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CHEMISTRY

Target : JEE (Main)

SOLID STATE

SOLID STATE

CONTENTS

JEE(MAIN) SYLLABUS

Classification of solids: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea); Bragg's Law and its applications; Unit cell and lattices, packing in solids (fcc, bcc and hcp lattices), voids, calculations involving unit cell parameters, imperfection in solids; Electrical, magnetic and dielectric properties.

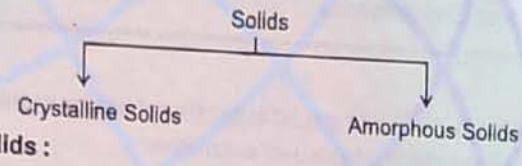
JEE(ADVANCED) SYLLABUS

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

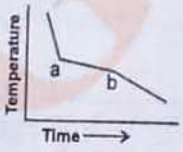
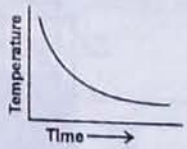
Solid State

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

- **Properties of Solids :**
  - (a) In solid state the particles are not able to move randomly.
  - (b) They have definite shape and volume.
  - (c) Solids have high density.
  - (d) Solids have high and sharp melting point which is depend on the strength or value of binding energy.
  - (e) They are very low compressible.
  - (f) They show very slow diffusion.
- **Types of Solids :**



- **Crystalline solids :**
  - (a) In this type of solids the atoms or molecule are arranged in a regular pattern in the three dimensional network.
  - (b) They have well defined geometrical pattern, sharp melting point, definite heat of fusion and anisotropic nature.
  - (c) Anisotropic means they exhibit different physical properties in all directions. e.g. The electrical and thermal conductivities are different directions.
  - (d) They are generally incompressible.
  - (e) The general examples of crystalline solids are as Quartz, diamond etc.
- **Amorphous Solids :**
  - (a) In this type of solids, the arrangement of building constituents is not regular.
  - (b) They are regarded as super cooled liquids with high viscosity in which the force of attraction holding the molecules together are so great, that the material becomes rigid but there is no regularity in structure.
  - (c) They do not have sharp melting points.
  - (d) They are isotropic as they exhibit same physical properties in all the directions.
  - (e) The general examples of this solids are as glass, Rubber, plastics etc.
- **Difference between crystalline and amorphous solids :**

Property	Crystalline solids	Amorphous solids
1. Shape	They have definite and regular geometrical form.	They do not have definite and regular geometrical form.
2. Melting point	They have definite melting point	They do not have definite melting point.
3. Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion.
4. Compressibility	They are rigid and incompressible.	These may be compressed to any appreciable extent.
5. Cutting with a Sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces. 	They are given irregular cleavage i.e.they break into two pieces with irregular surface. 
6. Isotropy and Anisotropy	They are anisotropic.	They are isotropic.

Solved Examples

Ex.1 A solid X melts slightly above 273K and is a poor conductor of heat and electricity. To which of the following categories does it belong :
(1) Ionic solid (2) Covalent solid (3) Metallic (4) Molecular **Ans. (4)**

Ex.2 In a crystal, the atoms are located at the position of :
(1) Zero P.E. (2) Infinite P.E. (3) Minimum P.E. (4) Maximum P.E. **Ans. (3)**

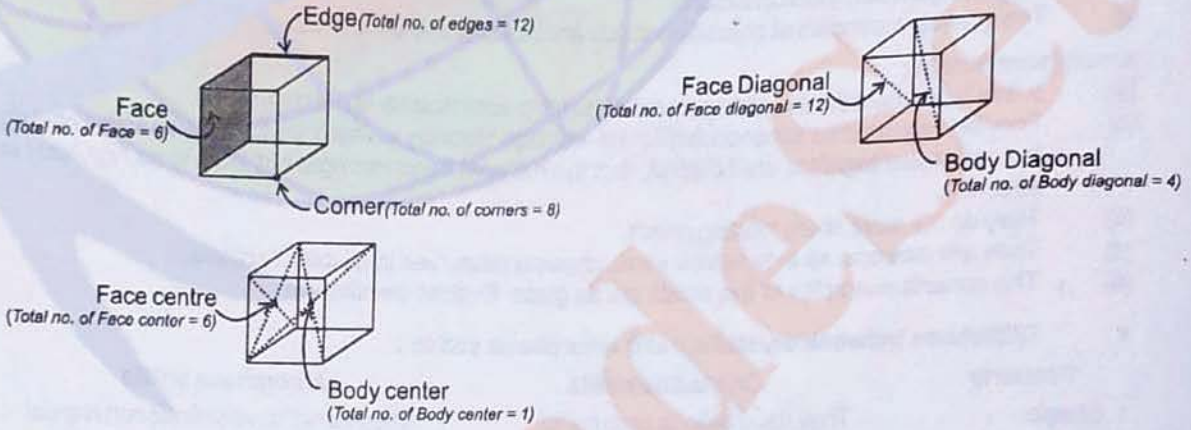
Ex.3 Graphite is an example of :
(1) Ionic solid (2) Covalent solid
(3) Vander waal's crystal (4) Metallic crystal **Ans. (2)**

