# MIND MAP

## Solid States

### Types of Solid

### Crystalline Solid

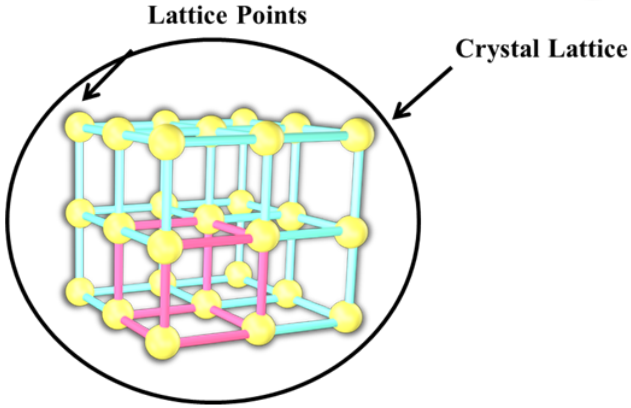
These are the solids having regular arrangement of constituent particles throughout the solid.

### Amorphous Solid

These are the solids which do not have regular arrangement of particles or have regular arrangement only in small distances.

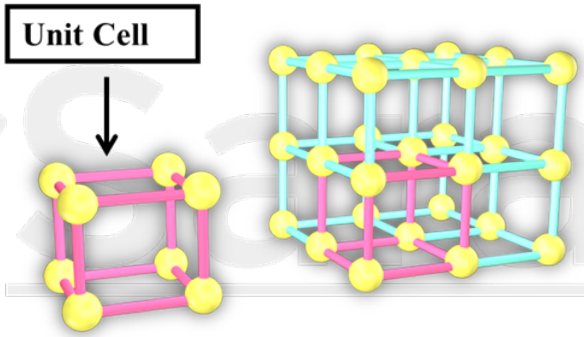
### Crystal Lattice

The diagrammatic representation of the three dimensional crystal, in which each constituent particle is represented by a point, is called a crystal lattice.




### Unit Cell

The smallest possible portion or part of the crystal lattice which repeats itself in different directions of the lattice is called the Unit Cell.




### Primitive Unit Cells

The unit cell in which the constituent particles are located only on the corner of the lattice is called Primitive Unit Cell.

### Face Centred Unit Cells

The unit cell which contains constituent particles on each face of the unit cell and other constituent particles on the corners is called the Face Centred Unit Cell.

### End Centred Unit Cells

In an End Centred Unit Cell, one constituent particle is present at the centre of opposite faces besides the ones located on the corners.

### Body Centred Unit Cells

The unit cell which contains one constituent particle at its body centre and other constituent particles are located on the corners is called Body Centred Unit Cells.

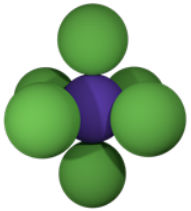
# MIND MAP

## Solid States

| Crystal System | Possible Variations | Axial Distance or Edge lengths | Axial angles | Examples |
|---|---|---|---|---|
| Cubic or Regular | Primitive, Body-centered Face centered | $a = b = c$ | $\alpha = \beta = \gamma = 90°$ | NaCl, Zinc blende, Cu Diamond, Alums |
| Tetragonal | Primitive, Body-centered | $a = b \neq c$ | $\alpha = \beta = \gamma = 90°$ | White tin, $SnO_2$, $TiO_2$, $CaSO_4$ |
| Orthorhombic or Rhombic | Primitive, Body-centered, Face-centered, End-centred | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90°$ | Rhombic sulfur, $KNO_3$, $BaSO_4$ |
| Hexagonal | Primitive | $a = b \neq c$ | $\alpha = \beta = 90°, \gamma = 120°$ | Graphite, ZnO, CdS, Ice |
| Rhombohedral or Trigonal | Primitive | $a = b = c$ | $\alpha = \beta = \gamma \neq 90°$ | Calcite ($CaCO_3$), Magnesite ($MgCO_3$), HgS (Cinnabar), Quartz, $NaNO_3$ |
| Monoclinic | Primitive, End-centred | $a \neq b \neq c$ | $\alpha = \gamma = 90°, \beta \neq 90°$ | Monoclinic sulfur, $Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$ |
| Triclinic | Primitive | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90°$ | $K_2Cr_2O_7, H_3BO_3$, $CuSO_4 \cdot 5H_2O$ |

### Coordination Number

The number of nearest particles around a specific particle in a given crystalline substance is called coordination number of that crystalline substance.



