SOLID STATE

INTRODUCTION

Matter can exist in three physical states namely ; solid, liquid and gas. Matter consists of tiny particles (atoms, ions or molecules). If the particles are very far off from one another, they behave like gases; nearer, they behave like liquids, and nearest, like solids. The three states of matter are thus known as the three states of aggregation from Latin word meaning **"Flacking together"**.

The fundamental difference between the three states of aggregation lies essentially in the difference of the relative amounts of energy possessed by the particles in the three states. The relative energies in the different states of matter are governed by two universal opposing tendencies associated with the particles :

(i) They have tendency of mutual attraction.

(ii) They have tendency of escape from one another which is known as escaping tendency.

Whether a given system would exist as a solid, liquid or gas depends upon the relative strengths of these opposing tendencies. If the escaping tendency is greater than the attraction between them, the molecules will be carried far from each other to distances which are large as compared with their diameters, the system will exists in gaseous state. But in the liquid state the molecular attraction exceeds the escaping tendency and in the solid state the forces of attraction are so much greater than those of escaping tendency that each particle is bound into a definite place in a rigid position by the mutual attraction of molecules. In other words, in the solid state, the system possesses the amount of energy of motion i.e. kinetic energy.

State of matter depends on.

(i) Tendency of relative motion at a particular temperature.

(ii) Intermolecular forces.

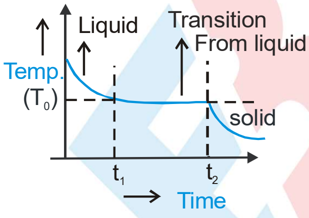
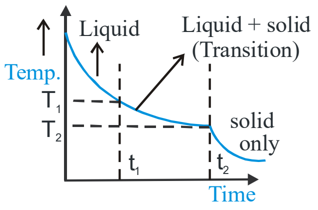
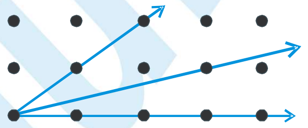
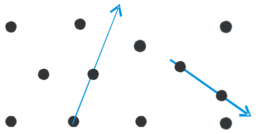
Properties	Solid	Liquid	Gases
(i) Motion of partical.	No free motion only vibration allow.	Random motion to a limited extent is allowed.	Totally random.
(ii) Inter molecular forces	Very strong	Intermediate strength	Very weak (≃ zero)
(iii) Average separation (volume)	x	Average separation is almost constant so almost fixed volume.	No fixed volume.
(iv) Shape	Definate shape as location of partical are fixed.	Average separation is fixed but location of partical is not fixed so no definate shape..	No fixed shape.
(v) Effect of change in pressure & temperature.	Are incompressible.	Liquid are also almost incompressible.	Highly compressible.
(vi) Heat capacities	Heat capacity is almost independent of process.	Same as solid.	Heat capacity is dependent on process.

THE SOLID STATE

The solid are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possesses the unique property of being rigid. Such solids are known as true solids e.g. NaCl, KCl, Sugar, Ag, Cu etc. On the other hand the solid which loses shapes on long standing, flows under its own weight and easily distorted by even mild distortion forces are called pseudo solids e.g. glass, pitch etc.

Some solids such as NaCl, Sugar, Sulphur etc. have properties not only of rigidity and incompressibility but also of having typical geometrical forms. These solids are called as crystalline solids. In such solids there is definite arrangements of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal. This is named as long-range order. This three dimensional arrangement is called **crystal lattice or space lattice**. Other solids such as glass, rubber, plastics etc. have rigidity and incompressibility to a certain extent but they do not have definite geometrical forms or do not have long range order are known as amorphous solids.

On the basis of arrangement of particle in the solid, these can be classified into crystalline & amorphous solids.

	Crystalline solid		Amorphous solids
	True solid		Pseudo solids, super cooled liquid [In between solid & liquid]
1	The constituent partical (atoms, molecule, ion) follow a definite repetiting arrangement.	1	No particular pattern is followed partical are random arranged.
2	These have long range order.	2	They have short range order no long range order are found.
3	These are produced by slow cooling under controlled condition of liquid. The crystalline structure is also dependent on conditions. Same substance can have different crystalline structure in different condition. Different crystalline structure of the same substance are called its polymorphic forms & this is known as polymorphism.	3	Rapid or suddenly cooling of the liquid generate the amorphous solid.
4	These have fixed or sharp melting point and enthalpy of fusion. Cooling Curve : 	4	These have a range of temperature in which they melts as. There melting point and enthalpy of fusion is not fixed. 
5	These are anisotropic : Physical properties will have different values in different direction.  Ex. : Ag, Fe, Cu, NaCl, H_2O (s), Dimond, Quartz, Sucrose (Sugar)	5	These are isotropic : All different physical properties are same in all different direction. Reason : Due to random arrangement of partical.  Ex. : Glass, Plastic, Amorphous silica, Rubber, Starch.

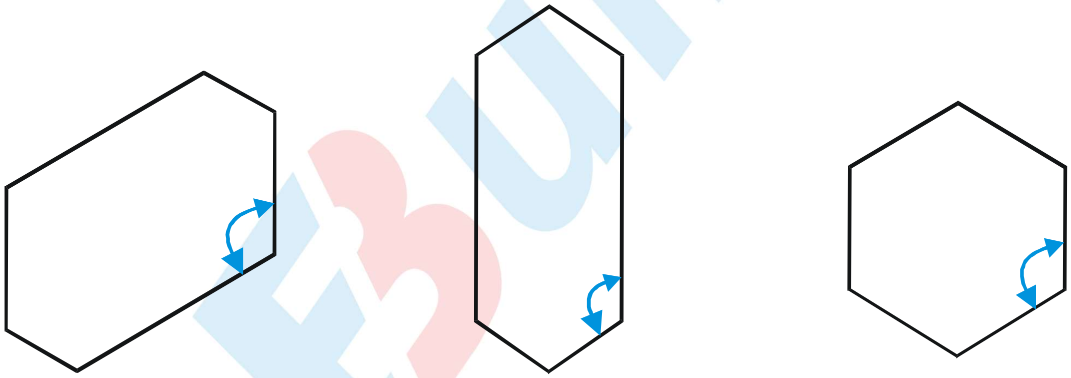
CRYSTALLINE STATE

"A crystal is a solid composed of atoms (ions or molecules) arranged in an orderly repetitive array".

Most of the naturally occurring solids are found to have definite crystalline shapes which can be recognised easily. These are in large size because these are formed very slowly thus particles get sufficient time to get proper position in the crystal structure. Some crystalline solids are so small that appear to be amorphous. But on examination under a powerful microscope it is also seen to have a definite crystalline shape. Such solids are known as micro crystalline solids. Thus the crystallinity of a crystal may be defined as "a condition of matter resulting from an or orderly, cohesive, three dimensional arrangement of its component particles (atoms, ions or molecules) in space". This three dimensional arrangement is called crystal lattice or space lattice. The position occupied by the particles in the crystal lattice are called lattice sites or lattice points. The lattices are bound by surface that usually planar and known as faces of the crystal.

"The smallest geometrical position of the crystal which can be used as repetitive unit to build up the whole crystal is called a unit cell."

The angle between the two perpendiculars to the two intersecting faces is termed as the interfacial angle which may be same as the angle between the unit cell edges. Goniometer is used to measure the interfacial angle. It is important to note that interfacial angle of a substance remains the same although its shape may be different due to conditions of formation.



Interfacial angles of crystal

This is known as law of constancy of interfacial angle or law of crystallography.

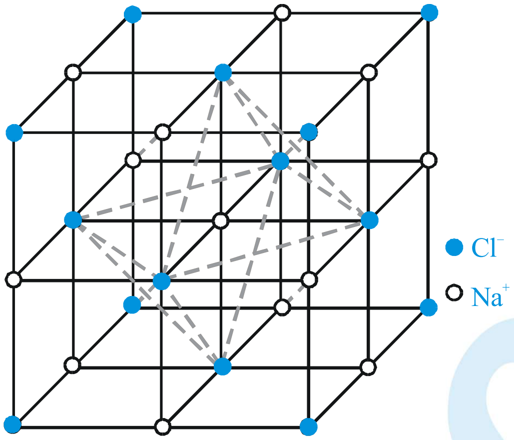
Types of the crystals

Crystal are divided into four important types on the basis of chemical bonding of the constituent atoms.