Ex.4 Amorphous solids :
(1) Possess sharp melting points
(2) Undergo clean cleavage when cut with knife
(3) Do not undergo clean cleavage when cut with knife
(4) Possess orderly arrangement over long distances **Ans. (3)**

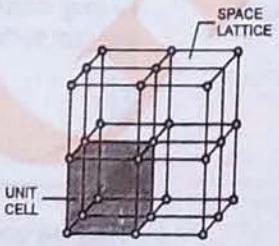
STUDY OF CRYSTALS :

- **Crystal :** A crystal is a homogeneous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.
- **Space lattice :** The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.
- **Unit cell :** The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.

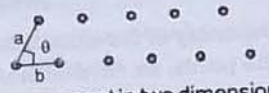
- **Properties of a cube :**



- **Face :** The plane surface of the crystal are called faces.
- **Edge :** An edge is formed by the intersection of two adjacent faces.
- **Interfacial angles :** The angle between the perpendiculars two intersecting faces called interfacial angles.



- **UNIT CELL IN TWO DIMENSIONS :**



Now in order to uniquely explain a regular arrangement in two dimensions we need the help of three parameters, two distance parameters and one angular parameter. Based upon their different relationships we can define different cases

Case 'A' (a = b) angle = 90°

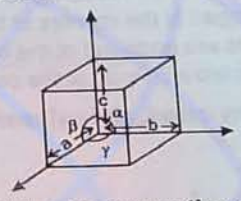
The unit cell in such a case is a **square**. Placing such square side by side we will obtain the entire two dimensional arrangement.

Case 'B'(a ≠ b) angle = 90°

The unit cell formed in this case is a rectangle.

- **UNIT CELL IN THREE DIMENSIONS :**

It has six parameters, 3-distance parameters and 3-angular parameter.



a, b, c are lengths of unit cell (also known as the crystallographic axes).
α, β, γ are known as the crystallographic angles.

- **DIFFERENT CLASSES OF CRYSTALS :**

Based on different permutations of a, b, c and α, β, γ we define different crystal classes.

Seven Crystal System

S.No.	Crystal System	Edge length	Angles	Unit cell found	Examples
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	SC, BCC, FCC (3)	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, Na_2O, CaF_2, KCl, Pb, Alum.
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	SC, BC (2)	Sn (white tin), SnO_2, ,TiO_2, ZnO_2, $NiSO_4$, urea.
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	SC, BC, FC, EC (4)	Rhombic sulphur, $BaSO_4$, KNO_3, $PbCO_3$, , $CaCO_3$ (aragonite)
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 120°$, $\neq 90°, \neq 60°$	SC, EC (2)	Monoclinic sulphur, $PbCrO_4$, Na_2SO_4, $10H_2O$, $Na_2B_4O_7.10H_2O$
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	SC (1)	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3
6	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma \neq 120°$	SC (1)	Graphite, ZnO, CdS, Mg, PbI_2, SiC.
7	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	SC (1)	$CaCO_3$ (Calcite), HgS(Cinnabar), $NaNO_3$, ICl.

Hint for memorise : CaTORacHMT

Note : In 3-D 14 different types of unit cell are found and these are also known as 14 **Bravais lattice.**

- **TYPES OF UNIT CELL :**

In every crystal class, the positioning of the lattice points may be different. Based upon these different positions occupied by the lattice points, we have different types of unit cells.

1. **Simple / primitive type of unit cell :** If lattice points or the particles of the solid are present only at the corners of the unit cell.
2. **Body centred unit cell :** lattice point are at the corners as well as at the body centre.
3. **Face centred unit cell :** lattice points are at corners as well as at each of the face centres.
4. **End centred unit cell :** lattice points are at the corners as well as at centre of any of two opposite faces.

