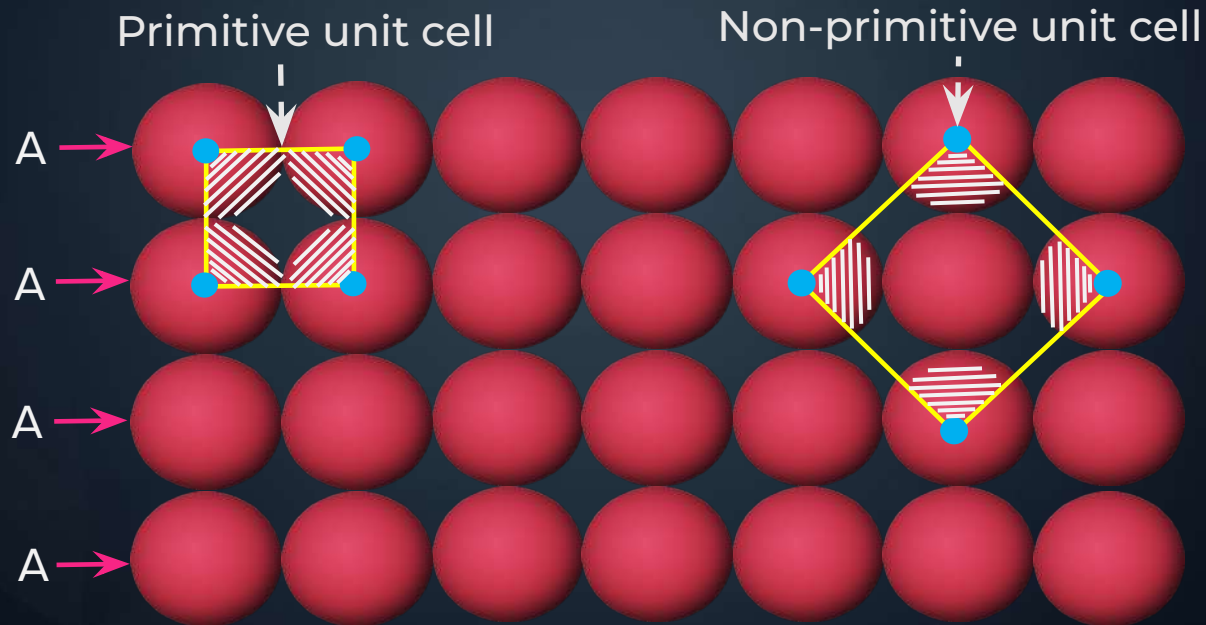
Square arrangement in
2-D lattice

AAA type packing



Structure in Solids

Square arrangement in
2-D lattice



AAA type of arrangement

Structure in Solids

Square arrangement in
2-D lattice

Square packing in 2-D

Unit cell

Primitive

Non-primitive

Effective
number of
particles (Z)

1

2

C.N.

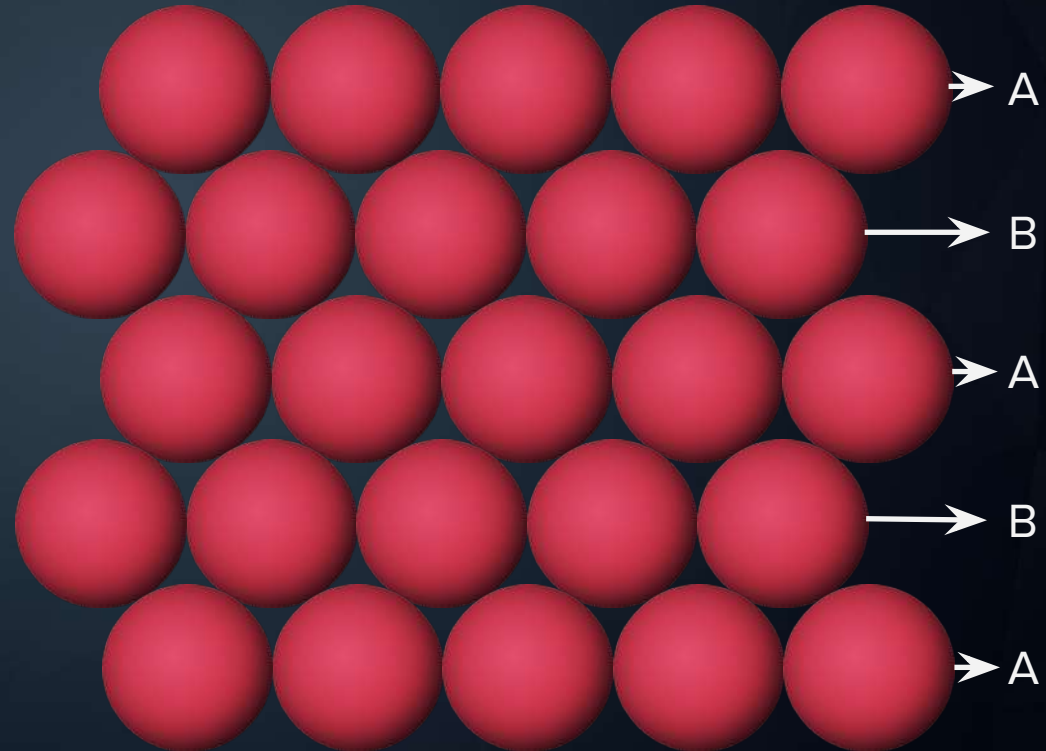
4

4

Structure in Solids

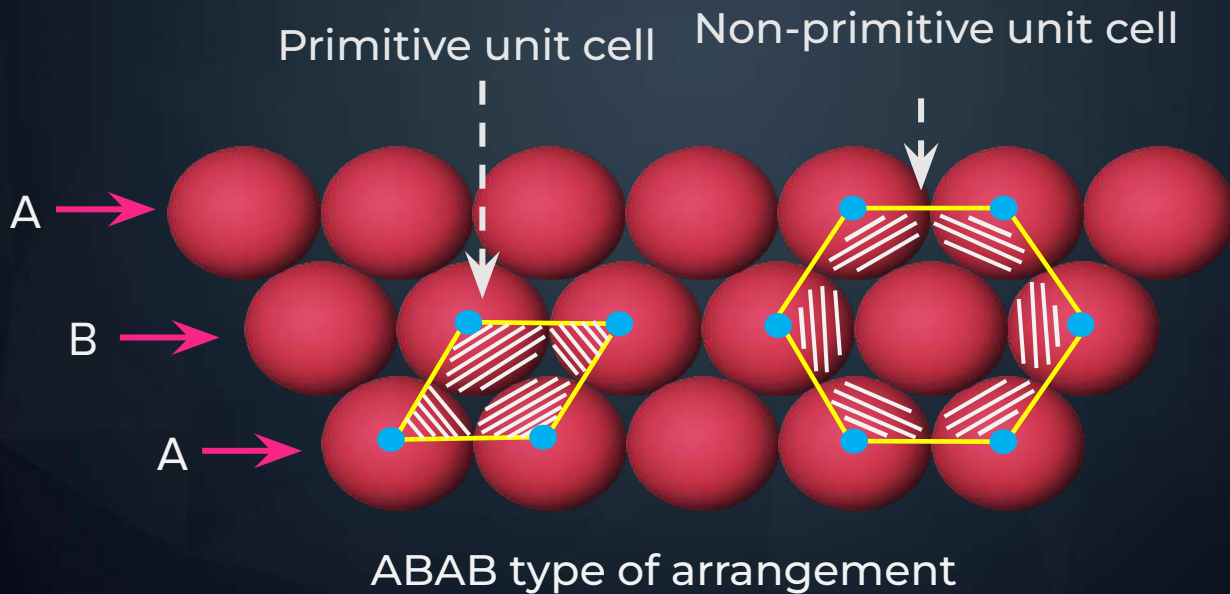
Hexagonal arrangement in
2-D lattice

1-D array are arranged such
that the spheres of one array
occupies the depression of
other array



Structure in Solids

Hexagonal arrangement in
2-D lattice



Structure in Solids

Hexagonal arrangement in
2-D lattice

Hexagonal packing in **2-D**

Unit cell

Primitive

Non-primitive

Effective
number of
particles (Z)

1

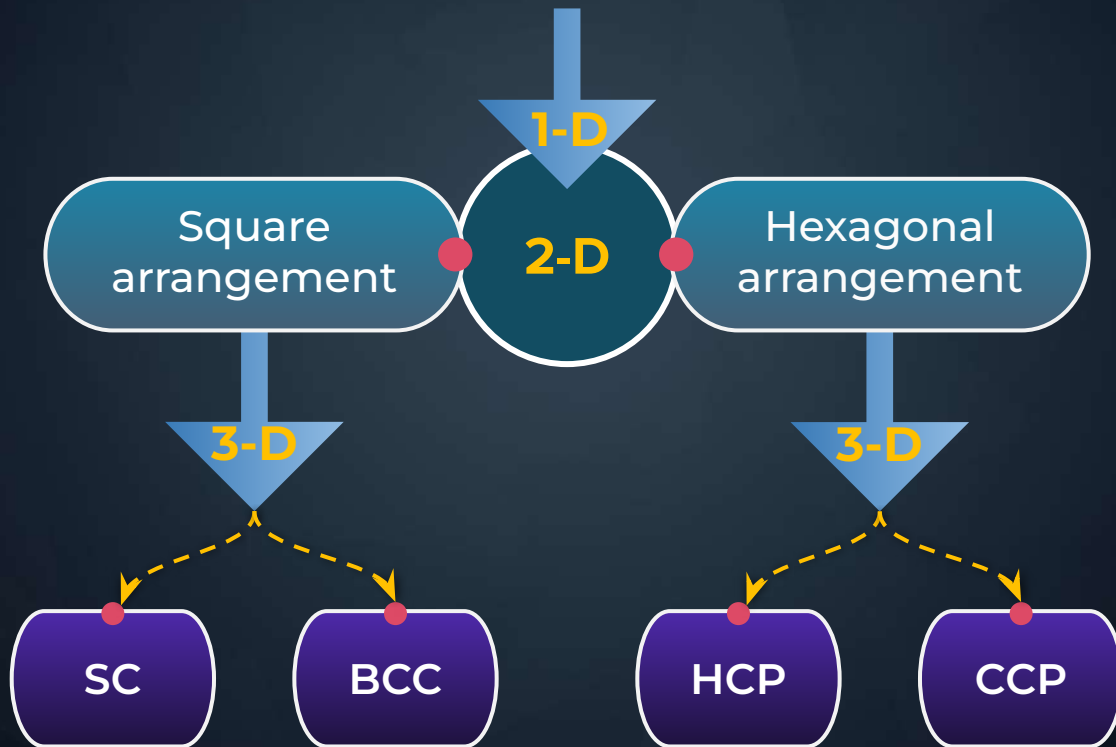
3

C.N.

6

6

Packing in 1D, 2D and 3D

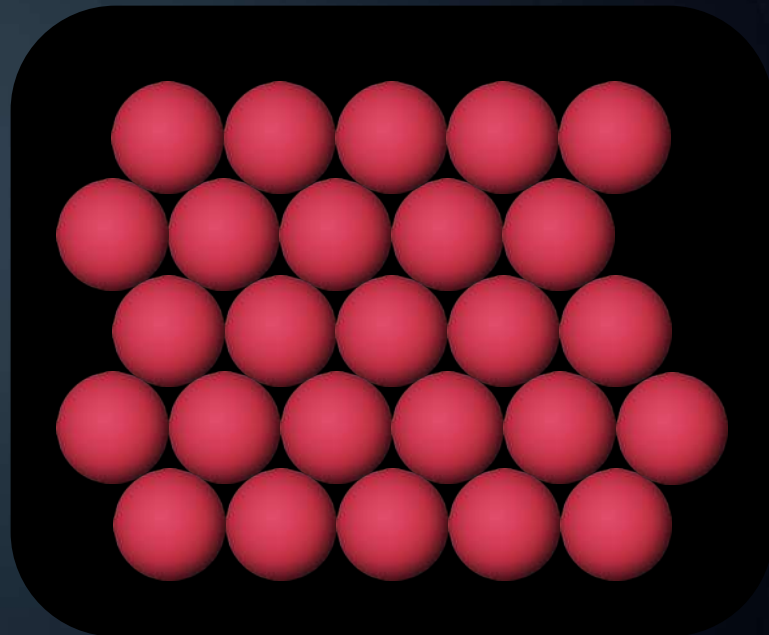


Arrangement of Hexagonal-Packed Sheets

To generate **close packing**, the 2D arrangement **must be hexagonal**.