IONIC CRYSTALS :

These are formed by a combination of highly electro-positive ions (cations) and highly electronegative ions (anions). Thus strong electrostatic force of attraction acts with in the ionic crystals. Therefore, a large amount of energy is required to separate ions from one another. The type of the crystal lattice depends upon (i) The size of the ion (ii)

The necessity for the preservation of electrical neutrality. Therefore alternate cations and anions in equivalent amounts are arranged in the ionic crystal Ex. NaCl, KF, CsCl etc.



Crystal structure of NaCl

COVALENT CRYSTALS

These are formed by sharing of valence electrons between two atoms resulting in the formation of a covalent bond. The covalent bonds extend in two or three dimensions forming a giant interlocking structure called network. Diamond and graphite are the good examples of this type.

MOLECULAR CRYSTALS

In these crystals, molecules occupy the lattice points of the unit cells, except in solidified noble gases in which the units are atoms, where the binding is due to vander Waal's' forces and dipole-dipole forces. Since vander Waal's forces are non-directional hence structure of the crystal is determined by geometric consideration only. Solid H_2, N_2, O_2, CO_2, I_2, sugar etc. are well known examples of such crystal in which vander Waal's forces are acting . Ice is the common example in which dipole-dipole forces of attraction (hydrogen bonding) are active. Many organic and inorganic crystals involve hydrogen bonds. Although these are comparatively weaker but play a very important role in determining the structures of substances Ex. polynucleotides, proteins etc.

METALLIC CRYSTALS

These are formed by a combination of atoms of electropositive elements. These atoms are binded by metallic bonds. It may be defined as :

The force that binds a metal ion to a number of electrons within its sphere of influences is known as metallic bond

OR

A bond which is formed between electropositive elements

OR

The attractive force which holds the atoms of two or more metals together in a metal crystal or in an alloy.

We know that the force of attraction between metal ions and valency electrons is very strong. This force of attraction is responsible for a compact solid structure of metal.

The important characteristics of the various types of crystals are given in the following table:

Some Important Characteristics of Various types of Crystals

S.No.	Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1	Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2	Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole -dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3	Hardness	Hard	Very hard Graphite is soft	Soft	Hard or soft
4	Brittleness	Brittle	Intermediate	Low	Low
5	Melting point	High	Very high	Low	Varying from moderate to high
6	Electrical	Semi conductor due to crystal imperfections, conductor is fused state	Non-conductor Graphiteis good	Bad conductor	Good conductors
7	Solubility in	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
8	Heat of Vaporisation (kj mol^{-1})	NaCl(s) 170-75	Graphite 718-43	$NH_3(s)$ 23.55	Cu(s) 304.59
9	Heat of fusion (kj mol^{-1})	NaCl 28.45	– –	NH_3 (s) 5.65	Cu(s) 13.016
10	Example	NaCl, KNO_3 CsCl, Na_2SO_4	Diamond, graphite, Quartz, (SiO_2), SiC	$H_2O(s)$, $CO_2(s)$, Sulphur, Sugar, Iodine,noble gases	Na, Cu, Ag, Fe, Pt, alloys

Ex. **Identify molecular solid, covalent solid, ionic solid : P_4(s), S_8 (s), SiC (s), Al_2O_3(s), He (s), Al_2Cl_6(s).**

Sol. Molecular solid → P_4(s), S_8 (s), He (s), Al_2Cl_6(s)

Covalent solid → SiC

Ionic solid → Al_2O_3(s).

ISOMORPHISM

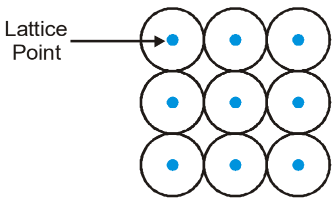
The occurrence of a given substance in more than one solid crystalline forms have different physical properties is known as polymorphism. This property when occurs in elements is known as allotropy.

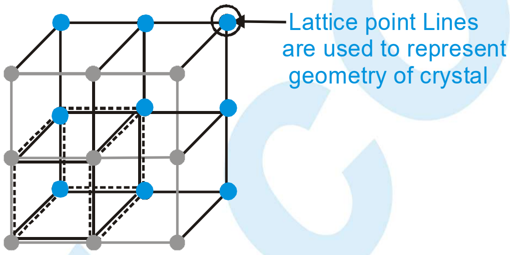
Sometimes we come across examples of chemically different solids which crystallise in the same crystalline shape. Such substances are said to be Isomorphous (same shape). Their chemical constitutions are very similar and in some cases crystals of one substance may continue to grow when placed in a saturated solution of the other e.g. potash alum and chrome alum crystals have the same shape and can be grown in each other's solutions. Mitscherlich deduced that isomorphous substances have similar chemical formula e.g. phosphates and arsenates are said to be isomorphous with one another viz.

1. $Na_2HPO_4.12H_2O$ and $Na_3AsO_4.12H_2O$
2. K_2SO_4, K_2CrO_4
3. $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$
4. $KMnO_4$, $KClO_4$
5. $K_2SO_4.Al_2(SO_4)_3.24H_2O$, $K_2SO_4.\ Cr_2(SO_4)_3.24H_2O$. However, the law is not without exceptions.

Space Lattice/Crystalline Lattice/3–D Lattice

Space lattice is a regular arrangement of lattice points showing how the particles are arranged at different sites in 3D–view.