Packing efficiency is defined as the ratio of volume occupied by the particles to the total volume of the crystalline substance.

$$\text{P. E.} = \frac{\text{Volume occupied by particles present in a crystal}}{\text{Volume of crystal}}$$

$$\text{P. E.} = \frac{\text{Volume occupied by particles present in Unit cell}}{\text{Volume of Unit cell}}$$

### Analysis of Cubic Crystal

Number of Corners

Number of Faces

Number of Edges

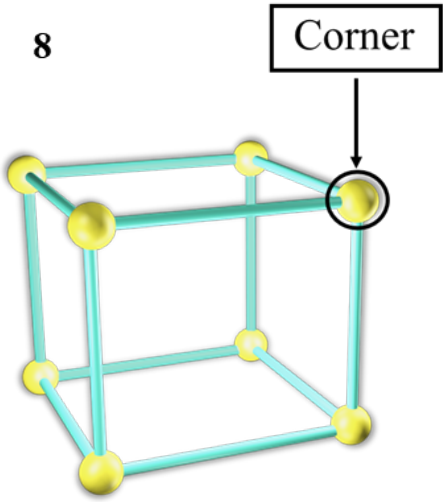
# MIND MAP

## Solid States

### Analysis of Cubic Crystal

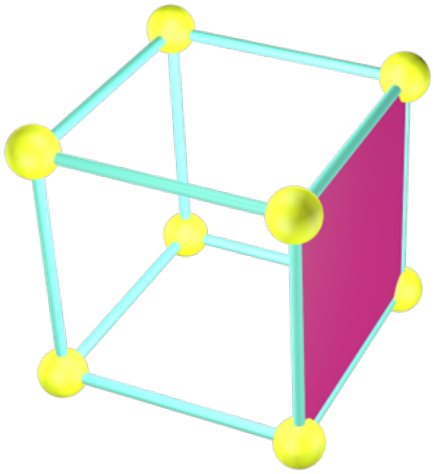
**1. Number of Corners**

8



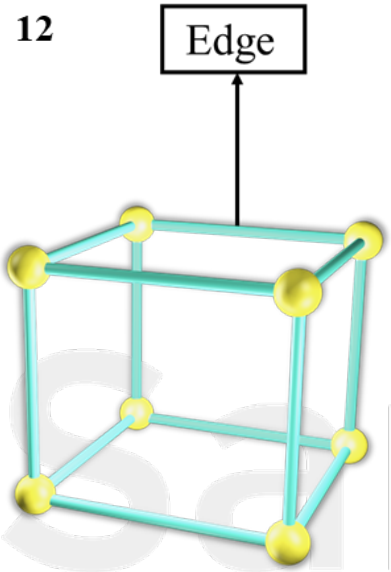

**2. Number of Faces**

6



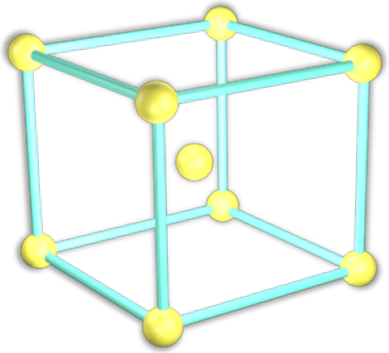
**3. Number of Edges**

12



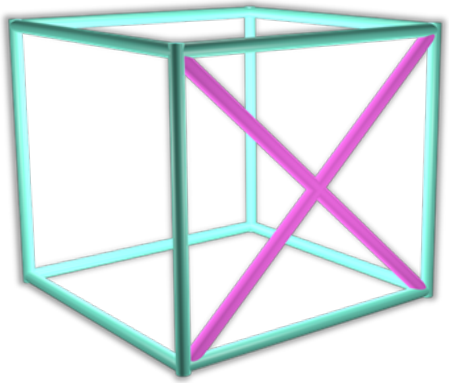

**4. Number of Cube Centre**

1



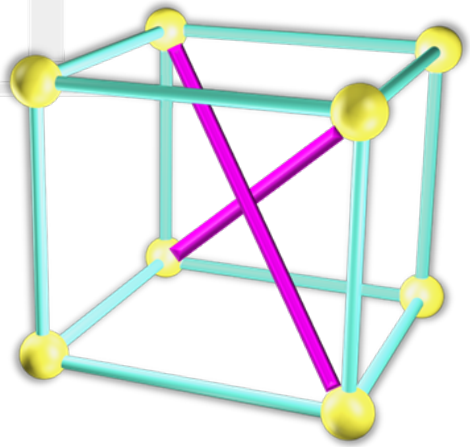
**5. Number of Face Diagonal**

12



**6. Number of Body Diagonal**

4



## Close Packing of Identical Solid Spheres

For solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours.

Although there are many ways to arrange the particles but the one in which maximum available space is occupied will be best suited which is known as Close Packing.

### The packing can be categorised as

1. Close Packing In One Dimension
2. Close Packing In Two Dimension
3. Close Packing In Three Dimension

### Close Packing In One Dimension

Each sphere is touched by other two spheres, hence coordination number of packing is two.

### Close Packing In Two Dimension

Two possible types of dimensional packing are

1. Square Close Packing In Two Dimension
2. Hexagonal Close Packing In Two Dimension

**MIND MAP**

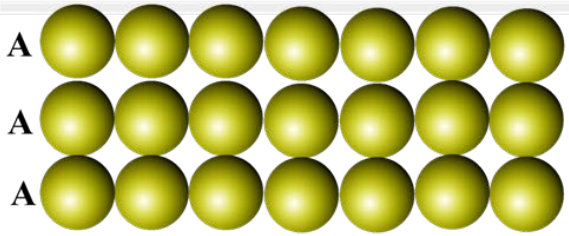
**Solid States**

### (1) Square Close Packing In Two Dimension

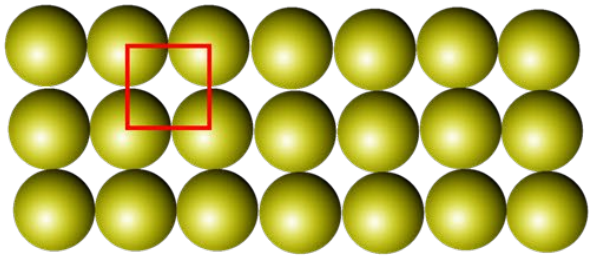
When two rows are placed in such a manner, that spheres of one row are placed immediately below the other, the resulting packing is called Two Dimensional Square Close Packing.