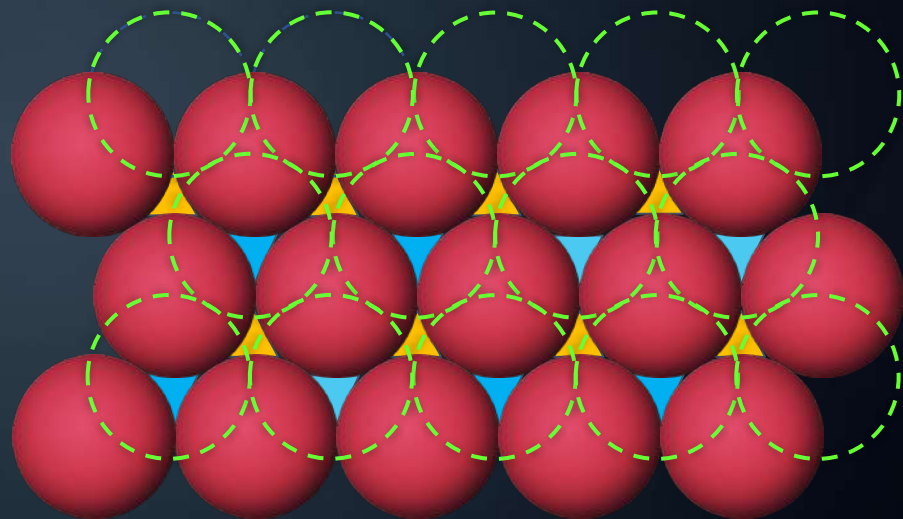


The sheets are arranged such that **depressions** of one sheet are **occupied** by the **spheres** of the other sheet.



Arrangement of Hexagonal-Packed Sheets

Only **50% depressions** of one layer can be occupied by the spheres of another layer (**II layer**).



Voids

Although the close-packed structures have the maximum packing efficiency, there are **empty spaces** in the arrangements.

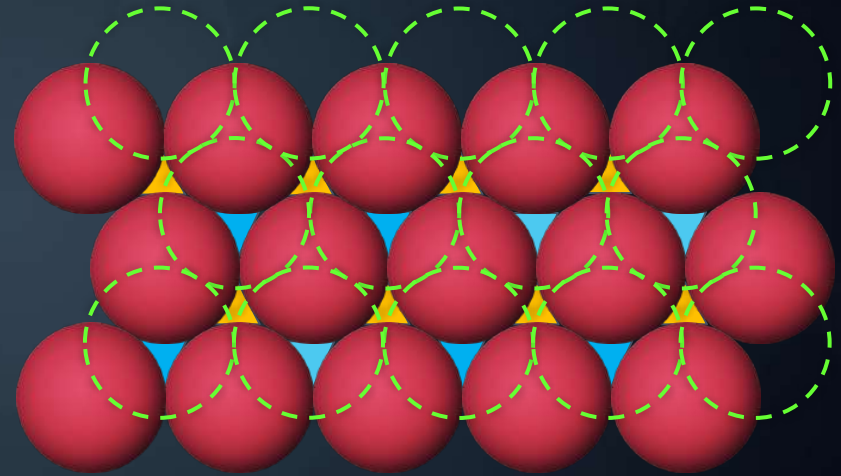
These empty spaces are known as **voids or interstitial voids**.

Types of Voids

On placing the second layer in the depressions of the first layer, two types of voids are generated.

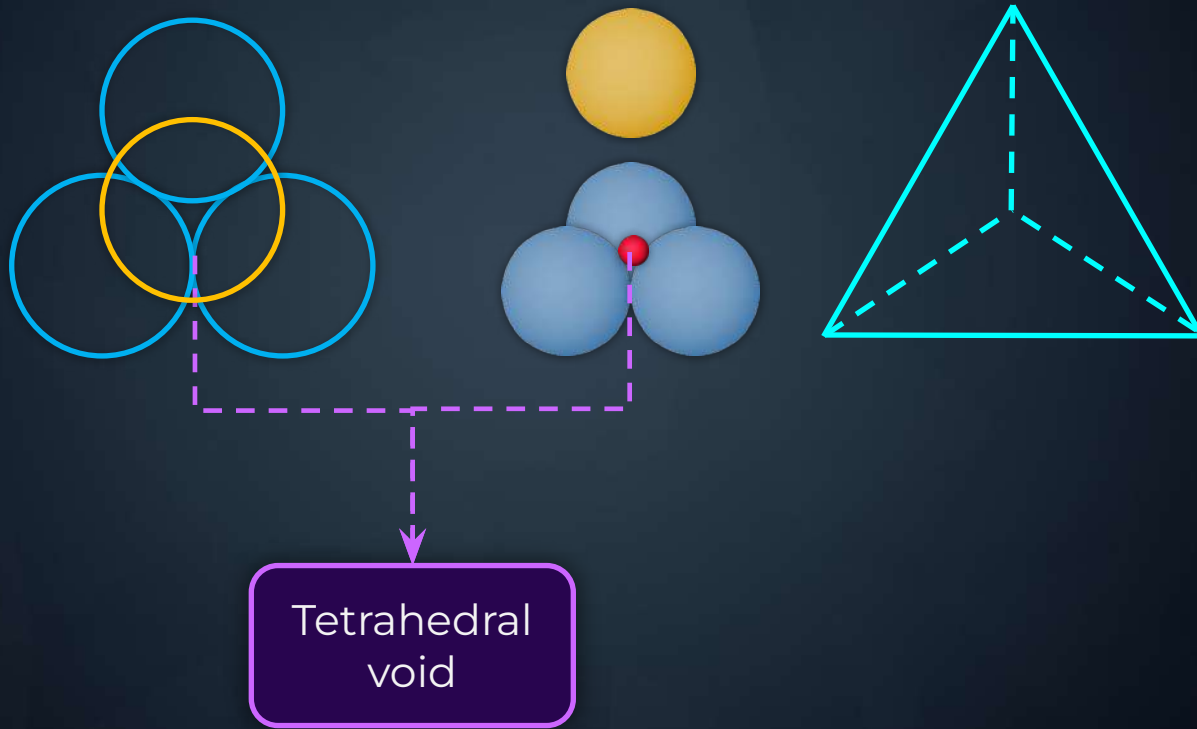
Tetrahedral
voids

Octahedral
voids

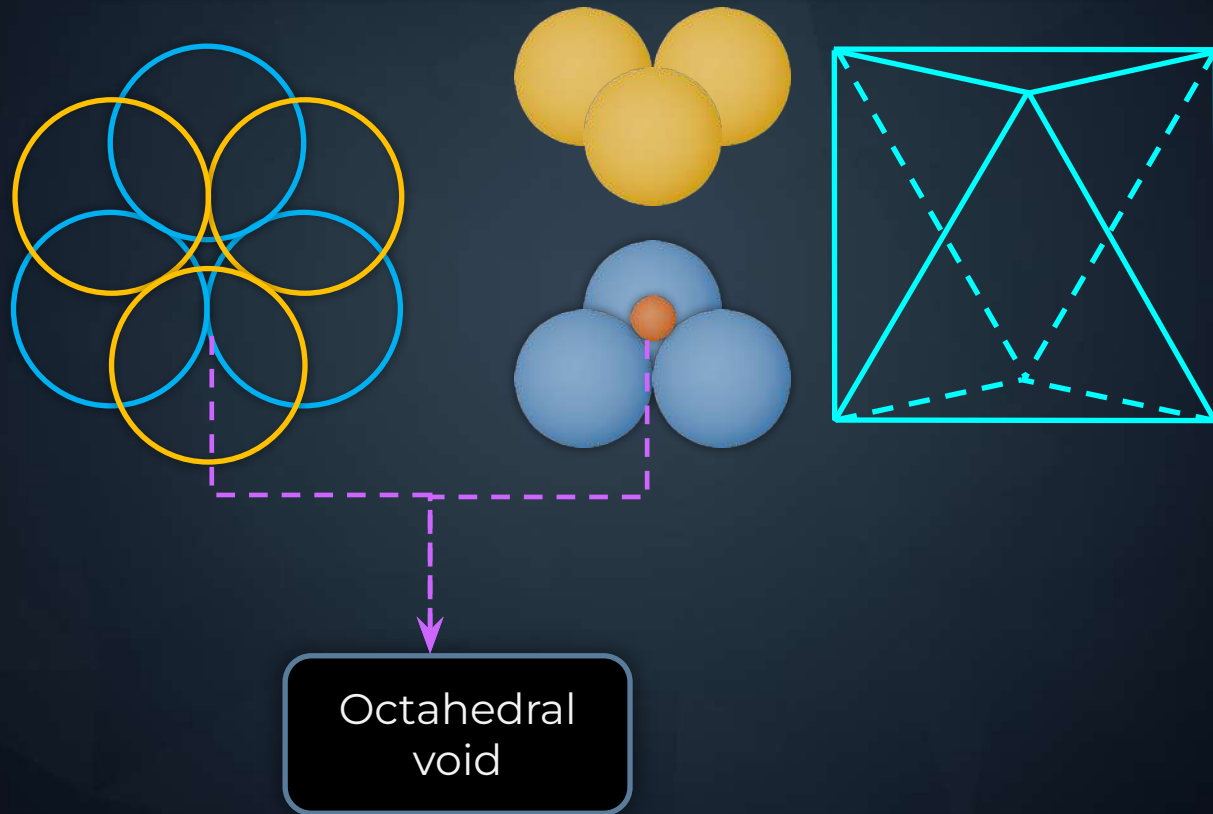


▲ Octahedral void
▼ Tetrahedral void

Tetrahedral Void



Octahedral Void



Two Methods to place 3rd layer on the 2nd layer

Spheres of 3rd layer
are placed on
tetrahedral **voids**

Spheres of 3rd layer
are placed on
octahedral voids

Hexagonal close
packing (**HCP**)

Cubic close
packing (**CCP**)

ABAB type

ABCABC type



Hexagonal Close Packing (HCP)

Sphere of the third layer occupy those **voids** of the second layer **under** which there are **sphere of the first layer i.e., T.V.**