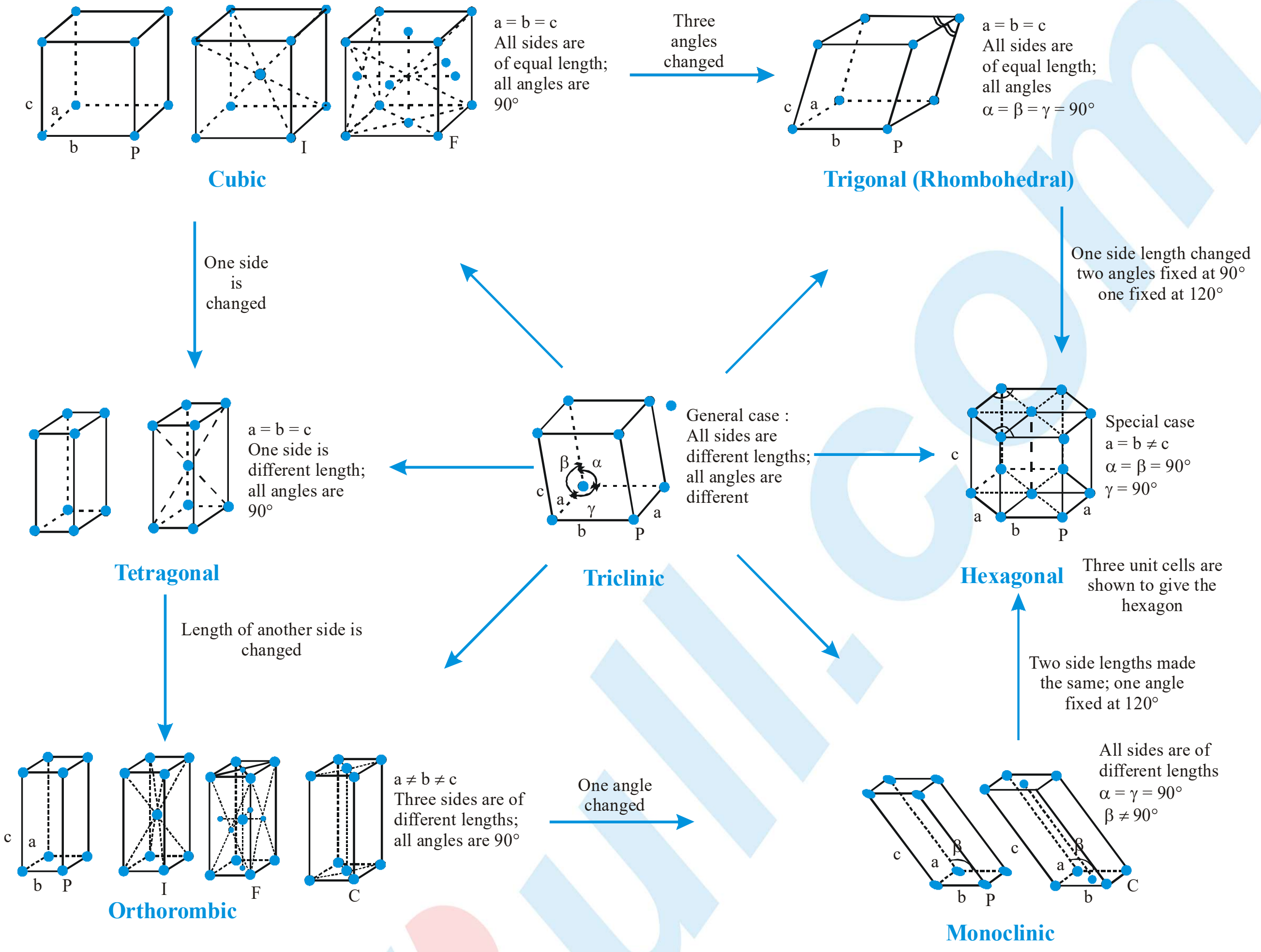


" The three dimensional distribution of component particles in a crystal can be found by X-ray diffraction of different faces of the crystal.

On the basis of the classification of symmetry, the crystals have been divided into seven systems. These can be grouped into 32 classes which in turn can be regrouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table.

The Seven Crystal Systems

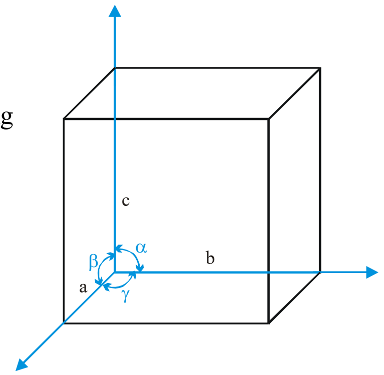
S.No.	Name of System	Axes	Angles	Bravais Lattices
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred = 4
5	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive, End - centred = 2
6	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\beta \neq 120°$	Primitive = 1 Total = 14



These crystal systems differ in length of unit cell edges **(a, b and c)** and the angles between the unit cell edges 4.

In cubic and trigonal (rhombohedral) systems, the three unit edges are of equal lengths but for the rest five systems it is not so. The interfacial angles are all 90^0 in the cubic, tetragonal and orthorhombic systems but it is not so for the rest four systems.

UNIT CELL (U.C.)



Unit cell of the crystalline substance is defined as the smallest repeating unit which shows the complete geometry of the crysta-lline substance. For eg. brick in wall. A unit cell is the smallest picture of the whole crystal. A unit cell is characterized by the edge lengths a, b and c along the three edges of the unit cell and the angles α, β and γ between the pair of edges bc; ca and ab respectively.

Characteristics of a Unit Cell :

(i) Its dimensional along the three edges, a, b and c. These edges may or may not be mutually perpendicular.

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

(iii) Each unit cell has characteristic relation between a, b and c or α, β, and γ to give rise different types of unit cell.

Thus, a unit cell is characterised by six parameters, a, b, c, α, β, and γ. These parameters of a typical unit cell are shown in figure.

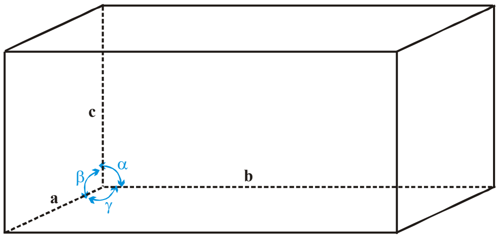


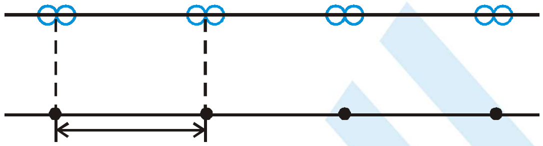
Illustration of parameters of a unit cell

A unit cell may also be defined as a 1D, 2D, 3D three dimensional group of lattice points that generates the whole lattice by repetition or stacking.

Note : Generally most symmetrical and smallest volume unit cell is selected.

1-Dimensional space lattice :

Uniformly separated lattice point in 1-D

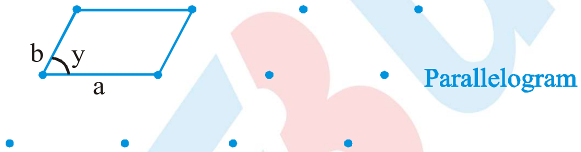


Figure

only one parameter is required → distance between two lattice point.

2-D Lattice :

Regular arrangement of point in plane 3 parameter required → Two edge lengths & angle between these two edge.



We can only shift the unit cell parallel not rotate it.

(i) Square unit cell → $a = b, \gamma = 90^\circ$

(ii) Rectangle unit cell → $a \neq b, \gamma = 90^\circ$

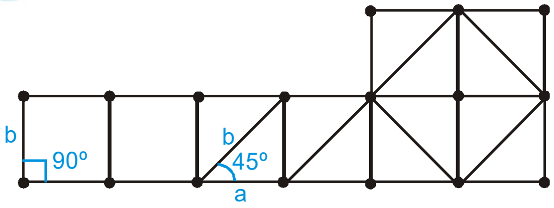
(iii) Hexagonal unit cell → $a = b, \gamma = 60^\circ$

(iv) Rhombic unit cell → $a = b, \gamma \neq 90^\circ$ & $\gamma \neq 60^\circ$

(v) Parallelogram → $a \neq b, \gamma \neq 90^\circ$

Most symmetrical → square unit cell.

Square unit cell :



Figure

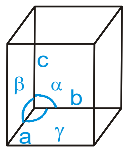
Primitive unit cell : Unit cell having lattice point only at the corner.

Non Primitive or centered unit cell : Unit cell having lattice point at corner as well as with in the unit cell.

3-D-Lattice

Seven Primitive unit cells in crystals

Cubic



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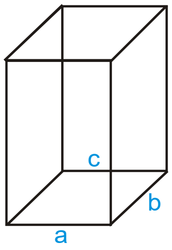
Tetragonal



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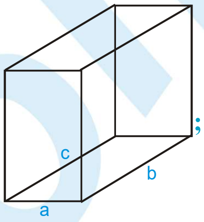
Orthorhombic



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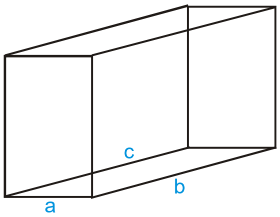
Monoclinic



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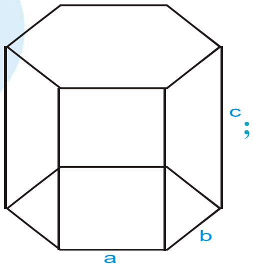
Hexagonal



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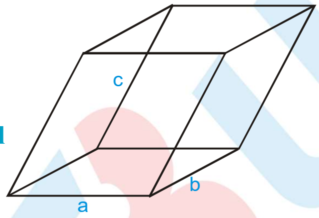
Rhombohedral



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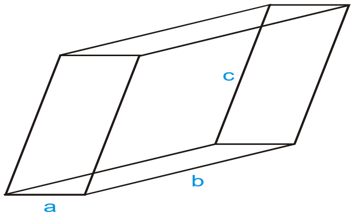
Triclinic



CO-ORDINATION NUMBER

The number of nearest particles around a specific particle in a given crystalline substance is called as co-ordination number of that crystalline substance.

PACKING EFFICIENCY OR PACKING DENSITY (P.E.)

Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance i.e. packing efficiency is equal to-

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

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

$$\text{P.E.} = \frac{n \times (4/3)\pi r^3}{V}$$

Where n = number of atoms present in unit cell

GEOMETRY OF A CUBE

Number of corners = 8

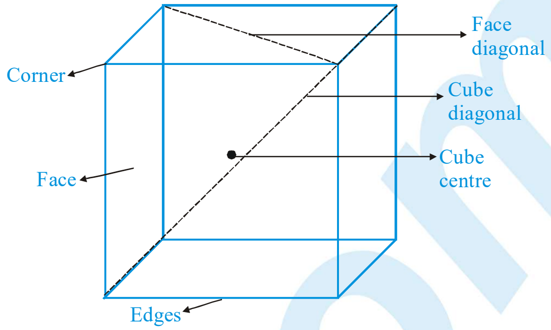
Number of faces = 6

Number of edges = 12

Number of cube centre = 1

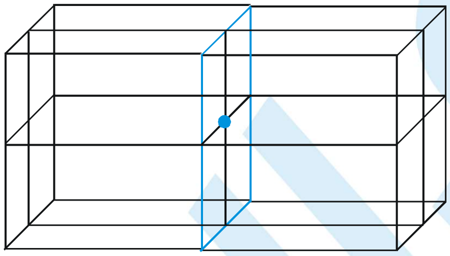
Number of cube diagonals = 4

Number of face diagonals = 12

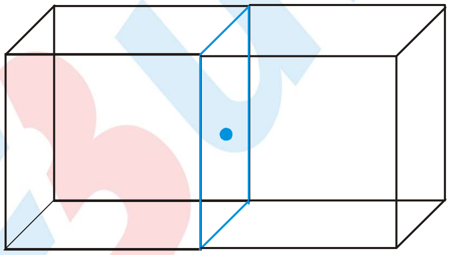


Contribution of an atom at different sites of cube :

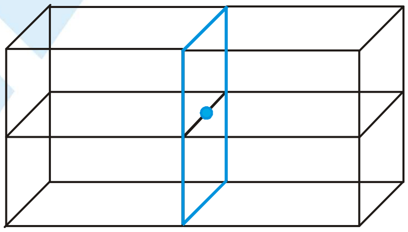
A corner of a cube is common in 8 cubes. So $\frac{1}{8}$ the part of an atom is present at this corner of cube.



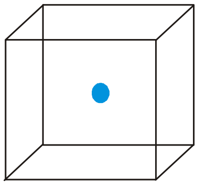
A face of a cube is common is 2 cubes. So $\frac{1}{2}$ the part of an atom is present at the face of a cube.



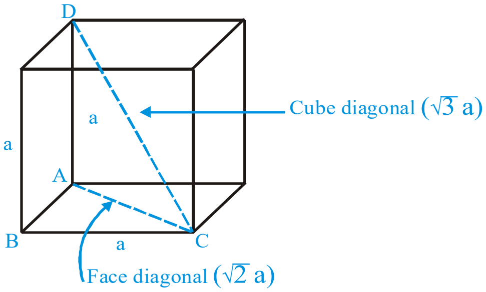
An edge of a cube is common in four cubes, so $\frac{1}{4}$ the part of the atom is present at the edge of a cube

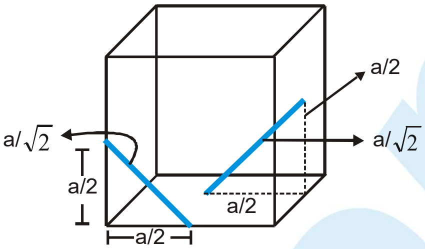


A cube centre is not common in any another cube, so one complete atom is present at the cube centre.



Length of face diagonal and cube diagonal





Distance between

2 adjacent face centres = $\frac{a}{\sqrt{2}}$

Distance between

2 adjacent edge centre = $\frac{a}{\sqrt{2}}$

Consider the triangle ABC, with the help of pyathogorous theorem

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a \qquad \text{(length of face diagonal.)}$$

Consider the triangle DAC, with the help of pythagoras theorem

$$DC = \sqrt{DA^2 + AC^2}$$

$$= \sqrt{a^2 + (\sqrt{2}a)^2}$$

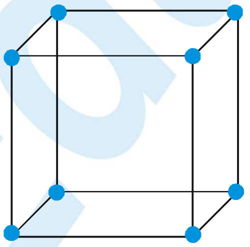
$$= \sqrt{3}a \quad \text{(length of cube diagonal)}$$

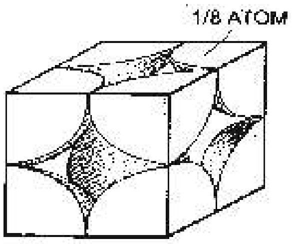
TYPE OF UNIT CELL (BRAVAIS LATTICE)

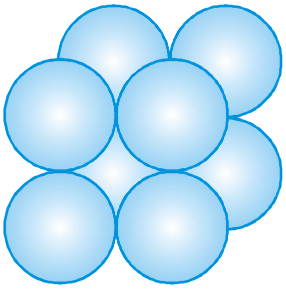
The distance between successive lattice planes of the same type is called the spacing of planes or interplanar distance between the planes. On the basis of this aspect, the lattices may be divided in following classes :

(1) Simple/Primitive/Basic Unit cell :

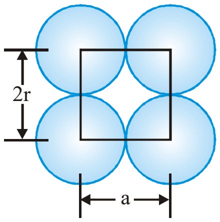
A unit cell having lattice point only at corners called as primitive or simple unit cell. i.e. in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (atoms) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.







(a) Relationship between edge length 'a' and atomic radius 'r' :



$a = 2r$

i.e. $r = \frac{a}{2}$ (One face of SCC)

(b) Number of atoms present in unit cell : In this case one atom or ion lies at the each corner. Hence simple cubic unit cell contains a total of $\frac{1}{8} \times 8 = 1$ atom or ion/unit cell.

(c) Packing efficiency (P. E.) :

$$\text{P.E.} = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} = \frac{n \times \frac{4}{3}\pi r^3}{V} \quad \left[\because \text{Volume of atom} = \frac{4}{3}\pi r^3\right]$$

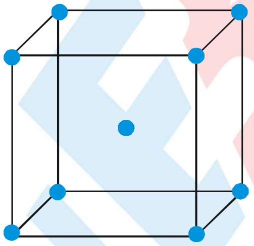
For SCC : $$\text{P.E.} = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} \quad \left[\because r = \frac{a}{2} \text{ and } V = a^3, n = 1\right]$$

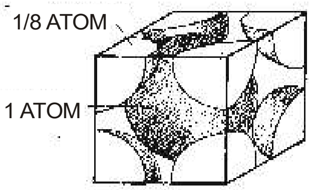
$$= \frac{\pi}{6} = 0.524 \quad \text{or} \quad 52.4\ \%$$

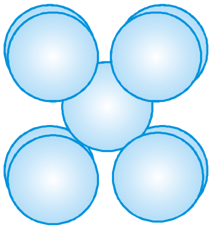
2. Body centred cubic (b.c.c.) cell : A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centered unit cell.

Here the central atom is surrounded by eight equidistant atoms and hence the co-ordination number is eight.

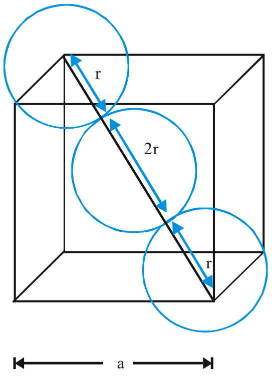
The nearest distance between two atoms will be $\frac{a\sqrt{3}}{2}$







(a) Relationship between edge length 'a' and atomic radius 'r' :-



In BCC, along cube diagonal all atoms touches each other and the length of cube diagonal is $\sqrt{3}a$.