Each of these arrangements corresponds to a unique and different type of arrangement. These 14 different arrangements are called the 14 Bravais lattices.

In any lattice, the surrounding of each and every lattice point is exactly identical.

- **MATHEMATICAL ANALYSIS OF CUBIC SYSTEM (TYPES AND ANALYSIS) :**

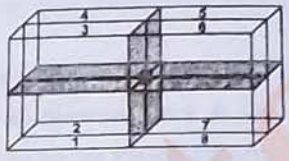
Simplest crystal is to be studied in cubic system. Three types of cubic systems are following.

(a) Simple Cubic (SC) : Atoms are arranged at the corners of the cube.

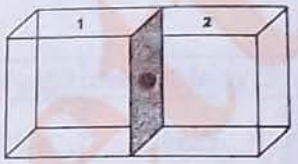
(b) Body Centered Cubic (BCC) : Atoms are arranged at the corners and at the centre of the cube.

(c) Face Centered Cubic (FCC) : Atoms are arranged at the corners and at centered of the each faces.

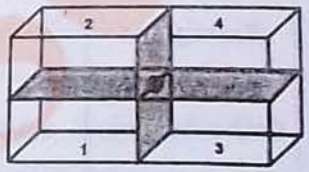
Contribution of different Lattice point in one Cubical unit cell :



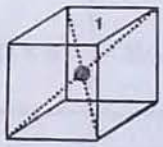
(i) Contribution from ***one corner lattice point*** = $\frac{1}{8}$ th.
(shared in 8 identical cubes)



(ii) Contribution from ***one face centered lattice point*** = $\frac{1}{2}$.
(shared in 2 identical cubes)



(iii) Contribution from ***edge centered lattice point*** = $\frac{1}{4}$ th.
(shared in 4 identical cubes)



(iv) Contribution from ***body centered lattice point*** = 1.
(it is present inside or at the centre of cube)

- **Number of atoms per unit cell / unit cell contents :**

The total number of atoms contained with in the unit cell for a simple cubic called the unit cell content.

(a) Simple cubic structure (sc) :

∵ Each corner atom is shared by eight surrounding cubes. Therefore, it contributes for $\frac{1}{8}$ of an atom.

$\therefore \quad z = 8 \times \frac{1}{8}$

(b) Body centered cubic structure (bcc) :

(i) Eight Corner atoms contribute one atom per unit cell.
(ii) Centre atom contribute one atom per unit cell.
(iii) So, total 1 + 1 = 2 atoms per unit cell.

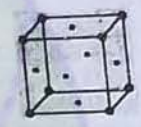
$$Z = 8 \times \frac{1}{8} + 1 = 2$$

(c) Face centered cubic structure (fcc) :

(i) The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell.

(ii) Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. Means

$$6 \times \frac{1}{2} = 3 \text{ atom per unit cell.}$$



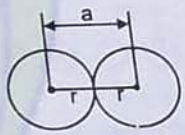
(iii) So, total Z = 3 + 1 = 4 atoms per unit cell.

- **ATOMIC RADIUS :**

It is defined as the half of the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.

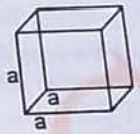
(a) Simple cubic structure [S.C.]

Radius of atom 'r' = $\frac{a}{2}$



(b) Face centered cubic structure (FCC) 'r' = $\frac{a}{2\sqrt{2}}$

(c) Body centered cubic structure (BCC) 'r' = $\frac{\sqrt{3}a}{4}$



$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$

Solved Examples

Ex.5 A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Drive the formula of the compound.

Sol. As A atoms are present at the 8 corners of the cube, therefore numbers of atoms of A in the unit cell

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

As B atoms are present at the face centres of the 6 faces of the cube, therefore, numbers of atoms of atoms of B in the unit cell $= \frac{1}{2} \times 6 = 3$

$\therefore$ Ratio of atoms A : B = 1 : 3

Hence, the formula of the compound is AB_3

Ex.6 A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at body centre. What is the formula of the compound ?

Sol. As atoms Y are present at the 8 corners of the cube, therefore, numbers of atoms of Y in the unit cell = 1/8 × 8 = 1

As atoms X are present at the body centre. therefore, numbers of atoms of X in the unit cell = 1

∴ ratio of atoms X : Y = 1 : 1

Hence, the formula of the compound is XY

Arrangement of the atom / particles of the solids in three dimensions :

Now having gained a knowledge of some of the terms, let us study how the different arrangements in space are brought about.

Firstly we will focus our attention on the solids containing only one type of lattice points.