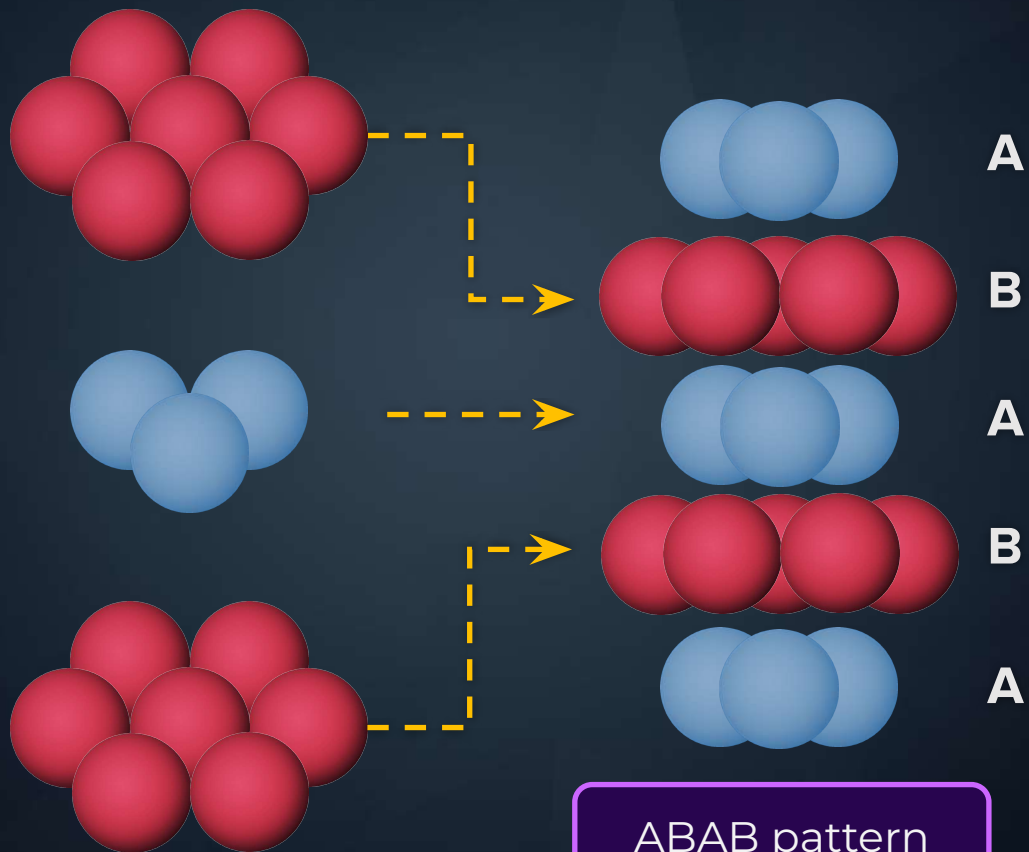


So, the third layer is **exactly identical** to the first layer. This generates the **ABAB - - - AB pattern.**

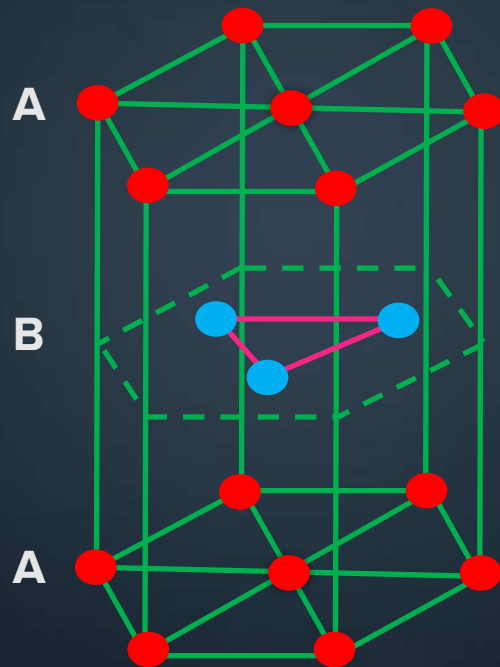


One type of void always remains **unoccupied, i.e., O.V.**

Hexagonal Close Packing (HCP)



Unit Cell



Effective Number of Particles in Hexagonal Unit Cell

Effective number of particles (Z)

$$= 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1$$

Corner particles of two hexagonal layers

For the centre particles of two hexagonal layers

For the particles of middle layer

Effective number of particles (Z)

$$= 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6$$

Coordination Number (C.N.)

$$\text{C.N.} = 12$$

Each sphere
touches

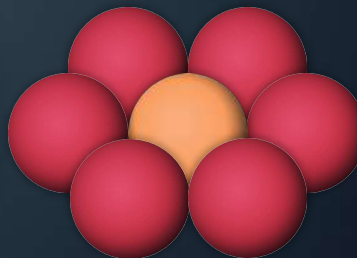
3 spheres
above the layer

+

6 spheres in
its layer

+

3 spheres
below the layer



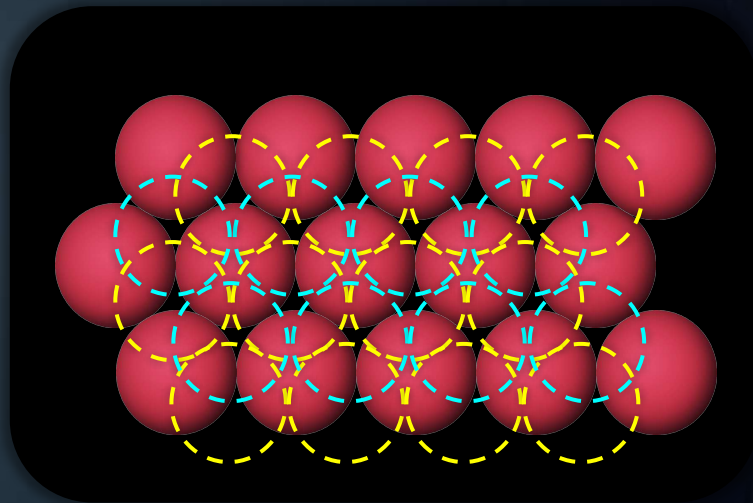
Cubic Close Packing (CCP)

The spheres of the third layer are placed such that they occupy **50% voids of the second layer**, under which there are **voids of the first layer, i.e., O.V.**

The third layer is **different** from the first layer as well as the second layer. Thus, it has an **ABCABC** type of arrangement.

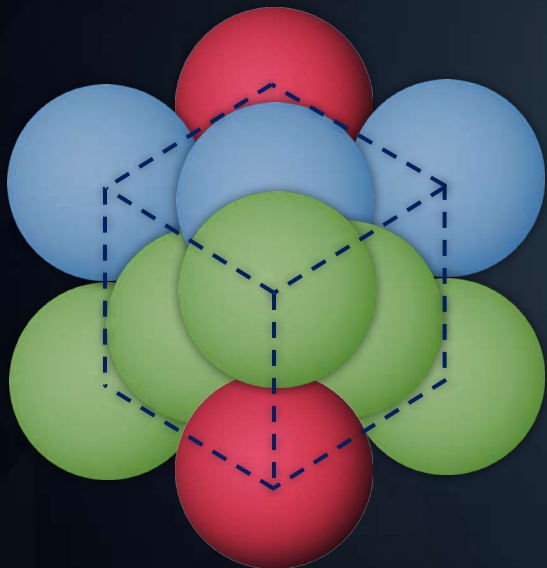


It is known as **cubical close packing**; the unit cell chosen is **face-centred cubic** (FCC).

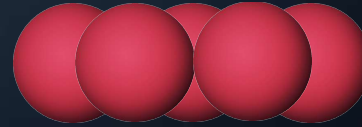
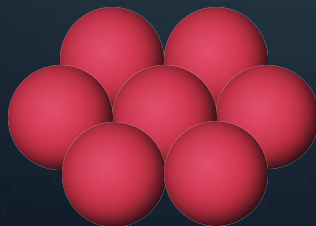
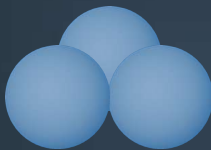
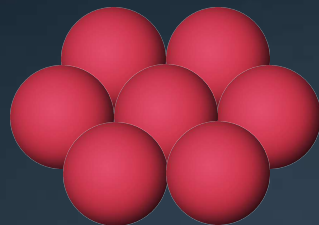


Cubic Close Packing (CCP)

ABCABC pattern



FCC unit cell



A

B

C

A

B

C

A

Coordination Number (C.N.)

C.N.

=

12

Each sphere touches

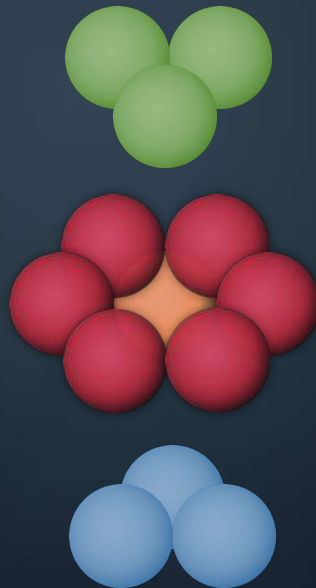
3 spheres
above the layer

+

6 spheres in
its layer

+

3 spheres
below the layer

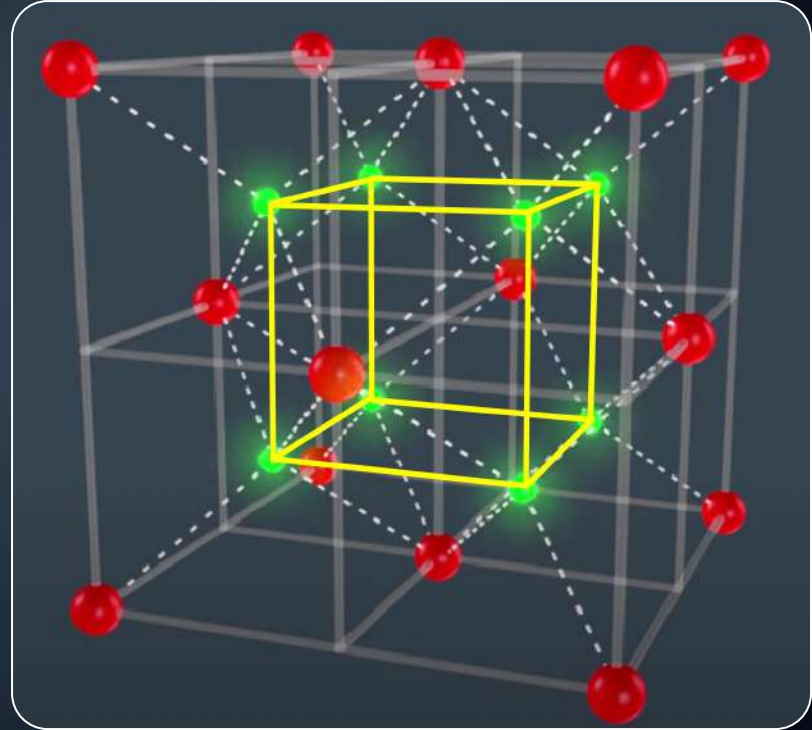


HCP and **CCP** are the **only** closely packed lattices (because of their efficiency, **74%**).

Tetrahedral Voids in FCC Unit Cell



FCC unit cell has
8 tetrahedral voids



● - Tetrahedral void

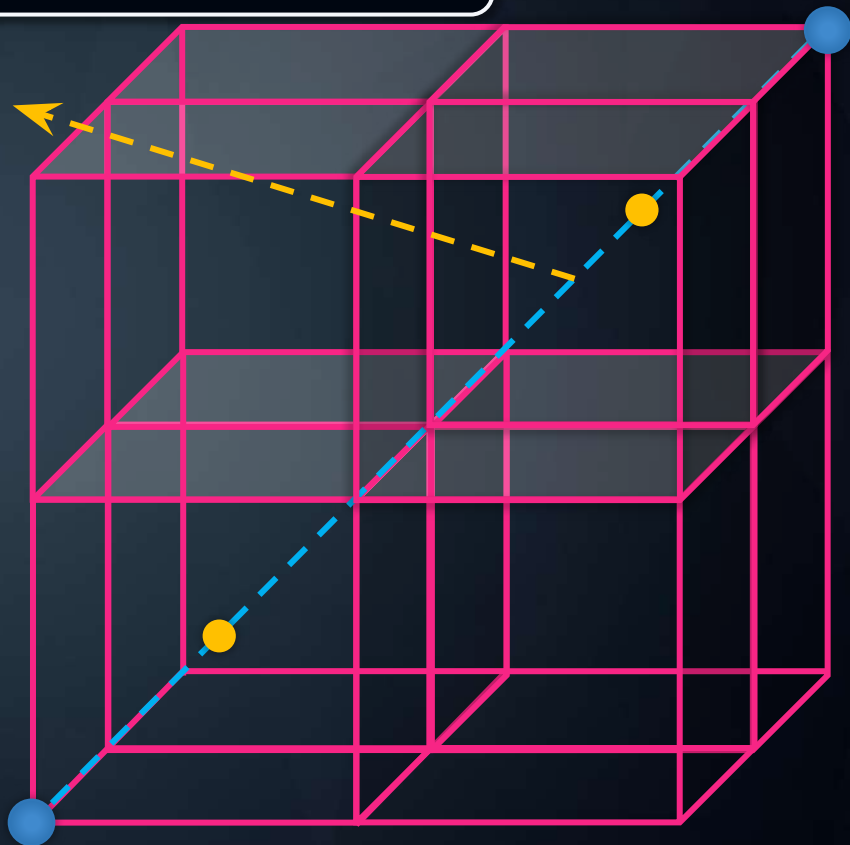
Tetrahedral Voids in FCC Unit Cell

Each tetrahedral void is present on the **body diagonal** of the FCC unit cell.