So, $\sqrt{3}a = 4r$

i.e. $r = \dfrac{\sqrt{3}a}{4}$

(b) Number of atom present in unit cell :

$$\left(\frac{1}{8}\times 8\right)+\left(1\times 1\right)=1+1=2 \text{ atoms/unit cell}$$

(Corner) (Body centre)

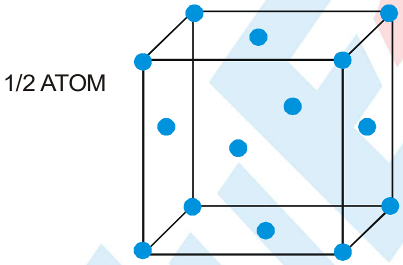
In this case one atom or ion lies at the each corner of the cube. Thus contribution of the 8 corners is $\left(\frac{1}{8}\times 8\right)=1$, while that of the body centred is 1 in the unit cell. Hence total number of atoms per unit cell is 1 + 1 = 2 atoms (or ions)

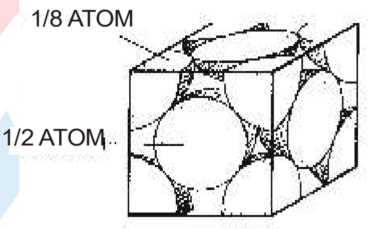
(c) Packing efficiency :

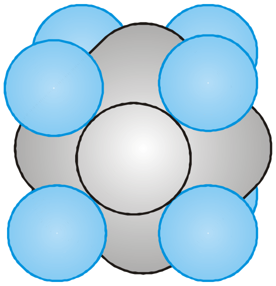
$$\text{P.E.} = \frac{n\times\frac{4}{3}\pi r^3}{V} = \frac{2\times\frac{4}{3}\times\pi\left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \qquad \left[\because\ n=2, r=\frac{\sqrt{3}a}{4}, V=a^3\right]$$

In B.C.C. 68% of total volume is occupied by atom or ions.

3. Face centred cubic (f.c.c.) cell : A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. Considering an atom at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number will be twelve and the distance between the two nearest atoms will be $\dfrac{a}{\sqrt{2}}$.







(a) Relationship between edge length 'a' and atomic radius 'r' :

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is $\sqrt{2}a$.

So $4r = \sqrt{2}a$

i.e. $r = \dfrac{\sqrt{2}a}{4} = \dfrac{a}{2\sqrt{2}} \qquad r = \dfrac{a}{2\sqrt{2}}$

(b) Number of atoms per unit cell :

$$\underbrace{\left(\frac{1}{8}\times 8\right)}_{\text{Corner}}+\underbrace{\left(6\times\frac{1}{2}\right)}_{\text{faces}}=1+3=4 \text{ atoms/unit cell}$$

In this case one atom or ion lies at the each corner of the cube and one atom or ion lies at the centre of each face of the cube. It may noted that only $\frac{1}{2}$ of each face sphere lie with in the unit cell and there are six such faces. The total contribution of 8 corners is $\left(\frac{1}{8}\times 8\right)$ = 1, while that of 6 face centred atoms is $\left(\frac{1}{2}\times 6\right)$ = 3 in the unit cell.

Hence total number of atoms per unit cell is 1 + 3 = 4 atoms (or ions).

(c) Packing efficiency :

$$\text{P.E.} = \frac{n\times\frac{4}{3}\pi r^3}{V} \qquad [\Theta \text{ for FCC } n=4,\ r=\frac{a}{2\sqrt{2}},\ V=a^3]$$

$$=\frac{4\times\frac{4}{3}\pi\times\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}=\frac{\pi}{3\sqrt{2}}=0.74 \quad \text{or} \quad 74\,\%$$

i.e. In FCC, 74% of total volume is occupied by atoms.

4. End Centered Unit Cell :

A unit cell having lattice point at the centres of only one set of opposite faces in addition to the lattice point at every corner called as end centered unit cell.

Note : This type of Bravais lattice is obtained only in orthorhombic and monoclinic type unit cell.

Number of atoms per unit cell in cubic close packed structure of atoms

Unit Cell	Number of atoms at			No. of atoms per unit cell	Volume occupied by particles (%)
	Corners	Centres	Faces		
Simple cube	$8\times\frac{1}{8}=1$	0	0	1	52.4
Body centred cube (BCC)	$8\times\frac{1}{8}=1$	1	0	2	68
Face centred cube (FCC)	$8\times\frac{1}{8}=1$	0	$6\times\frac{1}{2}=3$	4	74

Ex. The lattice parameters of a given crystal are a = 5.62 Å, b = 7.41 Å and c = 9.48 Å. The three coordinate axes are mutually perpendicular to each other. The crystal is :

(A) tetragonal **(B)** orthorhombic **(C)** monoclinic **(D)** trigonal.

Ans. **(B)**

Sol. $a \neq b \neq c$ & $\alpha = \beta = \gamma = 90°$ the crystal system is orthorhombic.

Ex. Tetragonal crystal system has the following unit cell dimensions:

(A) $a = b = c$ and $\alpha = \beta = \gamma = 90°$ **(B)** $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$

(C) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ **(D)** $a = b \neq c$ and $\alpha = \beta = 90°, \gamma = 120°$

Ans. **(B)**

Ex. In a face centered cubic arrangement of A and B atoms whose A atoms are at the corner of the unit cell and B atoms at the face centres. One of the A atom Is missing from one corner in unit cell. The simplest formula of the compound is

(A) A_7B_3 **(B)** AB_3 **(C)** A_7B_{24} **(D)** A_2B_3

Ans. **(C)**

Sol. $A = 7 \times \frac{1}{8} = \frac{7}{8}$; $B = 6 \times \frac{1}{2} = 3$

Formula = $A_{7/8}\ B_3$ or A_7B_{24}

Ex. A compound has cubical unit cell in which X atom are present at 6 corner, Y atom are at remaining corner & only at those face centers which are not opposite to each other & Z atoms are present at remaining face center & body center then find.

(i) Formula of compound (ii) Density if edge length = 2 Å.

Given : Atomic mass of X = 40 amu, Y = 60 amu, Z = 80 amu.

Sol. (i) $X = \frac{1}{8} \times 6 = \frac{3}{4}$,

$$Y = \frac{1}{8} \times 2 + \frac{1}{2} \times 3 = \frac{7}{4}$$

$$Z = \frac{1}{2} \times 3 + 1 + 1 = \frac{5}{2} = \frac{10}{4}$$

For formula : $X_{\frac{3}{4}}Y_{\frac{7}{4}}Z_{\frac{10}{4}} = X_3\ Y_7Z_{10}$

(ii) $1\text{ amu} = 1.67 \times 10^{-24}$ gram

$$1\text{ amu} = \frac{1}{6.02 \times 10^{23}}\text{ gram.}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\frac{3}{4} \times 40 + \frac{7}{4} \times 60 + \frac{10}{4} \times 80}{(2 \times 10^{-8})^3}\ \text{amu/cc} = \frac{335 \times 1.67 \times 10^{-24}}{8 \times 10^{-24}} = 69.8\ \text{gram/cc.}$$

CRYSTAL DENSITY OF THE CRYSTAL

If the length of edge of the unit cell is known we can calculate the density of the crystal as follow :

Let length of edge of the unit cell be ●.

∴ Volume of the unit cell = $●^3$ = V cm^3

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

Mass of the unit cell = Number of atoms present in a unit cell × Mass of one atom

= n × m g

But mass of one atom (m) $= \dfrac{\text{Atomic mass}}{\text{Avogadro Number}} = \dfrac{M}{N_A}$

Mass of the unit cell $= n \times \dfrac{M}{N_A}$ g, Density of the unit cell $= \dfrac{n \times \dfrac{M}{N_A}}{V}$ gm cm^{-3}

$\therefore$ Density of the unit cell $= \dfrac{n \times M}{V \times N_A}$ g cm^{-3}

$$\boldsymbol{\rho\,(\text{C.D.}) = \frac{n \times M}{V \times N_A}\ \text{g cm}^{-3}}$$

Ex. An element (atomic mass = 60) having face centred cubic crystal has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell (Avogadro constant, $N_A = 6.02 \times 10^{23}$ mol^{-1}) :-

Sol. Since element has fcc structure hence there are 4 atoms in a unit cell (or n = 4), Atomic mass is 60 (or M = 60), $N_A = 6.02 \times 10^{23}$ and $\rho = 6.23$ g cm^{-3}.