(i) Each sphere is touched by four other, hence coordination number is four.

(ii) Since all the rows are identical, the packing is called AAA ..... type packing.

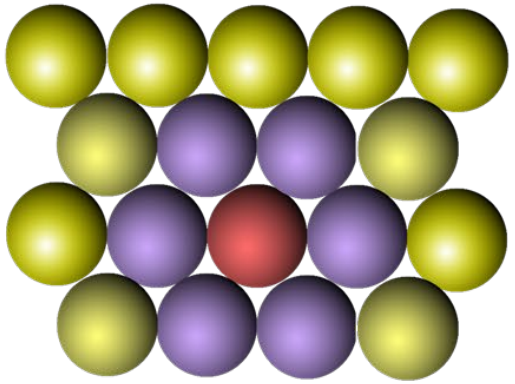



(iii) If centres of spheres are connected, square cells are formed , hence also called two dimensional Square Packing.

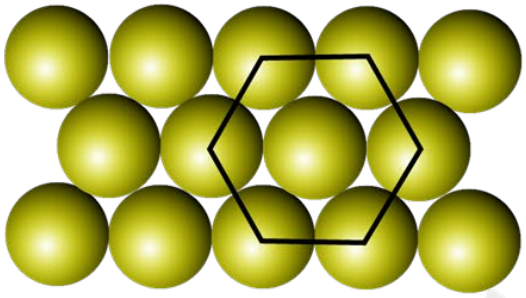


### (2) Hexagonal Close Packing In Two Dimension

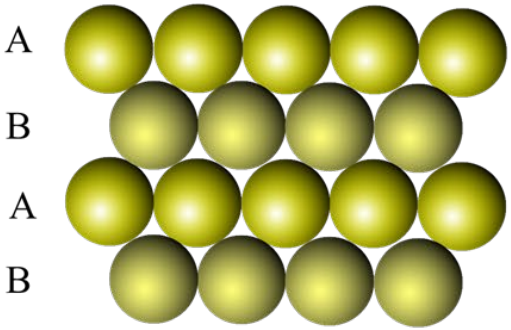
If various one dimensional close pack rows are placed in such a way that spheres of top row fits in depression of bottom row spheres, the resulting packing is called two dimensional hexagonal close packing structure.



(i) Each sphere is touched by six other, hence coordination number is six. If centres are joined, hexagonal unit cells are formed, hence this is called two dimensional hexagonal close packing.

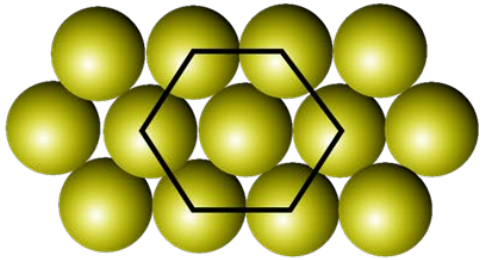


(ii) Every third row sphere comes exactly at top of first row sphere, hence the packing is called ABABAB ..... packing.

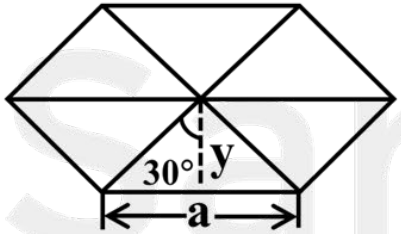



# MIND MAP

## Solid States



Z = 3




$$\tan 30° = \frac{a}{2 \times y}$$

$$\text{So } y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2}a$$

Base Area

$$= 6\left[\frac{1 \times a}{2} \times \frac{\sqrt{3} \times a}{2}\right]$$

$$= \frac{6\sqrt{3}a^2}{4}$$

## Close Packing In Three Dimension

When two dimensional packing structure are arranged one above the other, depending upon type of two dimensional arrangement in a layer and the relative positions of spheres in above or below layer, various types of three dimensional packing results.

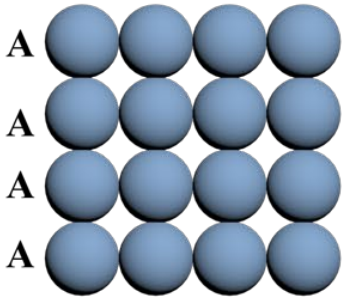
1. Simple Cubic Packing (A A A A .....)
2. Hexagonal Close Packing (AB AB AB .....)
3. Cubic Close Packing or Face Centred Cubic (ABC ABC...)