Each FCC unit cell has **4** body diagonals.

Each body diagonal contains **2** tetrahedral voids.

Body diagonal



Number of Tetrahedral Voids in FCC



Each tetrahedral void contributes **fully** to the unit cell and is **not shared** with other unit cells.



Total tetrahedral voids = **8**

For FCC unit cell

$$Z = 4$$

$$\text{T.V.} = 8$$

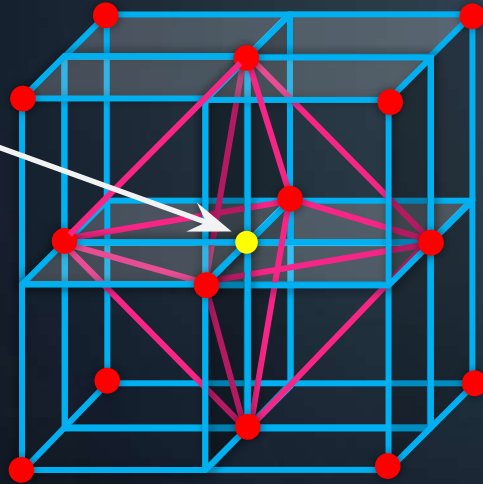
So,

$$\text{T.V.} = 2 \times Z$$

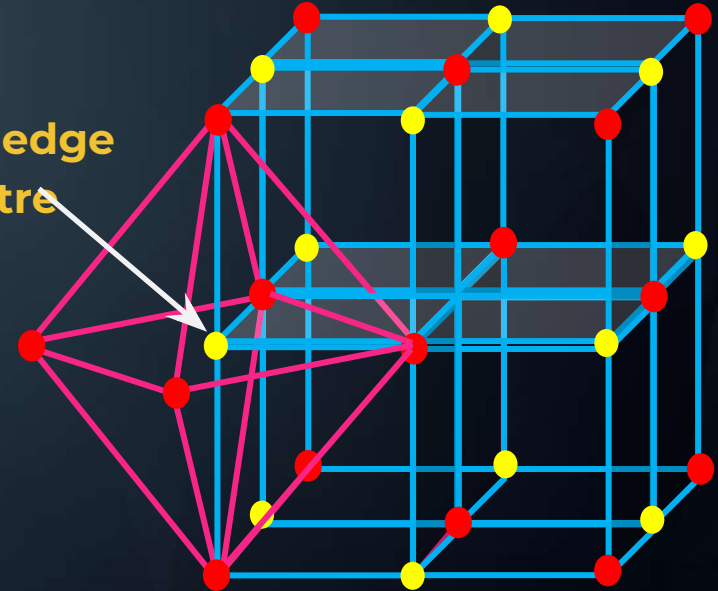
Octahedral Voids in FCC

Present at each **edge centre** and at the **body centre** of the FCC unit cell

O.V. at **body centre**



O.V. at **edge centre**



Number of Octahedral Voids in FCC or CCP

Number of octahedral
voids per unit cell

=

1

+

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

Void at body
centre

Void at edge
centre

=

4

Note

In general, in **close-packed structures** (HCP and FCC)

Number of **O.V.** = **Z**

Number of **T.V.** = **2 Z**

Z

Effective number of particles in one unit cell



Number of Voids in HCP

Tetrahedral Voids

Effective number
of particles per
unit cell (Z)

=

6

Number of
tetrahedral voids

=

$2Z$

Number of
tetrahedral voids

=

2×6
= **12**

Octahedral Voids

Effective number
of particles per
unit cell (Z)

=

6

Number of
octahedral voids

=

Z

Number of
octahedral voids

=

6



Remember

Unit cell	Z	Tetrahedral void ($2Z$)	Octahedral void (Z)
FCC	4	8	4
HCP	6	12	6

Ionic Compounds



Larger ions
(Generally anion)

Form the lattice



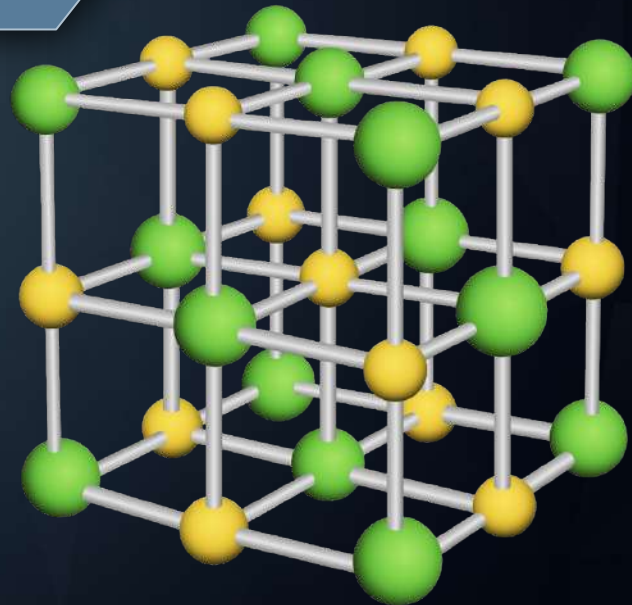
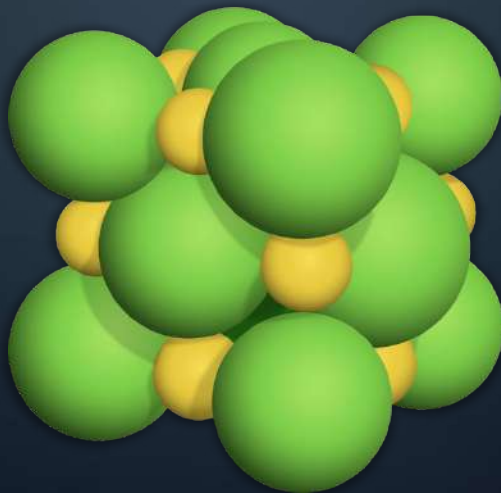
Smaller ions
(Generally cation)

Occupy the voids
such as T.V., O.V., etc.

Rock Salt (NaCl)

Cl^- forms a cubical closed-packing (CCP).

Na^+ ions occupy all the **octahedral voids**.





Rock Salt (NaCl)

Formula of unit cell: Na_4Cl_4

Effective number of Cl^- ions per unit cell

=

4

Formula of ionic compound

=

NaCl

Effective number of Na^+ ions per unit cell

=

4

Effective number of **formula units (Z)**

=

4

Rock Salt (NaCl)

Coordination number
of **cations**

=

6

Coordination number
of **anions**

=

6

Example: MgO, CaO, SrO,
BaO, and all alkali halides,
except CsCl, CsBr and CsI

Zinc Blende (ZnS)

Experimental
ratio,

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

=

0.3

0.225

≤

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

<

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

=

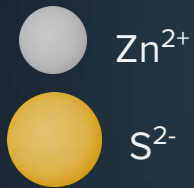
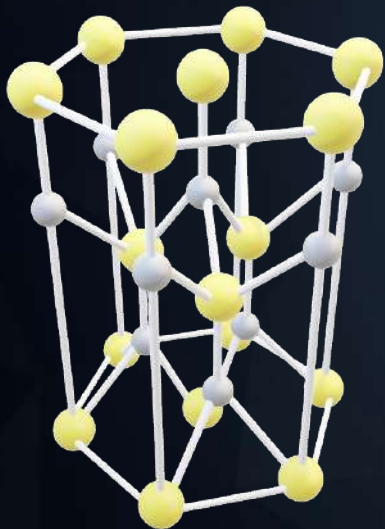
$$\frac{a}{\sqrt{2}}$$

Number of nearest
anions

=

12

Zinc Blende (ZnS)



S^{2-} ions form the
hcp lattice

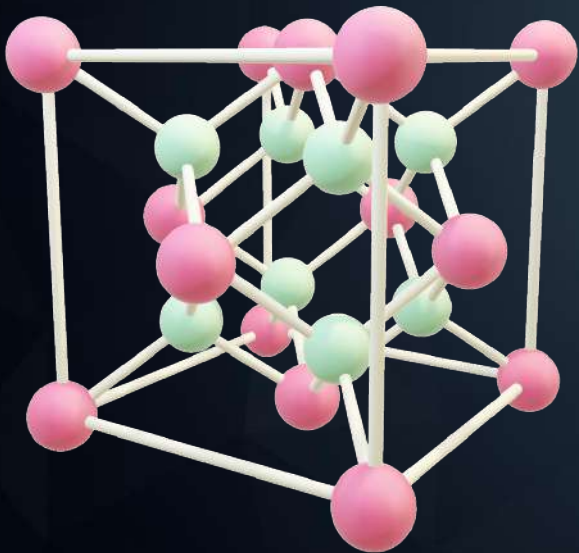
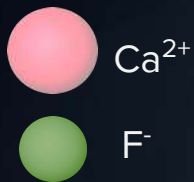
Number of S^{2-} ions = 6

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

Number of S^{2-} ions = 6

As total
tetrahedral
voids = 12

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

Other examples of
fluorite structure

BaF_2 , BaCl_2 , SrF_2 ,
 SrCl_2 etc.

So,

General
formula

=

AB_2

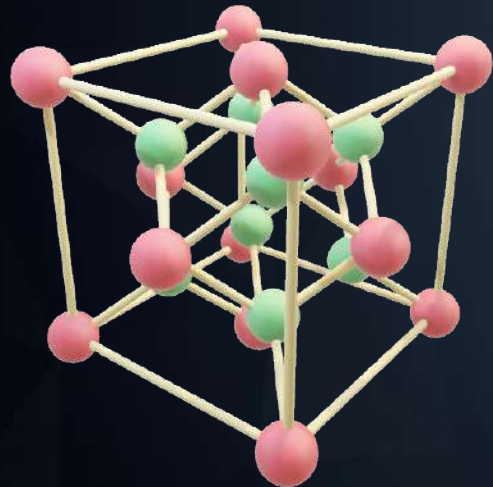
Fluorite Structure (CaF_2)

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

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

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

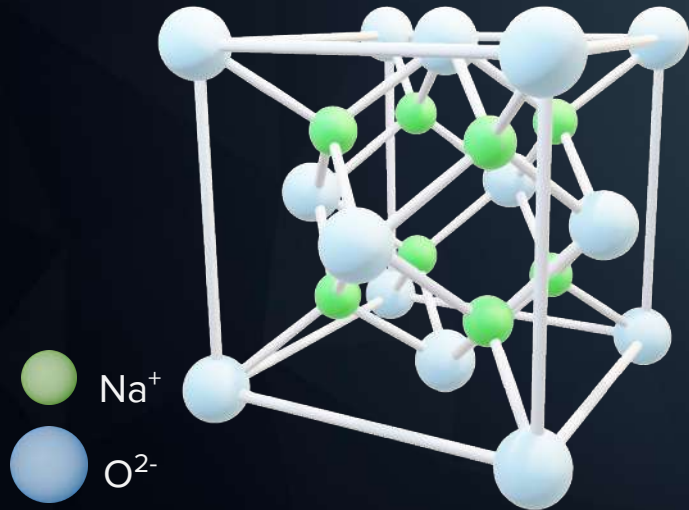
O^{2-} ions form the
FCC lattice

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

Examples

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

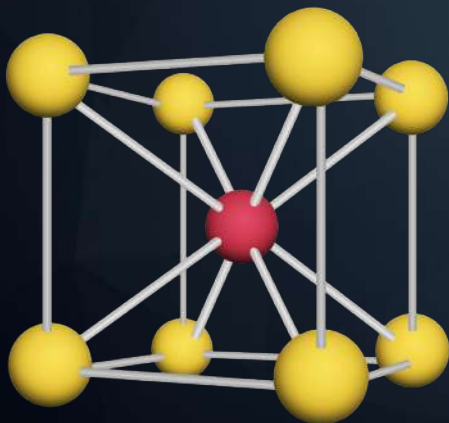
So,

General
formula

=

A_2B

Caesium Chloride (CsCl)