The solids which contain only one type of lattice points are:

- *metallic solids (eg. Iron)*
- *molecular solids (eg. dry ice)*
- *covalent network solids (eg. diamond)*

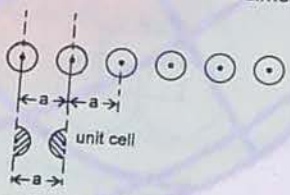
(Ionic solids do not fall into this category as they contain more than one type of particles,they will be studied in the later parts of the chapter)

All the atoms or particles of the solids will be represented by solid spheres, each of radius 'r'.

We will be taking these spheres of radius 'r' and explore how we can arrange these in three dimensions.Firstly we will begin with arrangement in one dimension.

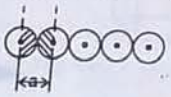
ARRANGEMENT IN 1-D : In one dimension it is possible to arrange the spheres in two possible ways.

1.



Not Stable [because the potential energy of the system is not minimum]

2.



a = 2r

Coordination number = 2

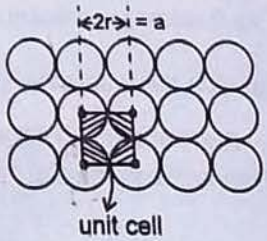
1-D close packing stable arrangement

This is the predominant way of packing in one dimension and as such most of the space lattices will show such an arrangement in one dimension along the planes of close packing.

ARRANGEMENT IN TWO DIMENSION :

In two dimensions also there are two ways of packing the spheres(in moving from one dimension to two dimensions it can be imagined that the two dimensional array will be made up of 1-D closed pack arrays / lines which are stacked one on top of other.

1. **Square packing :** If the one dimensional arrays are placed on top of one another, we get the square packing in two dimensions.



One sphere will be in contact with 4 other spheres.

area of square = $a^2 = 4r^2$

area of atoms in the square = $\frac{1}{4} \times \pi \ r^2 \times 4 = \pi r^2$

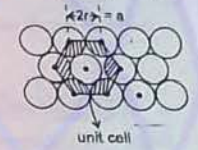
fraction of area occupied by spheres = $\frac{\pi r^2}{4r^2} = \frac{\pi}{4} = 78\%$

2. **Hexagonal close packing :** (in 2-D) If in a two dimensional arrangement,every one dimensional array is placed in the cavity of the just preceding array, we get the hexagonal packing in two dimensions.

area of hexagon $= 6 \times \frac{\sqrt{3}}{4} a^2 = 6 \times \frac{\sqrt{3}}{4} \times 4r^2 = 6\sqrt{3}\, r^2$

area of atoms $= \pi r^2 + \frac{1}{3} \times 6\pi r^2 = 3\pi r^2$

fraction of area occupied $= \frac{3\pi r^2}{6\sqrt{3}\, r^2} = \frac{\sqrt{3}\pi}{6} = 91\%$

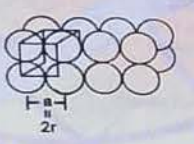


As is evident from the above calculations, the spheres are in closer contact in the hexagonal arrangement, hence the hexagonal arrangement is considered to be a better way of packing as compared to the square packing.

● **ARRANGEMENT IN THREE DIMENSIONS :**

1. **Simple cubical arrangement in three dimensions :**
(will be made up of 2-D sheets arranged one over other)

The simple cubical packing is obtained by arranging the square pack sheets of two dimension one over the other such that spheres of the second sheet are exactly (vertically) above the spheres of first sheet.




Simple cubic

(Note that $\begin{matrix} a = b = c \\ \alpha = \beta = \gamma = 90^\circ \end{matrix}$, hence crystal thus formed will belong to the cubic crystal class, and as the lattice points are only at the corners, hence the unit cell will be simple, therefore what we get is the **simple cubic**)

(i) Relation between 'a' and 'r'

$a = 2r$ (because atoms along the edge are touching each other)

(ii) Effective no. of atoms per unit cell :

$$(Z) = \frac{1}{8} \times 8 = 1$$

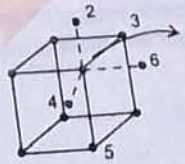
(iii) Packing fraction :

$$\text{Packing efficiency} = \frac{\text{Volume of atoms in a unit cell}}{\text{Total volume of a unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4}{3(2r)^3}\pi r^3 = \frac{4\pi r^3}{3 \times 8\, r^3} = 0.52 \text{ (or 52\%)}$$

***(Note :** This is not a very efficient way of packing as the packing fraction is very low)*

(iv) Coordination Number :
It is defined as the number of atoms touching any one particular atom. For simple cubic, coordination number = 6.



this sphere touches the numbered spheres as shown.