## Three Dimensional Close Packing From Two Dimensional Square Packing

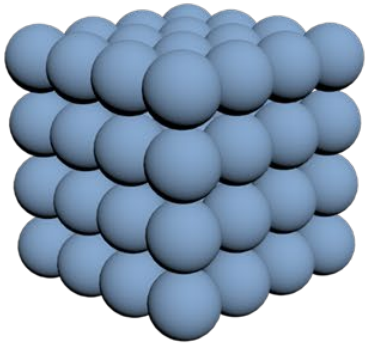
### Simple Cubic Packing In Three Dimension

The two dimensional square close packed layer are placed, in such a manner that spheres in each layer comes immediately on top of below layer.

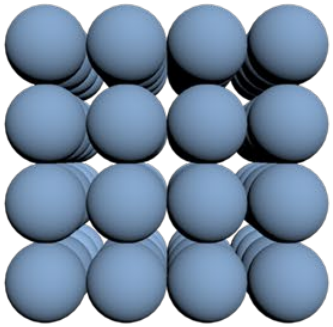
Front View & Top View




Side View



Perspective View



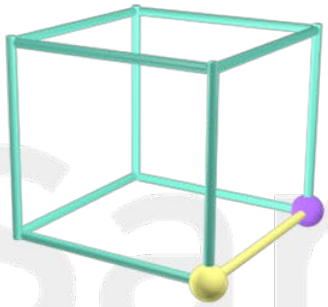
# MIND MAP

## Solid States

(i) In this packing, only 52% of available space is occupied by atoms.

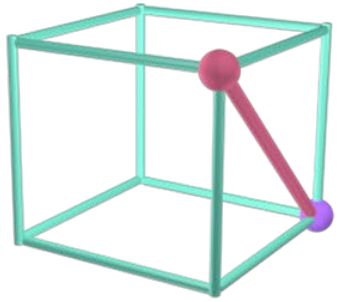
(ii) Coordination number = 6

First neighbour = 6 at a distance = a



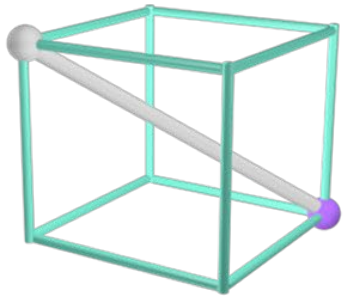
Second neighbour = 12

at distance = $\sqrt{2}a$



Third neighbour = 8

at distance = $\sqrt{3}a$

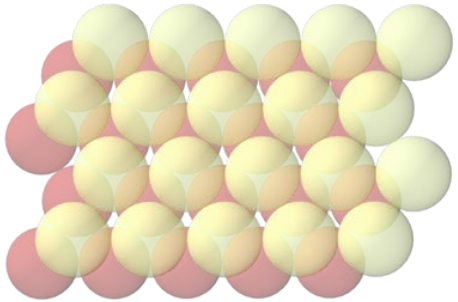


Three Dimensional Close Packing From Two Dimensional Hexagonal Packing

### Hexagonal Close Packing (HCP)

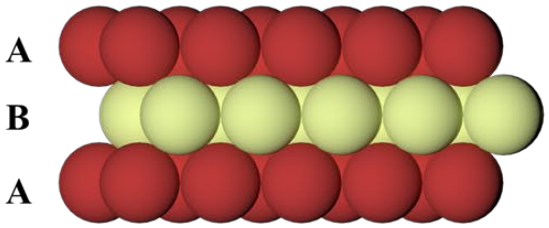
(i) The spheres of the second layer are placed in the depressions of the first layer.

(ii) The spheres of the third layer lie on the spaces of second layer in such a way that they lie directly above those in the first layer.

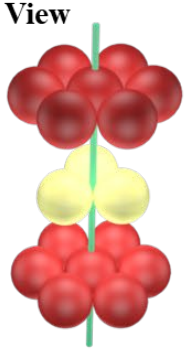


The third layer becomes identical to the first layer.

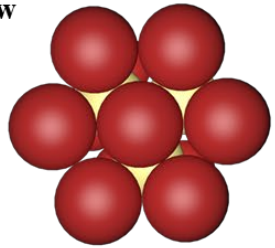
If this arrangement is continued definitely in the same order this is represented as AB AB AB....




Exploded View



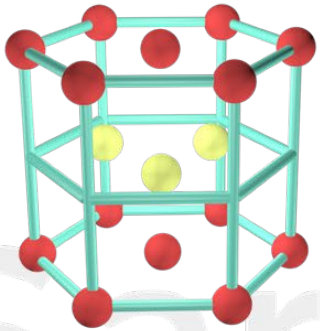
Top View



# MIND MAP

## Solid States

Unit Cell



### Effective no. of atoms (Z)

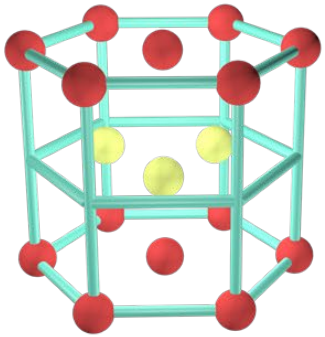
$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6}$$

$$= 3 + 1 + 2$$

$$= 6$$

$$\text{Packing efficiency} = \frac{6 \times \frac{4}{3}\pi \times R^3}{24\sqrt{2} \times R^3}$$

$$= \frac{\pi}{3\sqrt{2}} = 74\%$$



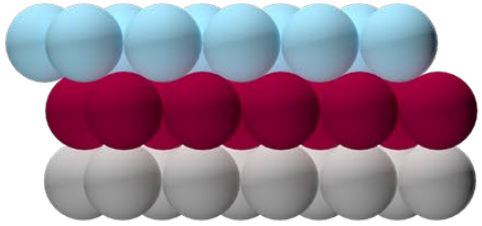
### Cubic Close Packing (FCC)