Cl^- ions form simple cubic lattice

Number of Cl^- ions per unit cell = 1

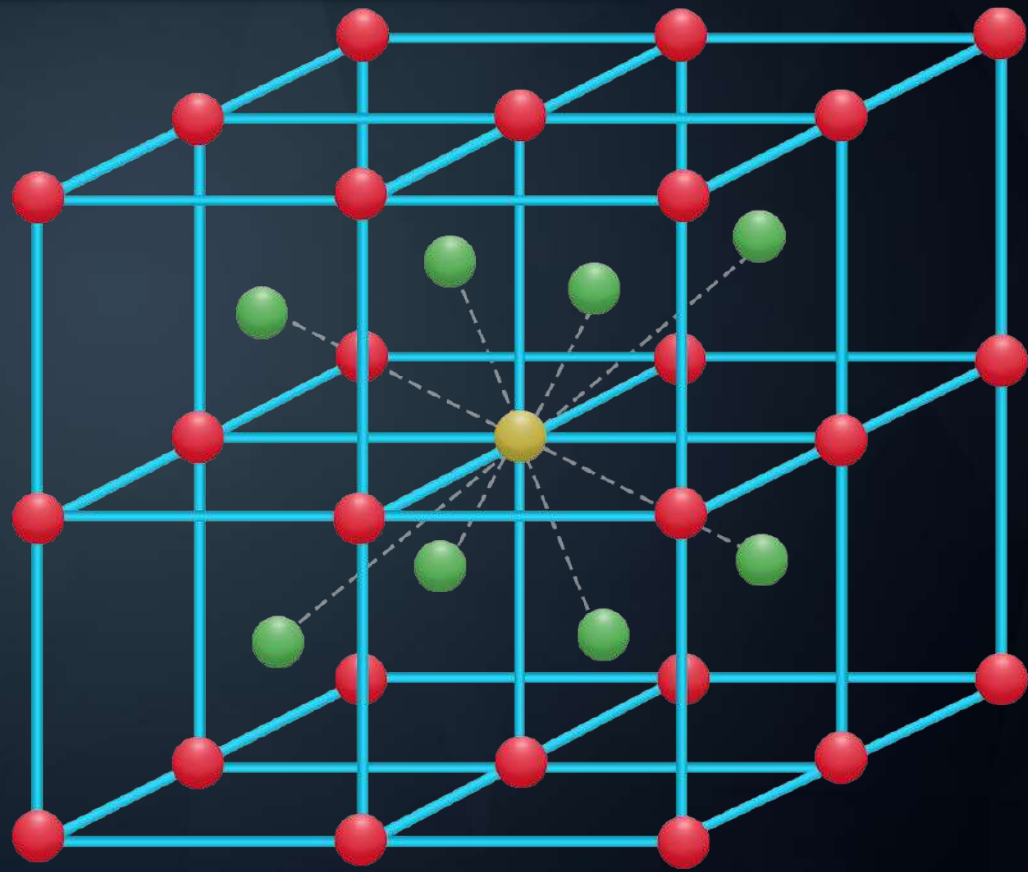
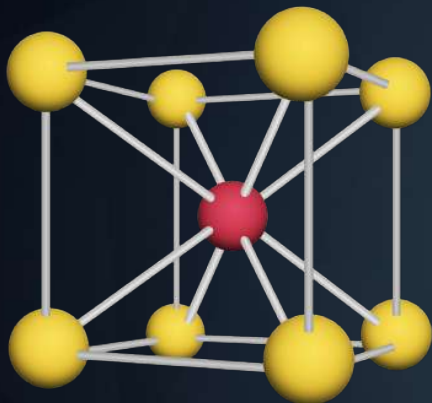
Cs^+ ions occupy cubical void

Number of Cs^+ ions = 1

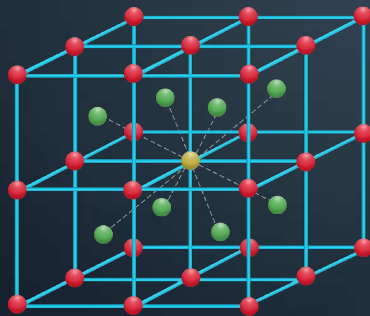
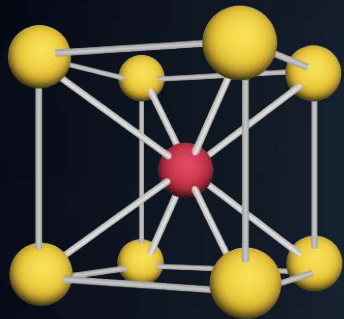
As total cubical void = 1

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,

$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}}$$

\approx

0.93

Other examples of
CsCl like structures

$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}}$$

$>$

0.732

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

Defects

Although crystalline solids have **short-range as well as long-range order** in the arrangement of their constituent particles, crystals are **not perfect**.

Usually, a solid consists of an aggregate of a large number of **small crystals**.



These small crystals have **defects** in them because crystallisation process occurs at a **fast or moderate** rate.

Defects

Single crystals are formed when the process of crystallisation occurs at an **extremely slow rate**.

Even these crystals are **not free from defects**.

The defects are basically **irregularities** in the arrangement of the constituent particles.

Defects in Crystals

In a **perfect crystal**, all atoms would be on their **correct lattice positions** in the structure.

A perfect crystal can exist only at the **absolute zero of temperature**, 0 K. **Above** 0 K, **defects** occur in the structure.

Imperfections can be because of:

1 **Conditions** under which crystals have been developed.

2 **Impurities**

3 **Temperature** (because of thermal conductivity some atoms/ions can get displaced).

Point Defects

Defects will only be **at** certain **lattice positions**.

Point defects
in ionic solids

Stoichiometric defects

Non-stoichiometric
defects

Impurity defects

Stoichiometric Defects

The **formula** of a compound remains **unchanged** despite the presence of these defects.

Also known as **thermodynamic** or **intrinsic defects**.

Point defects
in ionic solids

Stoichiometric
defects

Schottky

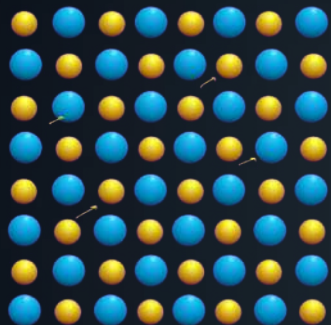
Frenkel

Non-stoichiometric
defects

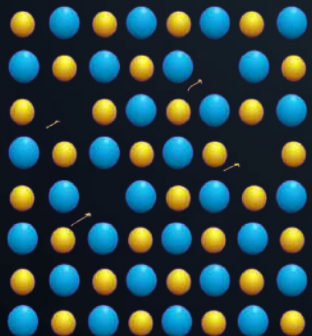
Impurity defects

Schottky Defect

Perfect
Crystal



Schottky
Defect



Schottky defect consists of **ion vacancy** in a crystal lattice, but the **stoichiometry** of the compound (and thus, electrical neutrality) is **retained**.

Characteristics

In **NaCl**, there is approximately **one Schottky defect per 10^{16} ions** at room temperature.

(i)

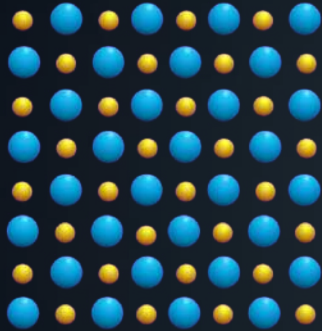
Shown by **ionic substances** in which the cation and anion are of almost **similar sizes**.
E.g.: NaCl, KCl, AgBr, and CsCl

(ii)

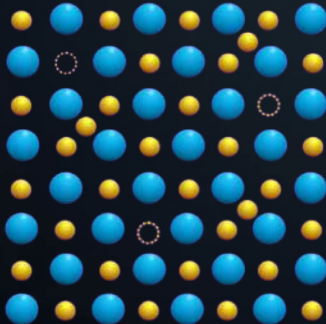
Schottky defect **decreases the density** of the substance.

Frenkel Defect

Perfect
Crystal



Frenkel
Defect



When ions are **displaced from normal lattice positions** and are present in some interstitial voids, it is known as Frenkel defect.

Frenkel defect is also known as **dislocation defect**.

Characteristics

(i)

Shown by **ionic solids** having **large difference** in size between the positive & negative ions.

E.g: ZnS, AgCl, AgBr, & AgI

(ii)

Density of a solid **does not change.**

Effect of Schottky & Frenkel Defect on Properties of Crystal

(i)

Stability of crystal

Defects ↑

Repulsions between
like-charged ions ↑

Stability ↓

(ii)

Electrical conductivity

Defects ↑

Mobility of ions
in the crystal ↑

Electrical
conductivity ↑

Non-Stoichiometric Defects

Point defects
in ionic solids

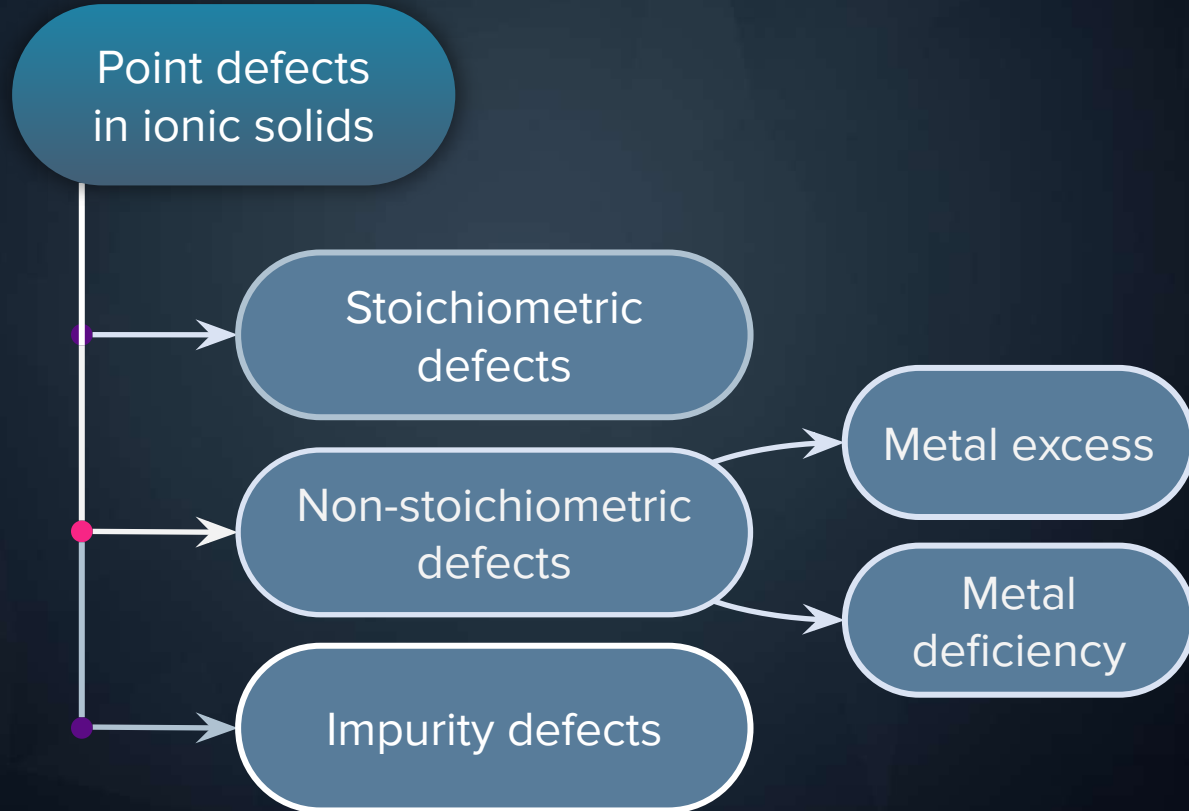
Stoichiometric defects

Non-stoichiometric
defects

Impurity defects

The formula
of compound
gets **modified**
because of the
presence of
these defects.