(v) Density of unit cell : *It is the ratio of mass of the spheres present in unit cell and total volume of unit cell.*

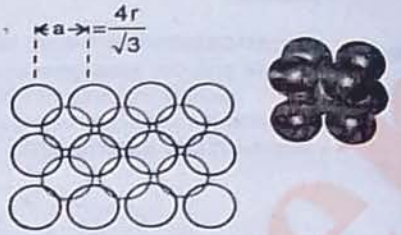
$$\text{Density of the unit cell} = \frac{\text{Mass of total atoms present in a unit cell}}{\text{Volume of that unit Cell}}$$

$$d = \frac{Z(M/N_A)}{a^3 \times 10^{-30}}\ gcm^{-3} \quad \Rightarrow \quad \boxed{d = \frac{ZM}{N_A\,(a^3 \times 10^{-30})}\ gcm^{-3}}$$

Where Z = no. of atoms in a unit cell
M/N_A = mass of a single atom
M = molar mass
N_A = Avogadro number (6.023×10^{23})

2. Body centred cubic :

The body centred cubic is a unique way of packing, as the 2D-arrays that can be imagined to constitute the space lattice are themselves formed in a unique way. The lattice points in the 2D array do not touch each other. The spheres start touching each other only upon moving from 2D to 3D, i.e when the 2D arrays are placed on top of each other in such a fashion that the spheres of the next plane are into the cavities of the first plane of spheres. The third plane of spheres is then exactly identical to the first plane of spheres.



(i) $a \neq 2r$ (as atoms along the edge are not touching each other) they touch along the body diagonal, hence $\sqrt{3}\,a = 4r$.

(ii) **Effective number of atoms (Z) = $1 + \frac{1}{8} \times 8 = 2$.**

(iii) **Packing fraction** $= \frac{2 \times \frac{4}{3}\pi r^3}{4 \times 4 \times 4r^3} \sqrt{3} \times \sqrt{3} \times \sqrt{3} = \frac{\pi\sqrt{3}}{8} \simeq 0.68 = 68\%$

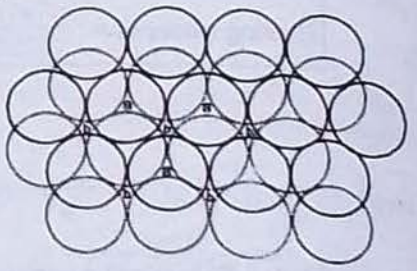
(iv) **Coordination No.= 8**

(the sphere at the body centre will be touching the spheres at the eight corners)

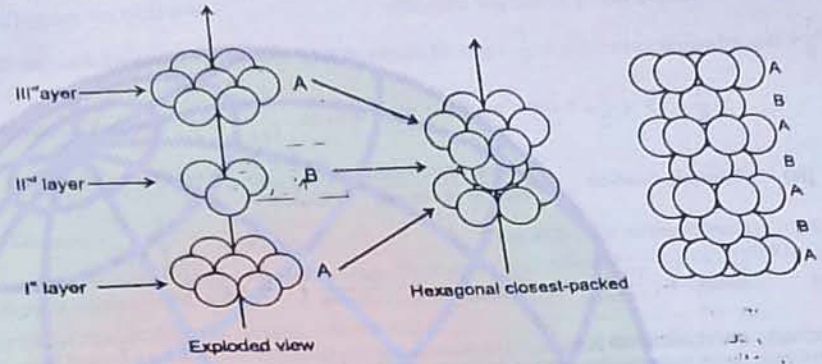
(v) **Density** $= \frac{ZM}{N_A a^3} = \frac{2M}{N_A a^3}$ $(\because Z = 2)$

3. Close packing in three dimensions :

(These are made up of two dimensional hexagonally packed sheets)
In second layer we have two kinds of voids.
(i) Voids of second layer below which there are spheres of first layer (all voids of type 'a').
(ii) Voids of second layer below which there are voids of first layer (all voids of type 'b').
For third layer, we have two possibilities.