In second way, the spheres of the third layer lie on the second layer in such a way that they lie over the unoccupied spaces of the second layer.

If this arrangement is continuous in the same order this is represented as ABC ABC ABC ....

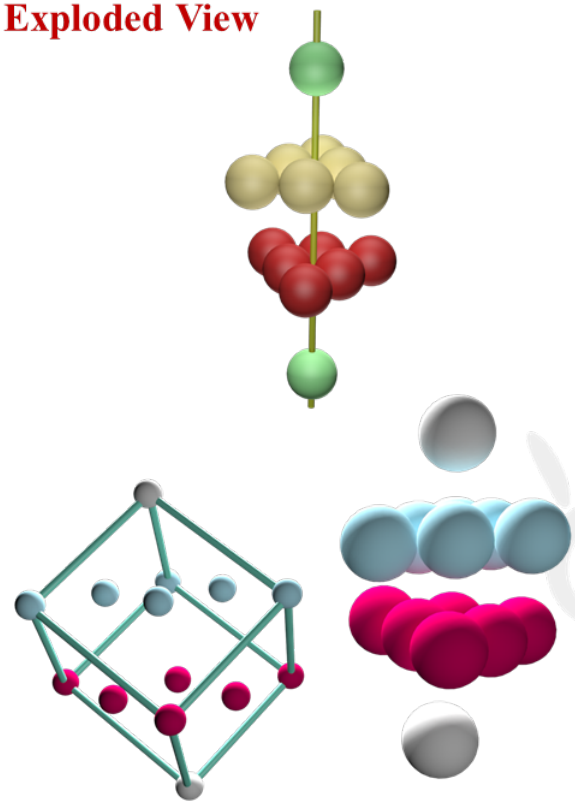
This type of arrangement represents Cubic Close Packed (CCP) structure.

Front View



This structure has 3-fold axes of symmetry which pass through the diagonal of the cube.

## Exploded View



4th layer spheres

3rd layer spheres

2nd layer spheres

1st layer spheres

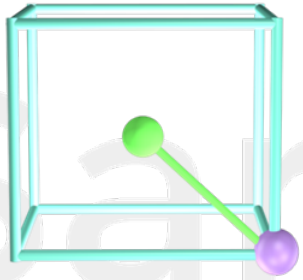
# MIND MAP

## Solid States

The spheres occupy 74% of the total volume and 26% is the empty space in both (hcp and ccp) structures.

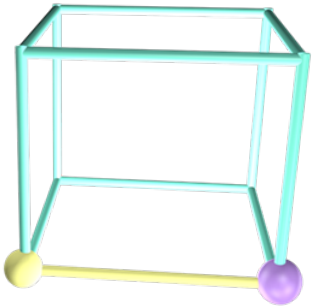
First neighbour = 12

at a distance = $(a/\sqrt{2})$



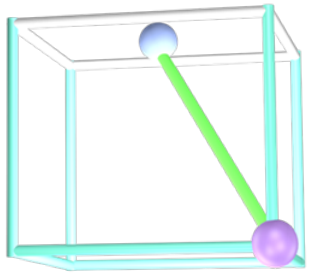
Second neighbour = 6

at distance = $a$



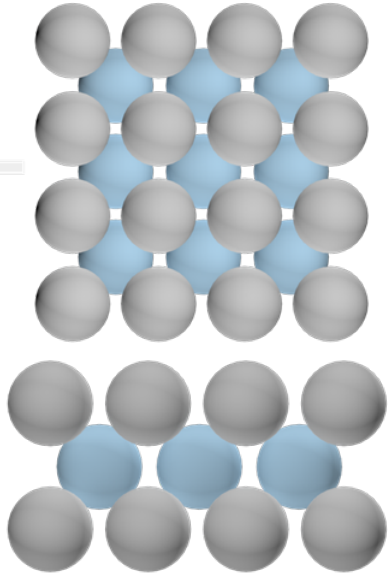
Third neighbour = 24

at distance = $\left(\sqrt{3/2}\, a\right)$



## Body Centred Cubic

There is another possible arrangement of packing of spheres known as Body Centred Cubic (BCC) arrangement.

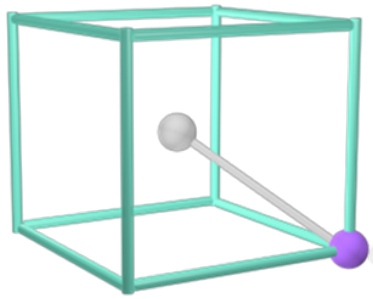


This arrangement is observed in square close packing .