✈ $\rho = \dfrac{n \times M}{V \times N_A}$

or $V = \dfrac{n \times M}{\rho \times N_A}$

$$= \frac{(4)\left(60 \text{ g mol}^{-1)}\right)}{\left(6.23 \text{ g cm}^{-3)}\right)\left(6.02 \times 10^{23} \text{mol}^{-1}\right)}]$$

$$= \frac{240 \times 10^{-23}\ \text{cm}^{-3}}{37.5046} = 6.4 \times 10^{-23}\ \text{cm}^3 = 64 \times 10^{-24}\ \text{cm}^3$$

Let ● be the length of the edge of the unit cell.

$\therefore$ ●^{3} = V = 64×10^{-24} cm^3 or ● = 4.0×10^{-8} cm

Ex. The density of KBr is 2.75 g cm^{-3}. The length of the edge of the unit cell is 654 pm. Show that KBr has face centred cubic structure.

Sol. Length of the edge of the unit cell = 654 pm = 6.54×10^{-8} cm

$\therefore$ volume (V) of the unit cell = $(6.54 \times 10^{-8}\ \text{cm})^3$

Molecular mass of KBr = 39 + 80

= 119 g mol^{-1}

Density of KBr = 2.75 g cm^{-3}

✈ $\rho = \dfrac{n \times M}{V \times N_A}$

or $n = \dfrac{\rho \times V \times N_A}{M}$

$$= \frac{\left(2.75 \text{ g cm}^{-3}\right)\left(6.54 \times 10^{-8} \text{cm}\right)^3 \left(6.023 \times 10^{23}\ \text{mol}^{-1}\right)}{119 \text{ g mol}^{-1}}$$

$$= \frac{2.75 \times (6.54)^3 \times (6.023)(10^{-1})}{119}$$

$= 3.9 = 4$

Since number of atoms (or ions) in a unit cell is four hence the crystal must be face centred cubic.

Ex. An element crystallizes in a structure having f.c.c. unit cell of an edge 200 pm. Calculate its density, if 200 g of this element contains 24×10^{23} atoms.

Sol. Length of the edge of the unit cell (●) = 200 pm = 2×10^{-8} cm

∴ Volume (V) of the unit cell

$= (2 \times 10^{-8}\text{ cm})^3 = 8 \times 10^{-24}\text{ cm}^3$

Mass of the element (M) = 200 g

Number of the atoms $(N_0) = 24 \times 10^{23}$

the number of atoms per unit cell (fcc) = 4

✈ $$\rho = \frac{n \times M}{V \times N_0}$$

$$= \frac{(4)\ (200\text{ g})}{(8 \times 10^{-24}\text{ cm}^3)(24 \times 10^{23})} = 41.7\text{ g cm}^{-3}$$

Ex. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If volume of this unit cell is $24 \times 10^{-24}\text{ cm}^3$ and density of the element is 7.2 g cm^{-3}. Calculate the number of atoms present in 200 g of the element.

Sol. Volume (V) of the unit cell

$= 24 \times 10^{-24}\text{ cm}^3$

Density of (r) of the element = 7.2 g cm^{-3}

Mass of the element = 200 g

Number of atoms (n) per unit cell = [The contribution of the 8 corner is (1/8) × 8=1 and two atoms on one of the diagonal is 2 × 1 = 2] i.e. 1 + 2 = 3 atoms

✈ $$\rho = \frac{n \times M}{V \times N_0} \quad \text{or} \quad N_0 = \frac{n \times M}{V \times \rho}$$

$$N_0 = \frac{(3)\ (200\text{ g})}{(24 \times 10^{-24}\text{ cm}^3)(7.2\text{ g cm}^{-3})}$$

$N_0 = 3.472 \times 10^{24}$ atoms

CLOSE PACKING OF IDENTICAL SOLID SPHERES

The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as closed packing.

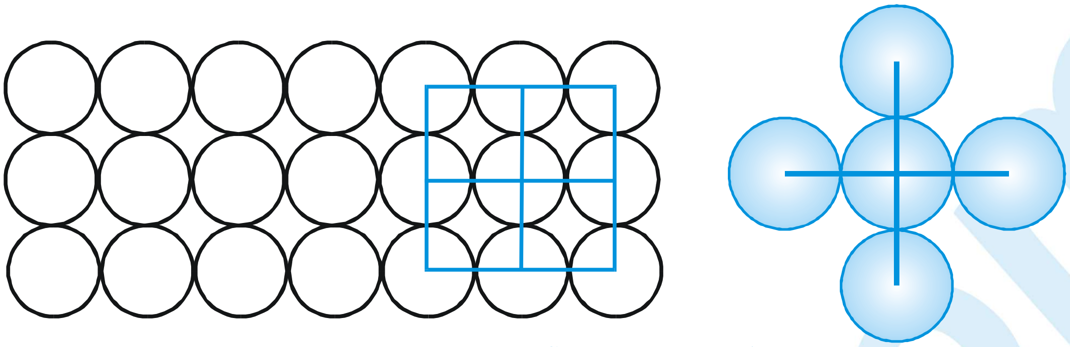
Now we describe the different arrangements of spherical particles of equal size.

When the spheres are packed in a plane i.e. There are two types of close packing.

(a) Two dimensionally close packing :

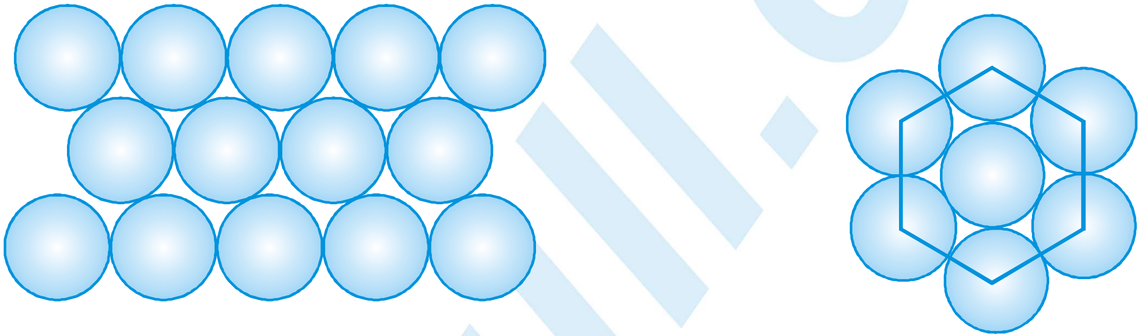
(i) The centres of the spheres lie one below another. This type of arrangement is called square close packing. In such packing one sphere touches four other spheres. In this case 52.4% of the volume is occupied. The remaining 47.6% of the volume is empty and is called void volume.

In square close packing co-ordination number is 4



Square close packing

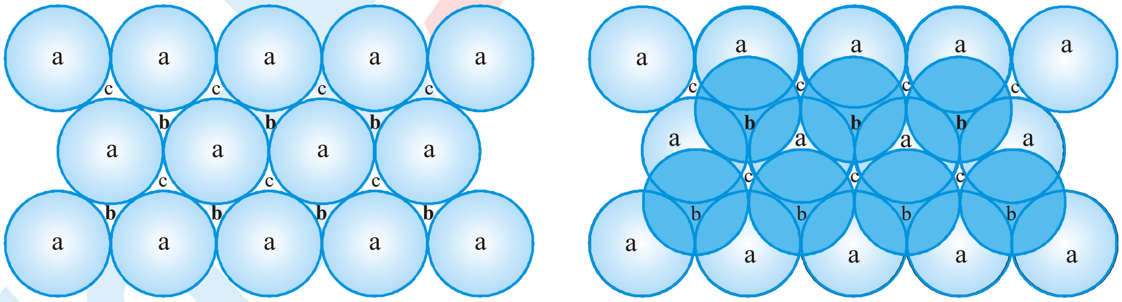
(ii) Another type of arrangement of atoms is shown below. This type of packing is called hexagonal close packing. In such packing one sphere touches six other spheres. In this case 60.4% of the volume is occupied. The remaining 39.6% of the volume is empty and is called void volume. Therefore this type of packing is more stable than the square close packing.