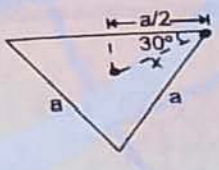
(A) If spheres of IIIrd layer are placed in voids of IInd layer below which there are spheres of Ist layer (voids of type 'a') then Ist layer and IIIrd layer are identical so this is called AB–AB pattern repeat or hexagonal close packing)

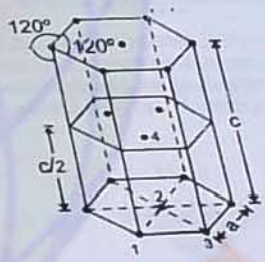


Hcp unit cell : $a = 2r = b$

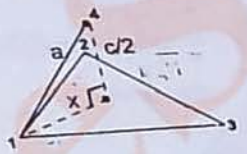
(I) Calculation of 'c' :

For the estimation of 'c', consider the spheres marked 1,2,3,4 in the unit cell as shown. These four spheres form a regular tetrahedron. The length of the perpendicular from '4' to the equilateral triangle 1-2-3 will be equal to c/2.





$$\cos 30^\circ = \frac{a}{2x}$$



$$x = \frac{a}{2\cos 30} = \frac{2a}{2\sqrt{3}} = \frac{a}{\sqrt{3}}$$

Apply pythagoras theorem.

$$x^2 + (c/2)^2 = a^2 \quad \Rightarrow \quad \boxed{c = \sqrt{\frac{2}{3}}\ 4r}$$

Volume of the hexagon = Area of base x Height.

$$= \frac{6\sqrt{3}}{4}\ a^2 \times c = \frac{6\sqrt{3}}{4}(4r^2) \times \sqrt{\frac{2}{3}}(4r) = 24\sqrt{2}\cdot r^3$$

(ii) **Effective no. of atoms per unit cell :**

$Z = \frac{1}{6} \times$ (no. of atoms at corner) $+ \frac{1}{2} \times$ (no. of atoms at face centres) $+ 1 \times$ (no. of atoms inside the body)

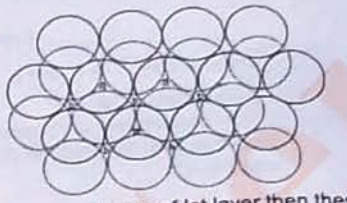
$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 1 \times 3 = 2 + 1 + 3 = 6$

(iii) **Packing fraction :** $= \frac{\text{volume of the atoms}}{\text{volume of unit cell}} = \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\, r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

(iv) **Coordination No. : C.N. = 12**

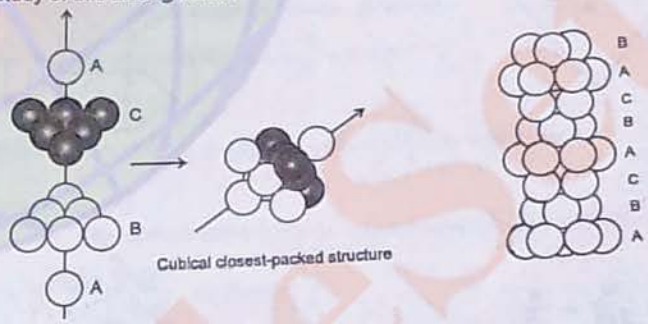
(v) **Density** $= \frac{\text{Mass}}{\text{Volume}} = \frac{ZM}{N_A \text{ (volume)}} = \frac{6M}{N_A \text{ (volume)}}$ $(\because Z = 6)$

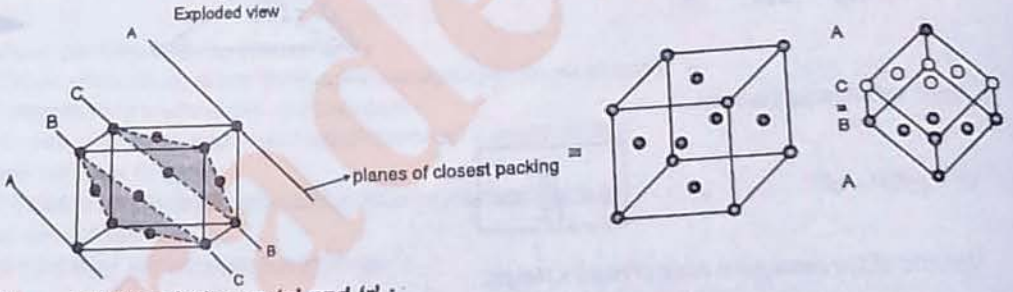
(B) ABC-ABC ARRANGEMENT :



If the third layer spheres are placed in those voids of second layer under which there are voids of the first layer of spheres (voids of type 'b'), then the first and the third layer of spheres will not be identical. Such an arrangement will lead to an ABC-ABC type of arrangement. It is also known as the cubical close packing (ccp) or also as the Face Centred Cubic structure (FCC).