Non-Stoichiometric Defects



Metal Excess Defect

Instead of anion, electron
occupies the lattice site of **anion**.

Example:
NaCl and **KCl** show such defects

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 the Na atoms to give NaCl



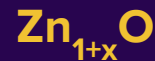
This happens due to **loss of electron** by Na atoms to form Na^+ ions.

The **released electrons** diffuse into the crystal and **occupy anionic sites.**



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

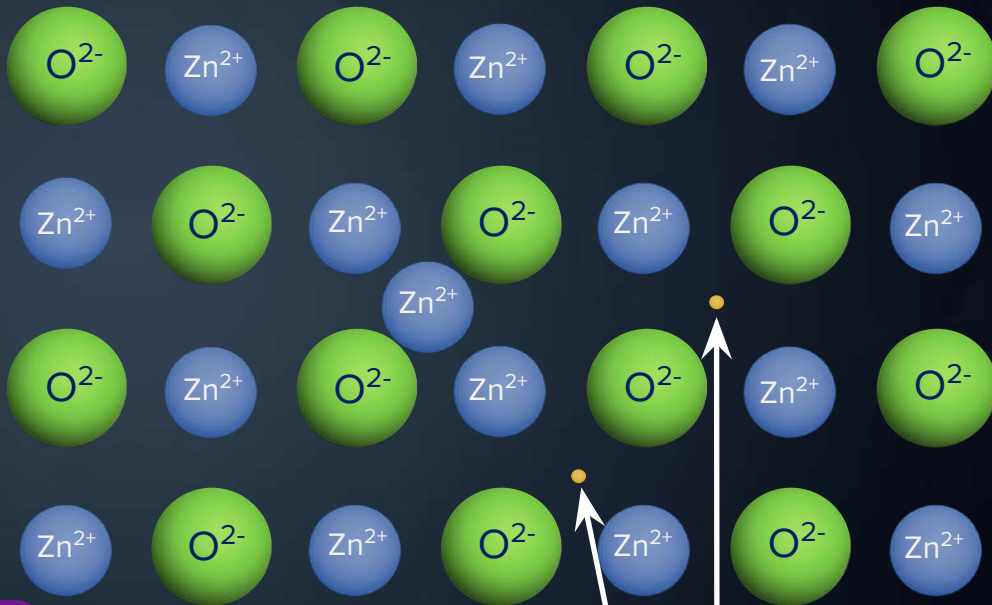
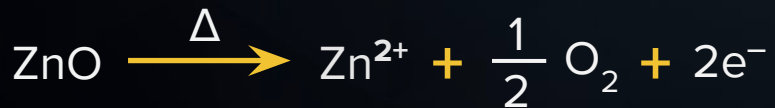
Metal Excess Defect



Zinc oxide is white in colour at room temperature.



On heating, it loses some O^{2-} ions in the form of O_2 and turns yellow.



electrons



Metal Excess Defect

The **electrical property**
and **colour** of a solid
gets modified.

The substance becomes
paramagnetic

E.g.: Crystal of NaCl is **yellow**, KCl
is **violet** or **lilac**, and LiCl is **pink**.



Metal Deficiency Defect

Example,

If a **positive charge is absent** from its lattice site, the charge can be balanced by an **adjacent metal ion** with an extra positive charge.

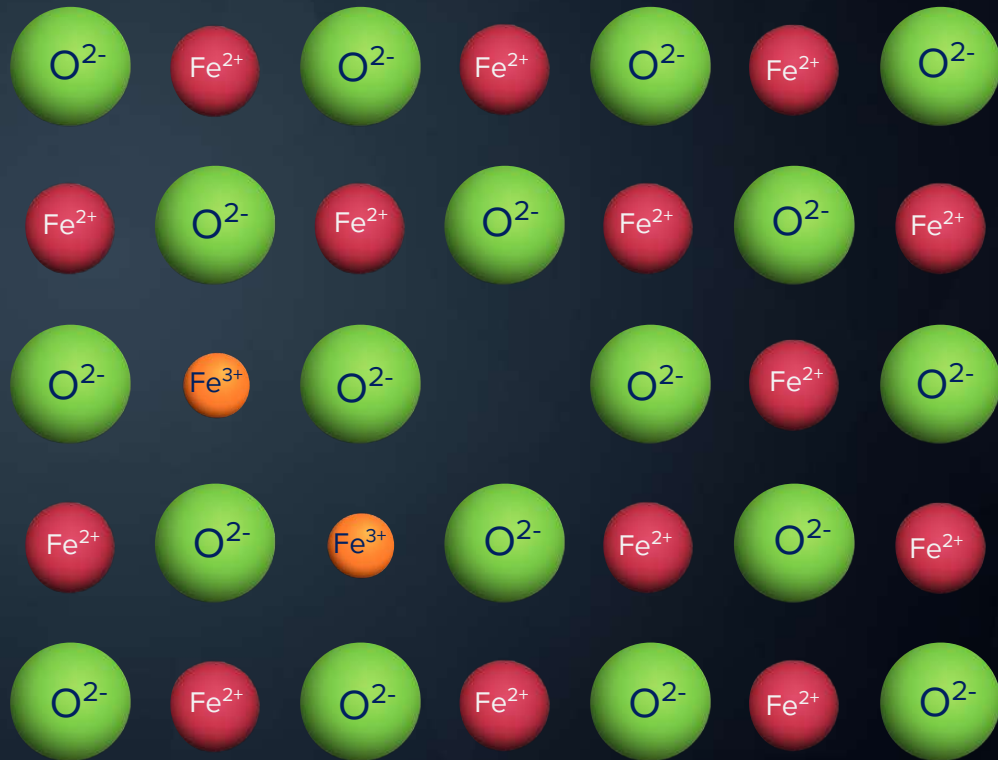
FeO is mostly found with a composition of **Fe_{0.93}O** to **Fe_{0.96}O**.



Loss of some Fe²⁺ ions is compensated by the presence of the required number of Fe³⁺ ions.

Metal Deficiency Defect

FeO



Impurity Defects

Point defects
in ionic solids

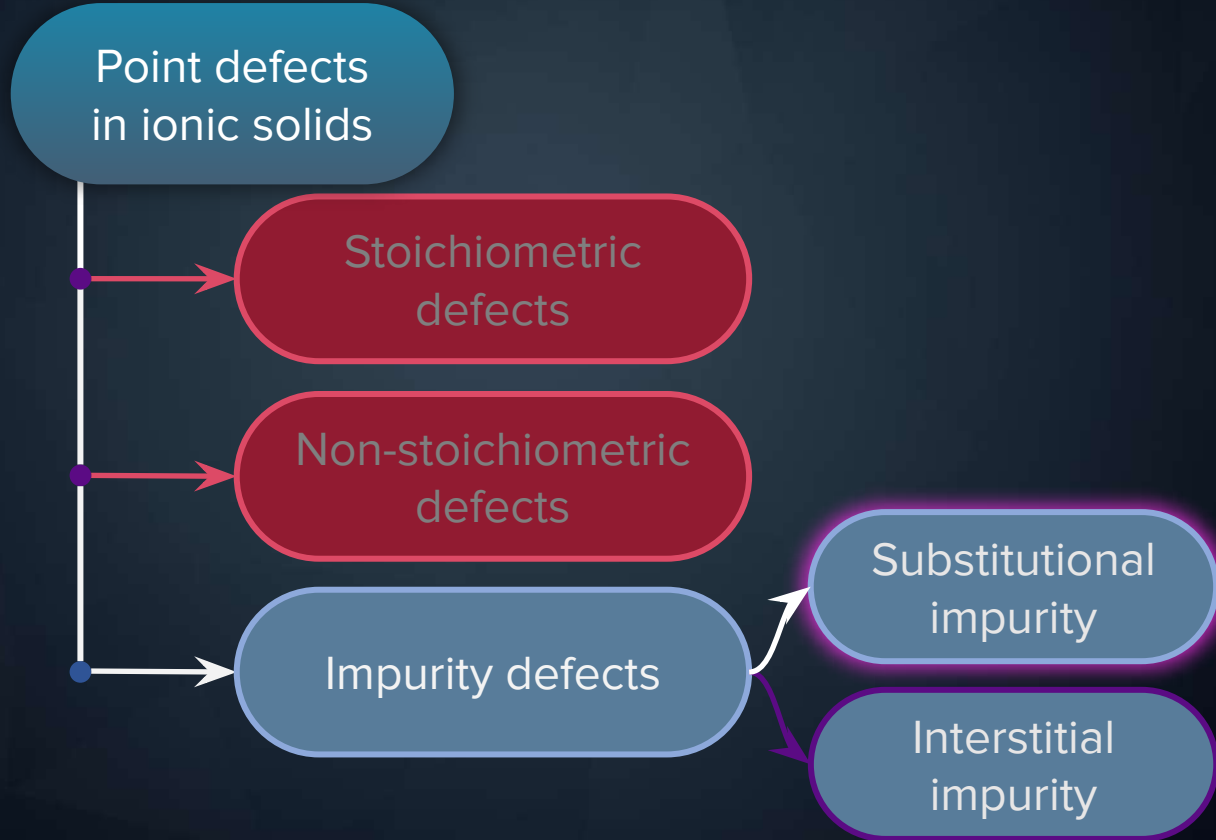
Stoichiometric
defects

Non-stoichiometric
defects

Impurity defects

Substitutional
impurity

Interstitial
impurity





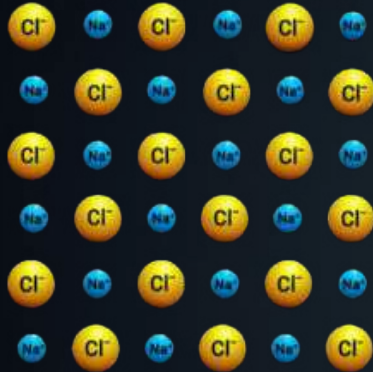
Substitutional Impurity Defects

Defects in ionic crystals, can be introduced by **adding impurities**.

Similar sized cation **substitute** the existing cation of ionic crystal.

Substitutional Impurity Defects

Perfect
Crystal



For example:

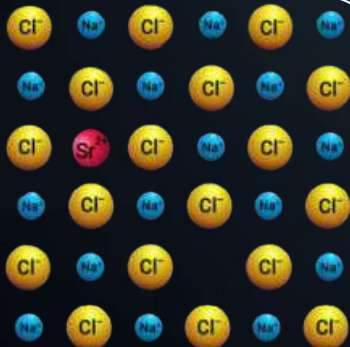
When molten **NaCl** is crystallised having a small amount of **SrCl₂**



Some **Na⁺** ions' locations are occupied by **Sr²⁺** ions



Impurity
Defect



Each **Sr²⁺** replaces **two Na⁺** sites by occupying a site of one Na⁺ and other site remaining vacant.