Hexagonal close packing

(b) Three Dimensionally close packing :

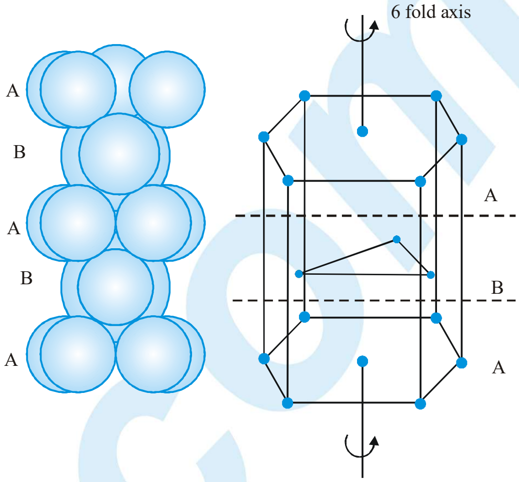
In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.



Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) **(B)** on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following two ways :

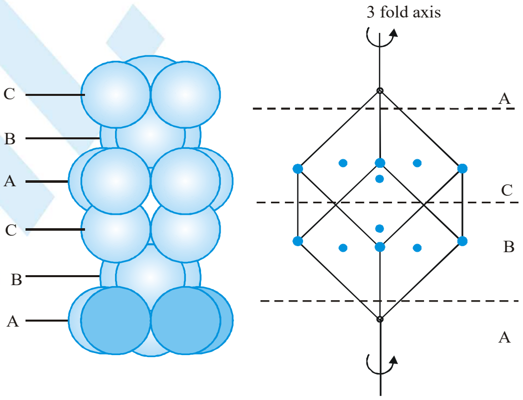
(i) In one way, the spheres of the third layer lie on the spaces of second layer **(B)** in such a way that they lies directly above those in the first layer(A). In other words we can say that the third layer becomes indentical to the first layer. If this arrangement is continued indefinitely in the same order this represented as A BA BA B ....

This type of arrangement represent hexagonal close packing (hcp) symmetry (or structure), which means that the whole structure has only one 6-fold axis of symmetry i.e. the crystal has same appearance on rotation through an angle of 60^0.



ABABAB ..... or hexagonal close packing (hcp) of spheres

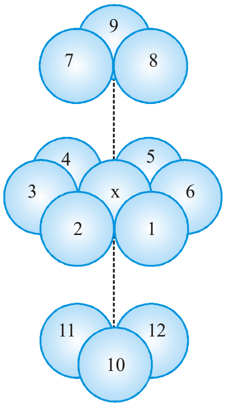
(ii) In second way, the spheres of the third layer **(C)** lie on the second layer **(B)** in such a way that they lie over the unoccupied spaces 'C' of the first layer (A). If this arrangement is continuous in the same order this is represented as ABC ABC ABC.... This type of arrangement represent cubic close packed (ccp) structure.



ABCABCA .... or cubic close packing (ccp) of spheres

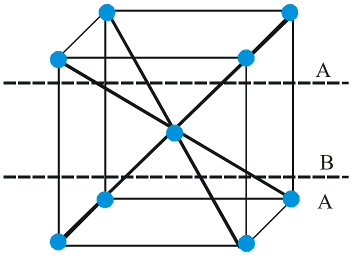
This structure has 3-fold axes of symmetry which pass through the diagonal of the cube. since in this system,there is a sphere at the centre of each face of the unit cell and hence this structure is also known as face-centred cubic (fcc) structure.

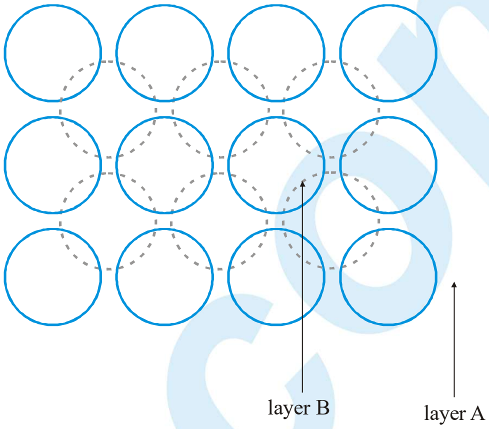
It may be noted that in ccp (or fcc) structures each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.



Coordination number of hcp and ccp structurs

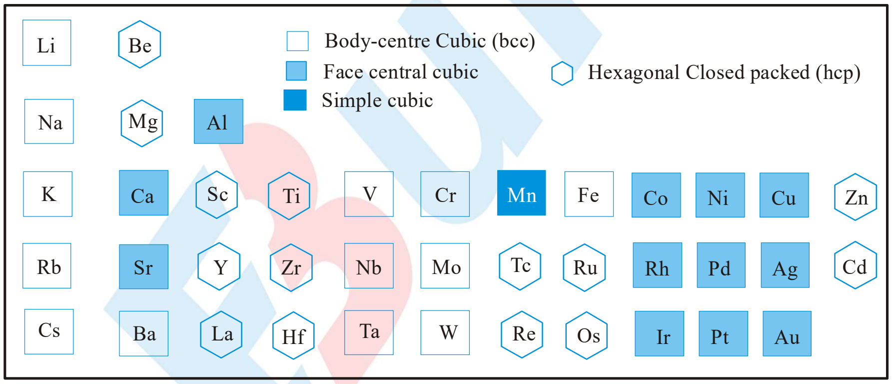
(iii) There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing (which is slightly opened that hexagonal close packing). In bcc arrangement the spheres of the second layer lie at the space (hollows or voids) in the first layer.





Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of IIIrd layer). Therefore coordination number of each sphere is 8 in bcc structure. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

Some examples of metals with their lattice types and coordination number are given in the following table.



☐ Body-centre Cubic (bcc)
▨ Face central cubic
■ Simple cubic
⬡ Hexagonal Closed packed (hcp)

☐ Li	⬡ Be										
☐ Na	⬡ Mg	▨ Al									
☐ K	▨ Ca	⬡ Sc	⬡ Ti	☐ V	☐ Cr	■ Mn	☐ Fe	▨ Co	▨ Ni	▨ Cu	⬡ Zn
☐ Rb	▨ Sr	⬡ Y	⬡ Zr	☐ Nb	☐ Mo	⬡ Tc	⬡ Ru	▨ Rh	▨ Pd	▨ Ag	⬡ Cd
☐ Cs	☐ Ba	⬡ La	⬡ Hf	☐ Ta	☐ W	⬡ Re	⬡ Os	▨ Ir	▨ Pt	▨ Au	

Three dimensional close packing

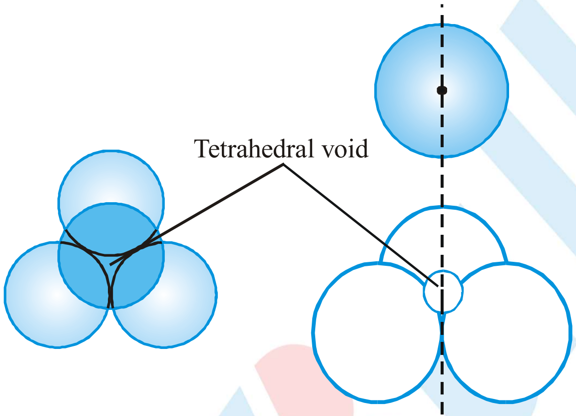
Contents	BCC	CCP/FCC	HCP
Type of packing packing but not close packing	ABAB....... close packing	ABCABC ...... close packing	ABAB ......
No. of atoms	2	4	6
Co-ordination no.	8	12	12
Packing efficiency	68%	74%	74%
Examples V & Cr group Fe	IA, Ba Co group, Ni group, Copper group, all inert gases except helium	Ca, Sr, Al d-block elements Be & Mg	Remaining

Note :- Only Mn crystallizes in S.C.C.