In the ABC – ABC pattern, the spheres of 4th layer are vertically above the spheres of Ist layer then these consecutive layers are different from each other, fourth layer will be idential to first layer so it will be called ABC – ABC repeat pattern. It is also called the ccp (cubical close packing) because a cubical type of unit cell is used for the study of this arrangement.





(i) **Relation between 'a' and 'r' :**

$a \neq 2r$

$\sqrt{2}a = 4r$ (as the spheres touch along the face diagonal)

(ii) **Effective no. of atoms :**

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

(iii) **Packing fraction :** $\frac{4 \times \frac{4}{3}\pi r^3}{4 \times 4 \times 4\,r^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$

(iv) **Coordination number : 12**

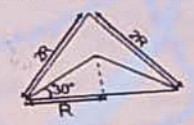
(v) **Density** $= \frac{Z \times M}{N_A \cdot a^3} = \frac{4 \times M}{N_A \times a^3}$

Note : *In close packings, whenever two consecutive layers are of different kinds(FCC, HCP) then packing efficiency will always be 74%*

- **TYPES OF VOIDS FOUND IN CLOSE PACKINGS :**

Eventhough the close packed structures have the maximum packing efficiency, there are indeed empty spaces in between, let us analyse the types of such voids and the maximum radius of a particle that can be placed in such voids.

1. **Triangular void (2-Dimensional 3 co-ordinate void)** The triangular voids are found in the planes of the close packed structures, whenever three spheres are in contact in such a fashion.

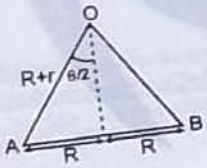


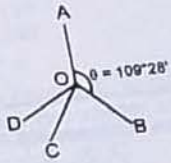
$\cos 30^\circ = \frac{R}{R+r}$ R = Radius of the sphere,

$\frac{\sqrt{3}}{2} = \frac{R}{R+r}$ r = maximum radius of a sphere that can be placed inside the void.

$\frac{2}{\sqrt{3}} = \frac{R+r}{R}$ $\Rightarrow$ **r = 0.155 R**

2. **Tetrahedral void (3-Dimensional 4 co-ordinate) :**
The tetrahedral void is formed whenever a sphere is placed on top of the triangular arrangement as in case of the triangular void.



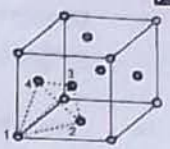


$1^\circ = 60'$ (minute)

$\sin \frac{\theta}{2} = \frac{R}{R+r}$

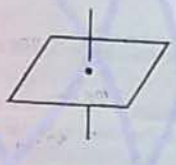
$\frac{R}{R+r} = \sin 54^\circ 44'$ $\Rightarrow$ $r = R\left\{\frac{1}{\sin\frac{\theta}{2}} - 1\right\}$ $\Rightarrow$ **r = 0.225 R**

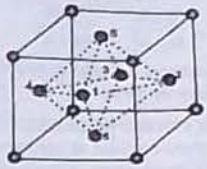
Location of tetrahedral voids in FCC unit cell :
The FCC unit cell has eight tetrahedral voids per unit cell. Just below every corner of the unit cell, there is one. As there are eight corners, there are eight tetrahedral voids.

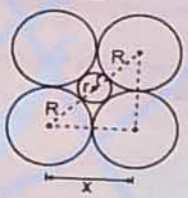


The spheres 1, 2, 3, 4 form a tetrahedral void.

3. **Octahedral void (3-Dimensional 6 coordinate void)** The octahedral void is formed whenever two spheres are placed, one on top and the other below a square arrangement of spheres







$x = 2R$

$\Rightarrow \quad x\sqrt{2} = 2R + 2r$

$\Rightarrow \quad 2R\sqrt{2} = 2R + 2r$

$\Rightarrow \quad R\sqrt{2} = R + r$

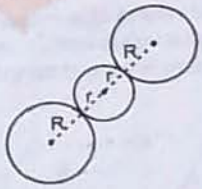
$\Rightarrow \quad r = (\sqrt{2} - 1)R$

Location of octahedral voids in a FCC unit cell :

In a FCC unit cell, there are four octahedral voids. *They are present at all the edge centres and at the body centre. The contribution of the edge centre void per unit cell is* $\frac{1}{4}$.