In bcc arrangement the spheres of the second layer lie at the space in the first layer.

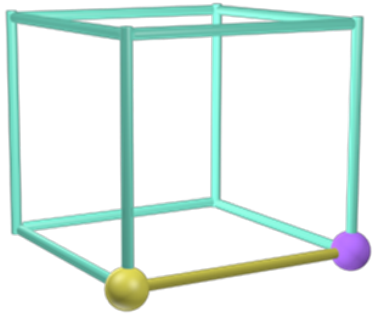
First neighbour = 8

at a distance = $\left(\frac{\sqrt{3}}{2}a\right)$



Second neighbour = 6

at distance = $a$

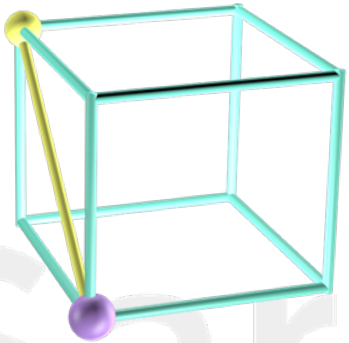


# MIND MAP

## Solid States

Third neighbour = 12

at distance = $(\sqrt{2}a)$



## Interstices or Voids or Holes In Crystals

When particles are closely packed in the crystals even then there is some empty space left in between the spheres. This is known as interstices (interstitial site or hole or empty space or Voids).

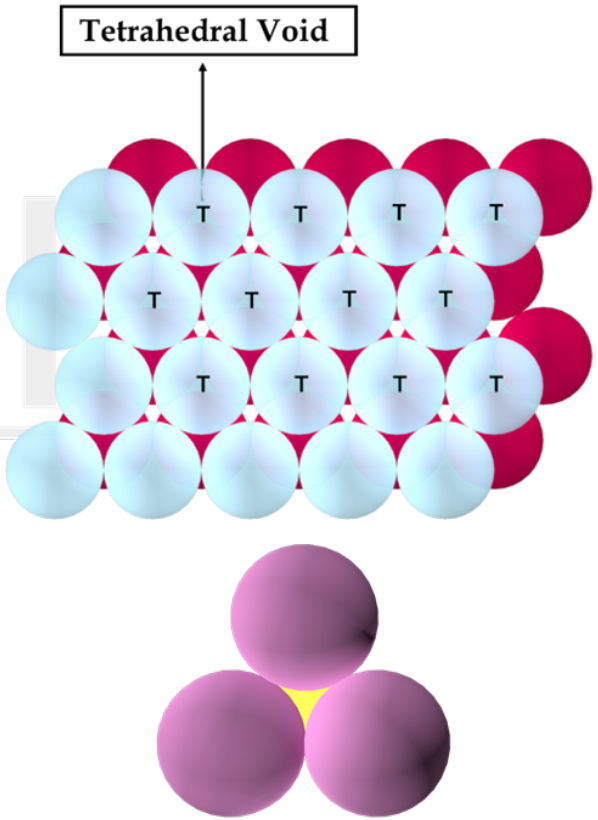
In three dimensional close packing (CCP & HCP), the interstices are of two types -

1. Tetrahedral Voids
2. Octahedral Voids

## Tetrahedral Voids

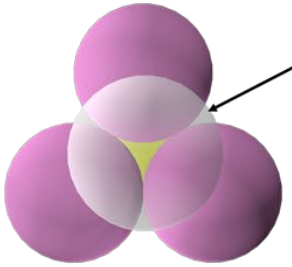
In HCP and CCP each sphere of second layer touches with three spheres of first layer.

They leave a small space in between spheres, which is known as Tetrahedral Site or Interstices.

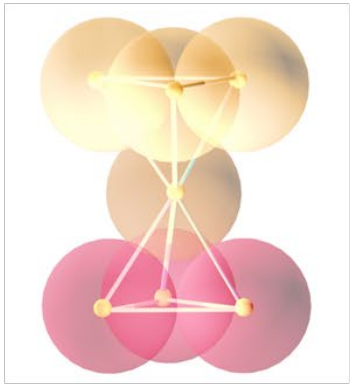


# MIND MAP

## Solid States



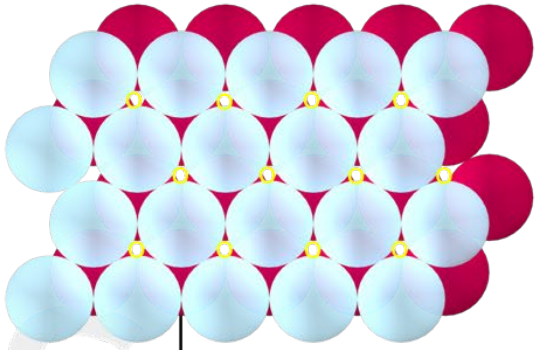

In another words, the vacant space between 4 touching spheres is called as Tetrahedral Void.