Substitutional Impurity Defects

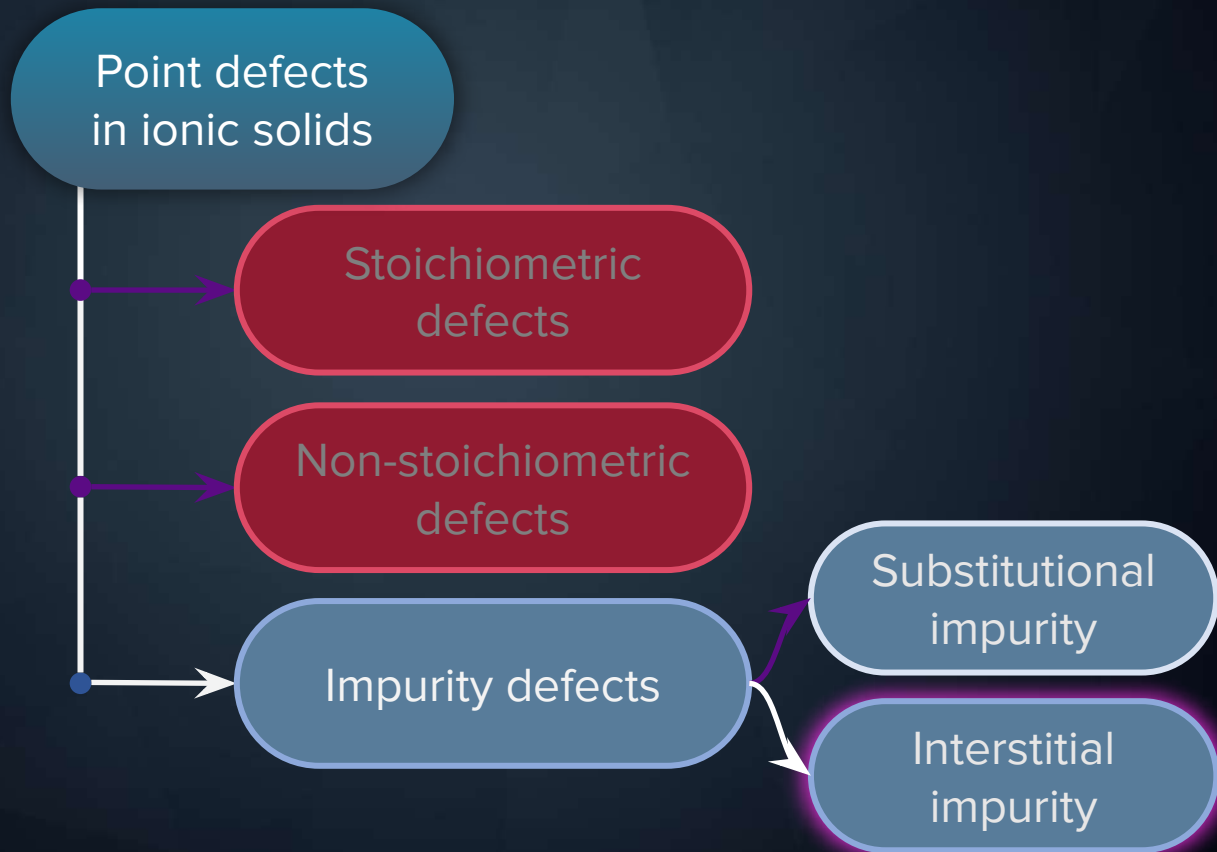
Number of cationic
vacancies generated

=

Number of Sr^{2+}
in the crystal

Other example:
solid solution of
 CdCl_2 and AgCl .

Impurity Defects



Interstitial Impurity Defect

When some **small foreign atoms** (like B, C, N, H) are **trapped** in interstitial voids of the lattice without any chemical reaction.

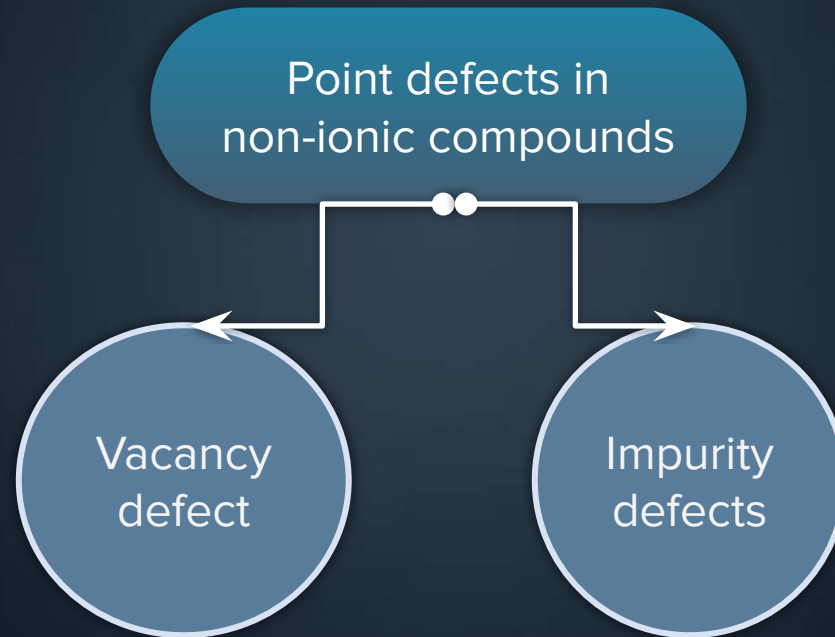
Formula remains the **same**.

d_{exp}

>

$d_{\text{theoretical}}$

Point defects in non-ionic compounds

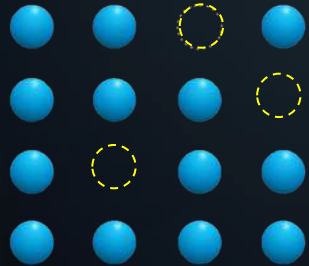


Vacancy Defect

**Perfect
Crystal**



**Vacancy
Defect**



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

Density of crystal **decreases**.

Interstitial Defect

**Perfect
Crystal**



**Interstitial
Defect**



Arises when some small **foreign atoms** (like B, C, N, H) are trapped in interstitial voids of the lattice without any chemical reaction.

Density of crystal **increases**.

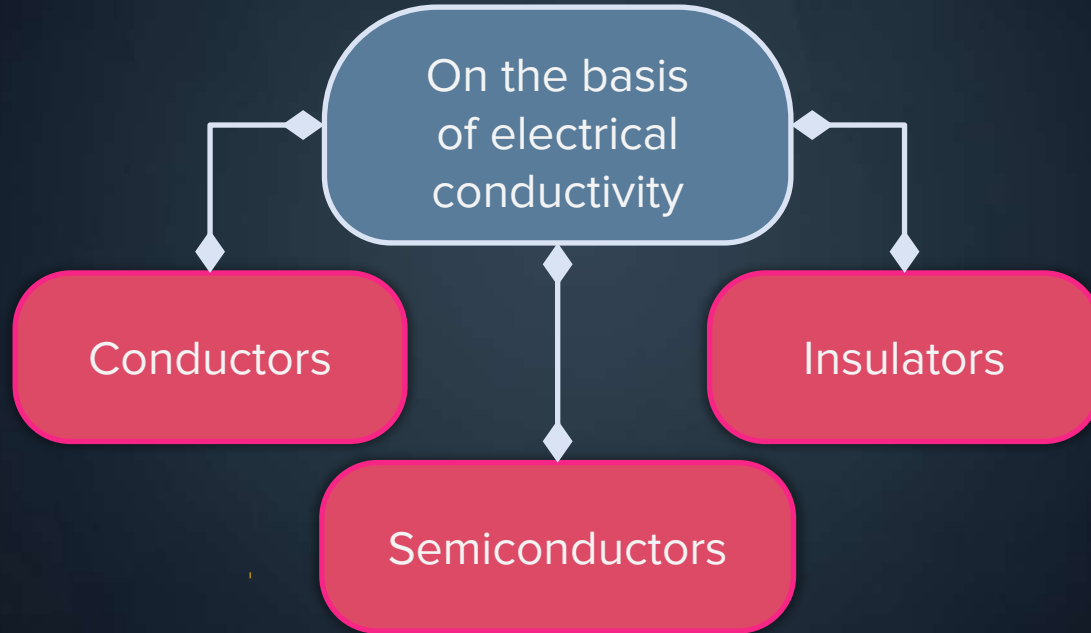


Electrical Properties of Solids

Solids exhibit an amazing range of **electrical conductivities**.

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

Classification of Solids

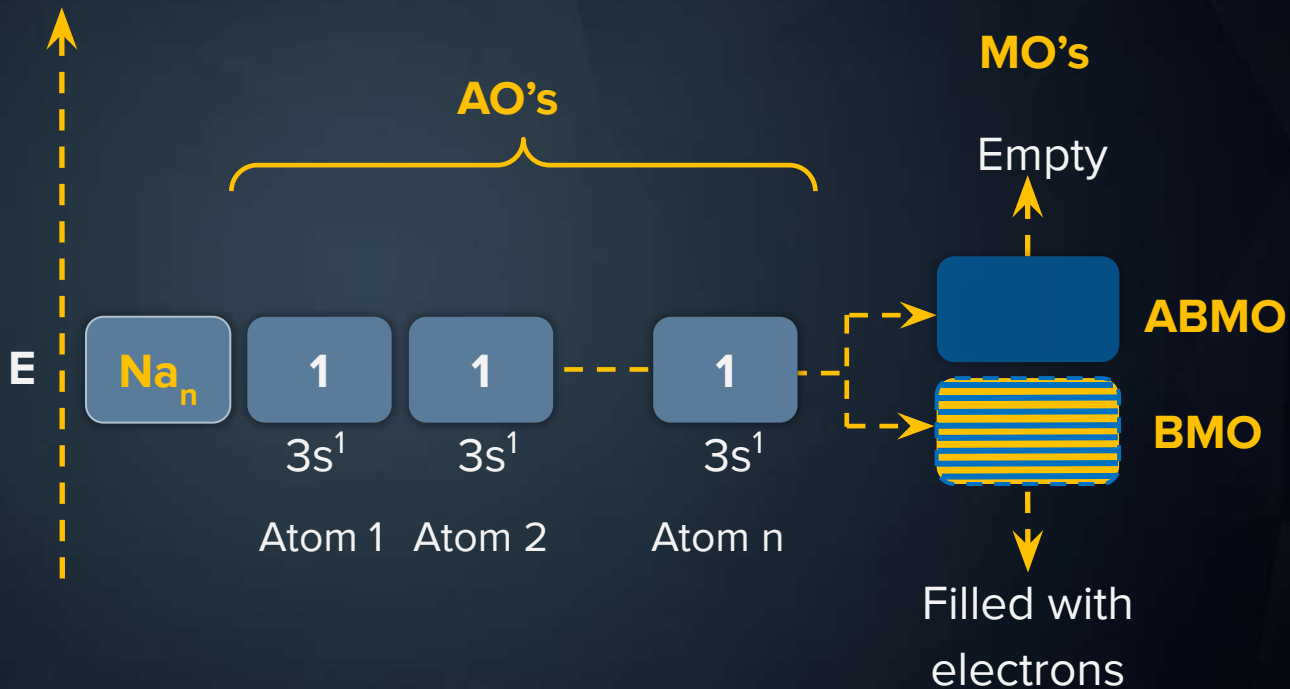


Electrical Properties of Solids

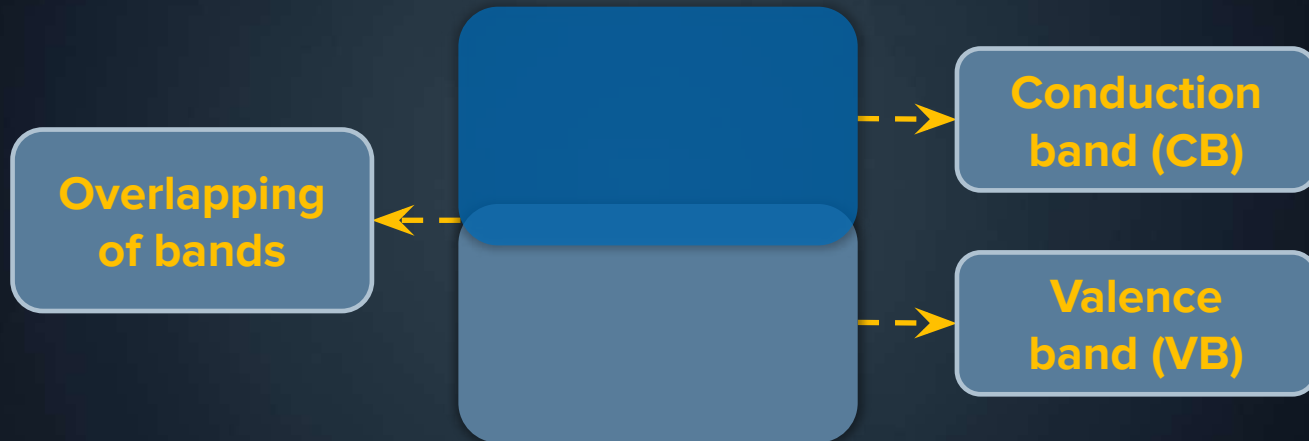
Type of solid	Conductivity range (ohm ⁻¹ m ⁻¹)	Examples
Conductor	10^4 to 10^7	Metal
Semiconductor	10^{-6} to 10^4	Germanium (Ge), Silicon (Si) etc.
Insulator	10^{-20} to 10^{-10}	MnO, CoO; NiO, CuO