Hence, total number of octahedral voids = $\underbrace{\left(12 \times \frac{1}{4}\right)}_{\text{edge centres}} + \underbrace{(1)}_{\text{body centre}} = 4$

4. **Cubical void (3-Dimensional 8-coordinate void)**
The cubical void is generally not found in closed packed structures, but is generated as a result of distortions arising from the occupancy of voids by larger particles.
Along body diagonal



$\sqrt{3}\,a = 2(R + r)$

$2\sqrt{3}R = 2(R + r)$

$r = (\sqrt{3} - 1)R$

$r = 0.732\,R$

Solved Examples

Ex.7 Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23)

Sol. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as $d = \frac{\sqrt{3}}{2}a$

or $\quad a = \frac{2}{\sqrt{3}}d = \frac{2}{1.732} \times 365.9 = 422.5$ pm

For bcc structure, $Z = 2$

For sodium, $M = 23$

$\therefore \quad D = \frac{Z \times M}{a^3 \times N_0} = \frac{2 \times 23\,\text{gmol}^{-1}}{(422.5 \times 10^{-10}\,\text{cm})^3 \times (6.02 \times 10^{23}\,\text{mol}^{-1})} = 1.51\ \text{g/cm}^3$

Ex.8 X-ray diffraction studies shows that copper crystallizes in an fcc unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm³. Calculate the atomic mass of copper.

Sol. $D = \frac{Z \times M}{a^3 \times N_0}$; $M = \frac{D \times a^3 \times N_0}{Z}$

For fcc lattice, Z = 4 hence, $\frac{(8.92\ g\ cm^{-3})(3.608 \times 10^{-8}\ cm)^3 (6.022 \times 10^{23}\ atoms\ mol^{-1})}{4\ atoms} = 63.1\ g\ mol^{-1}$

∴ Atomic mass of copper = 63.1

Ex.9 Density of Li atom is 0.53 g/cm³. The edge length of Li is 3.5 Å. Find out the number of Li atoms in a unit cell ($N = 6.023 \times 10^{23}$, M = 6.94)

Sol. The aim is to find Z in the formula

$D = \frac{Z \times M}{a^3 \times N_0}$

$Z = \frac{D \times a^3 \times N_0}{M} = \frac{0.53\ g\ cm^{-3} \times (3.5 \times 10^{-8}\ cm)^3 \times (6.023 \times 10^{3}\ mol^{-1})}{6.94\ g\ mol^{-1}} = 1.97 \simeq 2$

Ex.10 Transition metals, when they form interstitial compounds, the non-metals (H, B, C, N) are accomodated in:
(1) Voids or holes in cubic-packed structure (2) Tetrahedral voids
(3) Octahedral voids (4) All of these **Ans. (4)**

Ex.11 In a close pack array of N spheres, the number of tetrahedral holes are -
(1) 4N (2) N/2 (3) 2N (4) N **Ans. (3)**

Ex.12 In antiflourite structure, the negative ions -
(1) Occupy tetrahedral voids (2) Occupy octahedral voids
(3) Are arranged in ccp (4) Are arrange in hcp **Ans. (3)**

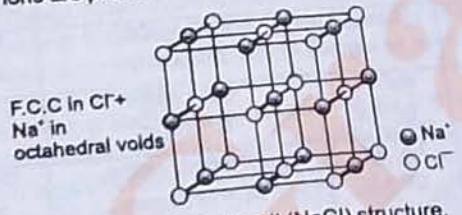
● **IONIC SOLIDS :**

Ionic solids are characterised by the presence of atleast two types of particles,viz: the cation and the anion,even the simplest of ionic solids contains one cation and one anion.
The Cations are generally found to be of smaller size, and the anions of larger sizes. The anions thus form the lattice by occupying the lattice positions and the cations are found inside the voids in such structures. The types of void occupied by the cation would depend upon the the ratio of its radius to that of the anion, popularly termed as the radius ratio. Hence, radius ratio = r_+ / r_-

C.No.	Limiting radius ratio	Type of Void Occupied
3	0.155 – 0.225	Triangular
4	0.225 – 0.414	Tetrahedral
6	0.414 – 0.732	Octahedral
8	0.732 – 0.999	Cubical

Examples of Ionic crystals :

(a) Rock Salt (NaCl) Coordination number (6 : 6) NaCl crystallizes in the face centred cubic structure. The chloride ions are present at all the lattice position and the sodium ions occupy all the octahedral voids.



Rock salt (NaCl) structure.

Every sodium is in contact with four chloride ions, and every chloride is in contact with four sodium ions

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