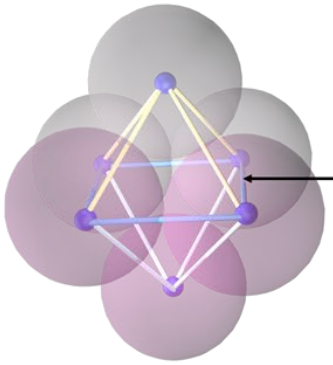
### Octahedral Voids

HCP and CCP also form another type of interstices which is called as Octahedral Site.

In another words, the vacant space between 6 touching spheres is called as Octahedral Void.

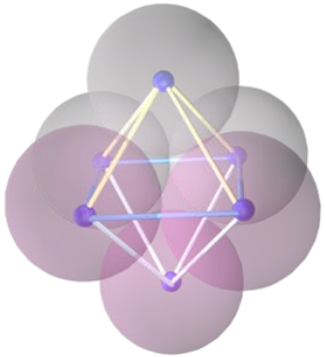


Octahedral Void



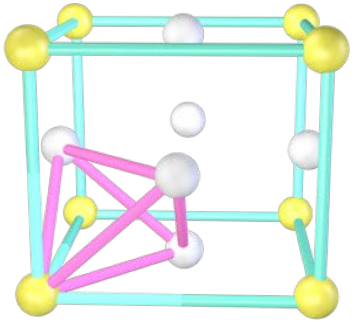
Octahedral geometery

An Octahedral Site does not mean that the hole is Octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged Octahedrally.

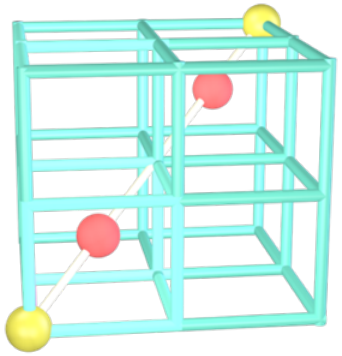


### Positions of Tetrahedral Voids In FCC Unit Cell

In FCC, one corner and its three face centred atom of faces meet at that corner to form a Tetrahedral Void.



In FCC, two Tetrahedral Voids are obtained along one Cube diagonal.

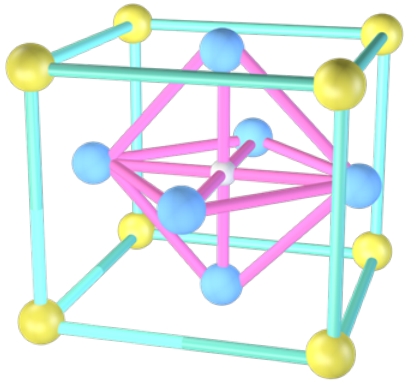


In FCC total number of atoms = 4

In FCC total number of Tetrahedral Voids = 8

## Positions of Octahedral Voids In FCC Unit Cell

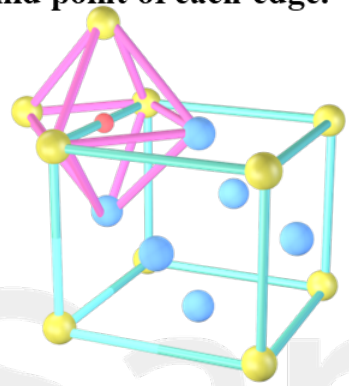
In FCC, 6 face centres form a Octahedral Void at Body Centre.



# MIND MAP

## Solid States

One more position of Octahedral Void is at mid point of each edge.



Each Octahedral Void located at mid point of edge contributes 1/4 to the unit cell.

The Octahedral Void situated at the centre contributes 1.

In FCC, total number of Octahedral Voids are

$(1 \times 1) + (12 \times \frac{1}{4}) = 1 + 3 = 4$

Cube Centre edge

In FCC, number of particles = 4

$\therefore$ Effective number of Octahedral Void per particle = 1

## Tetrahedral And Octahedral Voids In HCP

(i) Number of Tetrahedral Void/unit cell = 12

(ii) Number of OV/unit cell = 6

Note

In any closed packing of maximum efficiency, there are two TV & one OV per particle.

## Packing In Ionic Solid

(i) Normally anions are bigger than cations hence ionic solids are considered as the packing of anions and cations are supposed to occupy the voids.

(ii) Oppositely charged particles should lie closer and similarly charged particles should be away each other.

(iii) Each ion tend to maximise its coordination number (Number of oppositely charged ions around it).

Point (ii) and (iii) contradict each other because on increasing the CN, the repulsion between like charges will also increase.

Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

## Limiting or Ideal Radius Ratio $\left(\frac{r^+}{r^-}\right)$

The minimum $\frac{r^+}{r^-}$ values for the existence of a cation in a particular void is called limiting radius ratio for that void.

| Voids | CN | Limiting $r^+/r^-$ | Range $r^+/r^-$ |
|---|---|---|---|
| Triangular | 3 | 0.155 | 0.155 – 0.225 |
| Tetrahedral | 4 | 0.225 | 0.225 – 0.414 |
| Octahedral | 6 | 0.414 | 0.414 – 0.732 |
| Cubic | 8 | 0.732 | 0.732 – 1 |