Band Theory

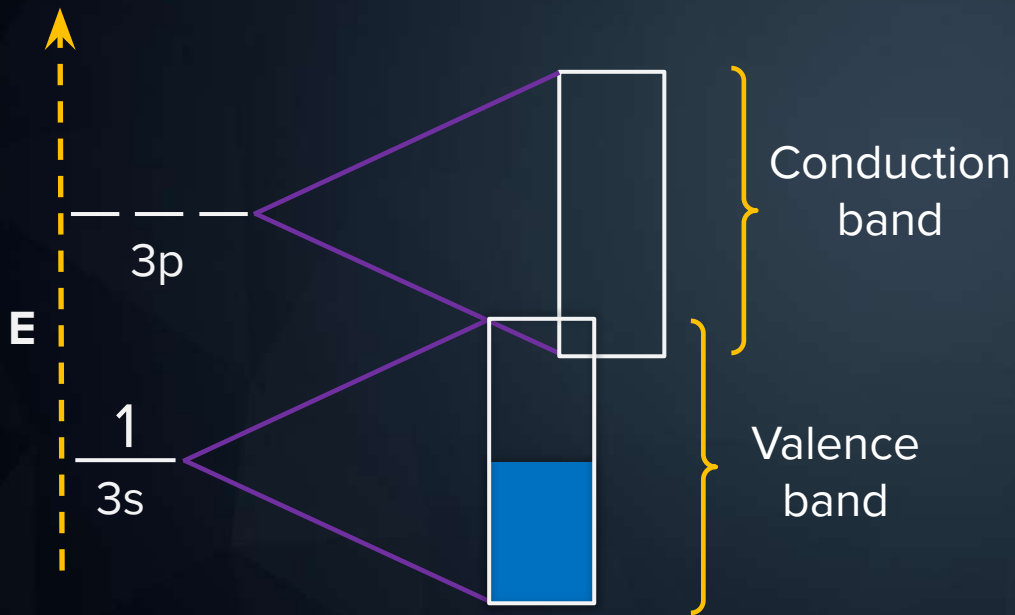
**Overlap of
atomic orbitals**
in solids
gives rise to
**bands
of energy
levels.**



Overlapping of Bands



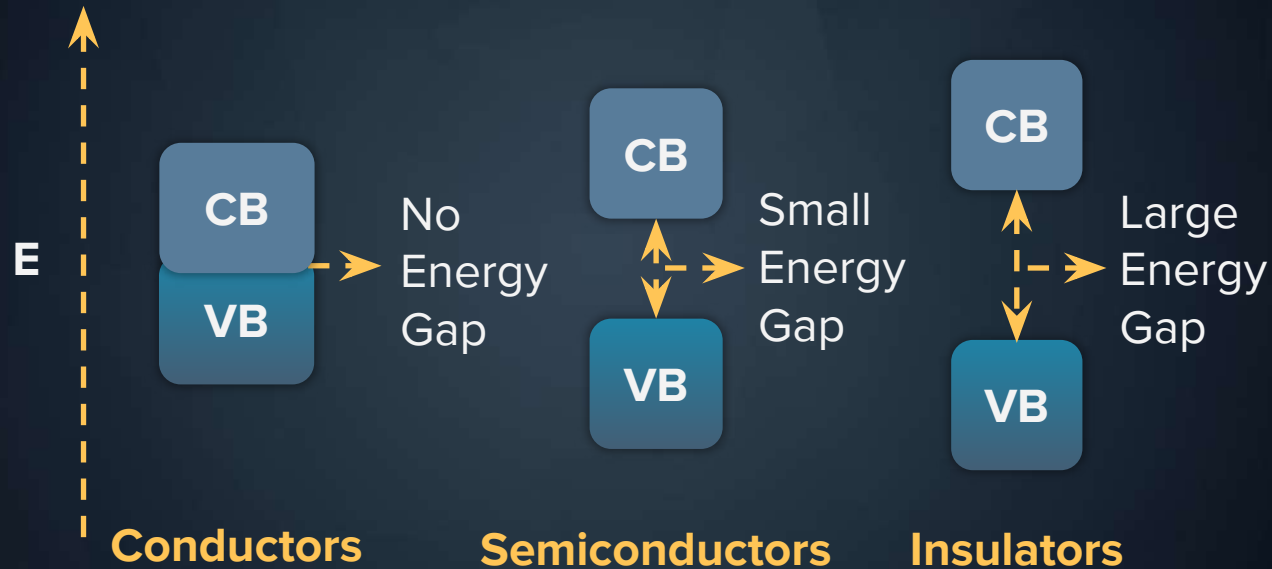
Band of Orbital in Crystal of Sodium



Band Gap

Energy difference
between the valence
band and the
conduction band

Electrical Conductivity



Metals

Temperature ↑



Thermal vibrations
of the nuclei produce
electrical **resistance**



Electrical
conductivity ↓

Semiconductors

Temperature ↑

Electrical
conductivity ↑

On heating

**Electron easily
jumps** from
VB to CB



Magnetic Properties

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



Each electron in an atom behaves like a tiny magnet.

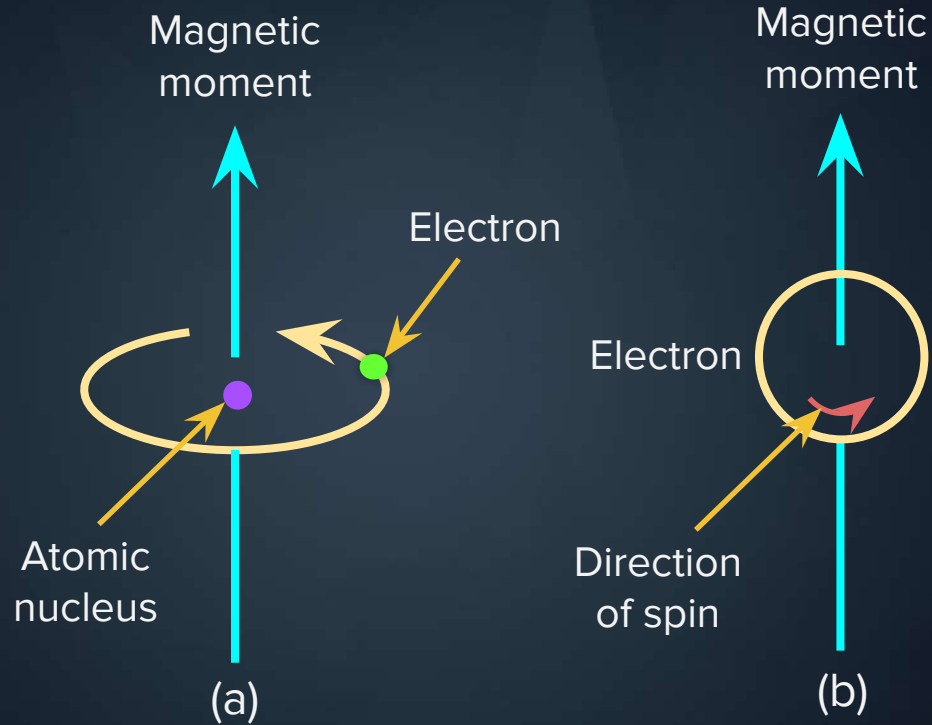
Magnetic moment of an electron originates from **two types of motion**.

(1)

Its **orbital** motion around the nucleus.

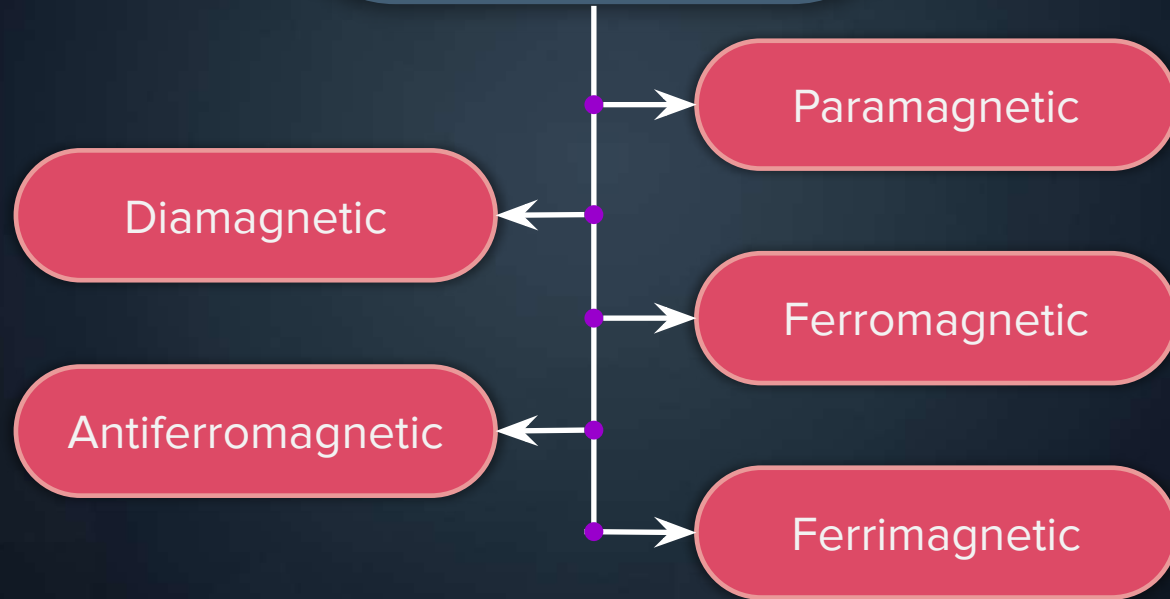
(2)

Its **spin** around its own axis.



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

On the basis of their
magnetic properties,
substances are





Paramagnetic Substances

Substances that are **attracted by the external magnetic field**



Atoms, ions or molecules containing **unpaired electron** show this property.

Examples

O₂, Cu²⁺, Fe³⁺ etc. These substances **lost their magnetism** in the **absence** of magnetic field.



Diamagnetic Substances

Substances that are
repelled by magnetic field



They **do not** have **unpaired electrons**.

Examples

Cu^+ , 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.

In an unmagnetised piece of a ferromagnetic substance, the 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 effect** is produced.

Ferromagnetic Substances

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

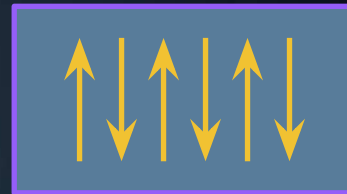


Examples

Fe, Ni, Co, and CrO_2

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.

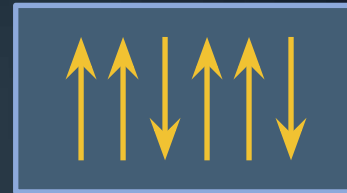


Example

MnO

Ferromagnetic Substances

Substances in which the magnetic moments of the domains are aligned in **parallel & anti-parallel** directions in **unequal numbers**.



They are **weakly attracted** by magnetic field 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.