## Structure of Ionic Solids

1. Common Salt
   NaCl
2. Zinc Blende
   ZnS
3. Caesium Halide
   CsCl
4. Fluorite
   $CaF_2$
5. Antifluorite
   $Li_2O$
6. Corundum
   $Al_2O_3$
7. Rutile
   $TiO_2$
8. Pervoskite
   $CaTiO_3$
9. Spinel and Inverse Spinel
   $MgAl_2O_4$

# MIND MAP

## Solid States

## Structure of NaCl

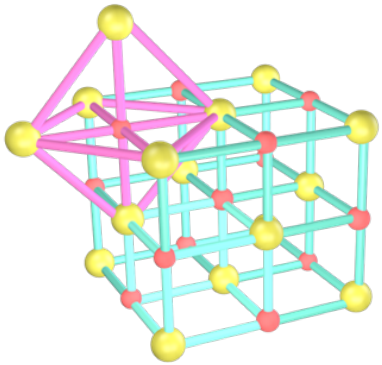
The bigger Cl– forms Cubic Close Packing and small Na+ occupy positions of all Octahedral Voids.

The radius ratio $\frac{r^+}{r^-}$ lie in the range 0.414 – 0.732.

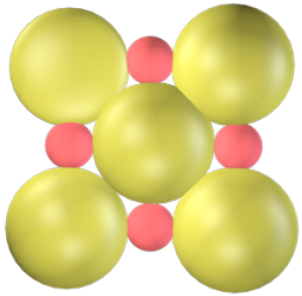
(i) Each $Na^+$ is surrounded by six $Cl^-$ and each $Cl^-$ is surrounded by six Na+ ion. [6:6 coordination]

(ii) No. of $Na^+$ and $Cl^-$ in each unit cell is 4.

(iii) Number of formula units of NaCl per unit cell is equal to 4.



## Structure of a face



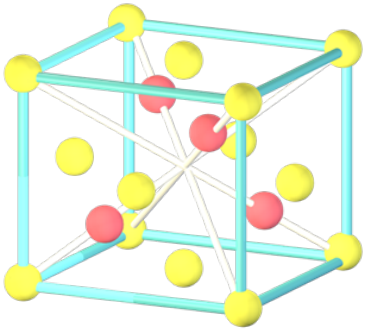
## Zinc blende (Sphalerite) Structure

Larger anions $S^{2-}$ form ccp arrangement and smaller cations $Zn^{2+}$ fill alternate Tetrahedral Voids.

(i) C.N. of $Zn^{2+} = 4$ ; C.N. of $S^{2-} = 4$
[4 : 4 coordination]

(ii) Formula units of ZnS per unit cell = 4.

(iii) $r_{Zn^{2+}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$



## Caesium Halide Structure

$Cl^-$ at the corners of Cube and $Cs^+$ in the center.

(i) C.N. of $Cs^+ = 8$ ;C.N. of $Cl^- = 8$
[8 : 8 coordination]

(ii) Formula units of CsCl per unit cell = 1

(iii) $r_{Cs^+} + rCl^- = \frac{a\sqrt{3}}{2}$

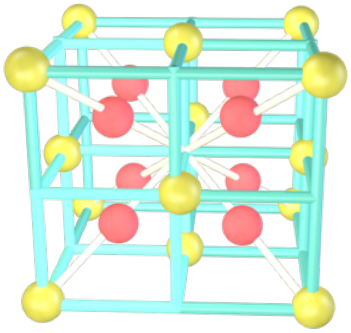
## Fluorite Structure

($CaF_2$) $Ca^{2+}$ forming CCP arrangement and $F^-$ filling all Tetrahedral Voids.

(i) C.N. of $F^- = 4$ ;C.N. of $Ca^{+2} = 8$
[8 : 4 coordination]

(ii) Formula units of $CaF_2$ per unit cell = 4

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



# MIND MAP

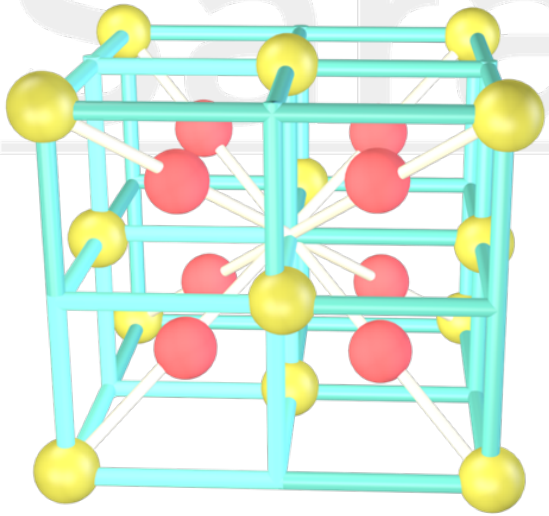
## Solid States

## Antifluorite Structure

($Li_2O$) $O^{2-}$ ion forming CCP and $Li^+$ taking all Tetrahedral Voids.

(i) C.N. of $Li^+ = 4$ C.N. of $O^{2-} = 8$

(ii) Formula units of $Li_2O$ Per unit cell = 4



The crystal is FCC for C atom & alternate tetrahedral voids are also occupied by carbon atoms.

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

$= 8$

CN = 4

$$\frac{\sqrt{3}a}{4} = 2r = d_{C-C}$$