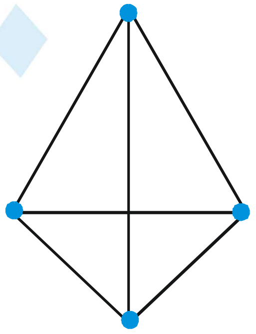
INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

It has been shown that the particles are closely packed in the crystals even than there is some empty space left in between the spheres. This is known as interstices (or interstitial site or holest or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types : (i) tetrahedral interstices and (ii) octahedral interstices.

(i) **Tetrahedral interstices :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp) each sphere of second layer touches with three spheres of first layer. Thus they, leave a small space in between which is known as **tetrahedral site or interstices**. or The vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may by noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.



A tetrahedral interstices



Tetrahedron geometry

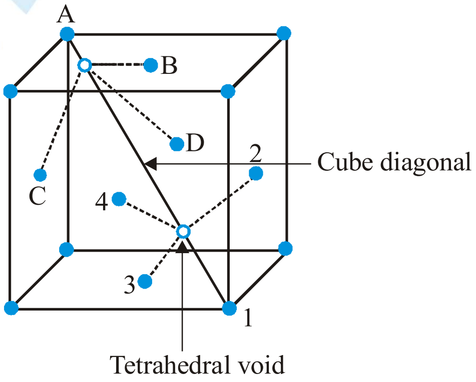
In FCC, one corner and its there face centres form a tetrahedral void

In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral void are present.

In FCC total number of atoms = 4

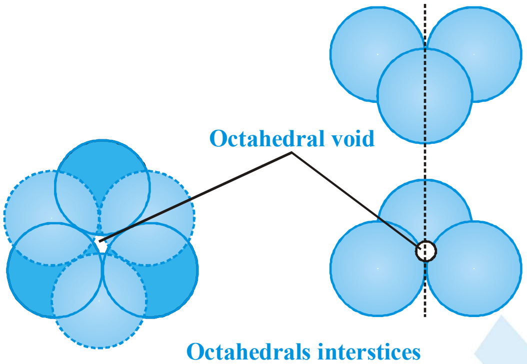
In FCC total number of tetrahedral voids = 8

So, we can say that, in 3D close packing 2 tetrahedral voids are attached with one atom.

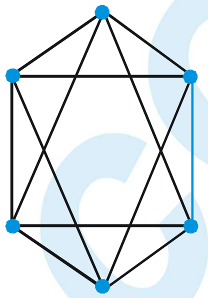


(ii) **Octahedral - interstices :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site) which is called octahedral site (or interstices). or The vacant space between 6 touching spheres is called as octahedral void.

In the figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers.



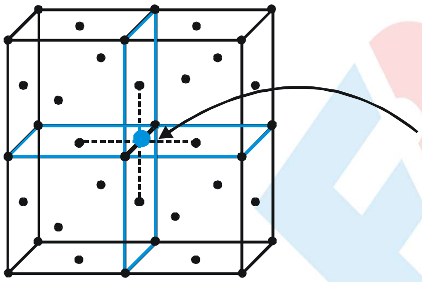
Octahedrals interstices



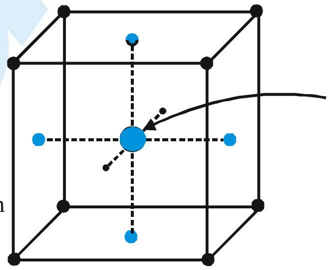
Octahedral Geometry

In FCC, 6 face centres form a octahedral void

The apices of these triangles point are in opposite directions. On super imposing these triangles on one another a octahedral site is created. It may be noted that 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.



Octahedral void (at the edge)
($\frac{1}{4}$th part of Octahedral void is obtained at each edge)



Octahedral void (at the body centre)

In FCC, total number of octahedral voids are $\underset{\text{(Cube centre)}}{(1\times 1)} + \underset{\text{(edge)}}{\left(12\times\frac{1}{4}\right)} = 1+3=4$

In FCC, number of atoms = 4
In FCC, number of octahedral voids = 4
So, we can say that, in any type of close packing one octahedral void is attached with one atom.

Ex. Element A is every element of FCC, atom B is present at every Octahedral void, atom C is present at 25% of Tetrahedral void. Find out the possible molecular formula of the compound ?

Sol. Atom A is every element of FCC = 4 atoms of A
Atom B is present at every octahedral void = 4 atoms of B

Atom C is present at 25% of tetrahedral void = $8\times\frac{25}{100}$ = 2 atom of C

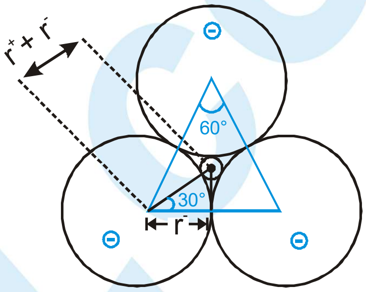
So, the possible molecular formula is $A_4B_4C_2 = A_2B_2C$.

LIMITING RADIUS RATIOS

An ionic crystal contains a large number of cations and anions. Generally cations are Smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability. The stability of the ionic crystal may be described in terms of radius ratio i.e. the ratio of the radius of cation (r) to that of anion (R) is (r/R). The range of (r/R) may be expressed as limiting radius ratio. This value is important to determine the arrangement of the ion in different types of crystals.

Evidently radius ratio (r/R) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.)

(i) **Triangular :** All anions touches each other and co-ordination number is 3



$$\text{Cos}\theta = \frac{r^-}{r^- + r^+}$$

$$\text{Cos } 30° = \frac{\sqrt{3}}{2} = \frac{r^-}{r^- + r^+}$$

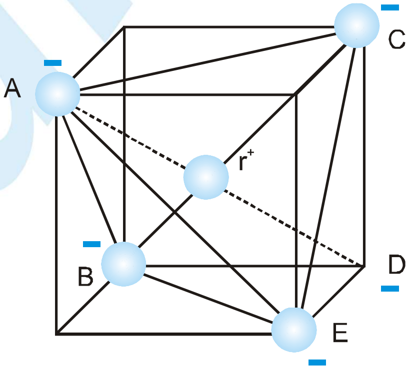
$$\sqrt{3}r^- + \sqrt{3}r^+ = 2r^-$$

$$\sqrt{3}r^+ = \left(2 - \sqrt{3}\right)r^-$$

$$\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = \frac{2-1.73}{1.73} = \frac{0.27}{1.73} = 0.155$$

$$\text{L.R.R.} = 0.155 = \frac{r^+}{r^-} < 1$$

(ii) **Tetrahedral void :** All anions touches each other and co ordination number of cation is 4.



Face diagonal AC = $\sqrt{2}a = 2r^-$

$$r^- = \frac{a}{\sqrt{2}} \text{ or } a = \sqrt{2}r^-$$

Triangle ACD -

$$AD^2 = AC^2 + CD^2$$

$$AD^2 = \left(\sqrt{2}a\right)^2 + (a)^2 = 2a^2 + a^2 = 3a^2$$

$$AD = \sqrt{3}\ a$$

According to cube diagonal AD

✈ $$\frac{\sqrt{3}a}{2} = r^+ + r^-$$

$$\therefore \quad \sqrt{3}a = 2r^+ + 2r^- = AD$$

Put the value of a = $\sqrt{2}\ r^-$

$$\sqrt{3} \times \sqrt{2}\ r^- = 2r^+ + 2r^-$$

$$\frac{\sqrt{3} \times \sqrt{2}\ r^-}{2r^-} = \frac{2r^+ + 2r^-}{2r^-}$$

$$\frac{\sqrt{3}}{\sqrt{2}} = \frac{r^+}{r^-} + 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}}{\sqrt{2}} - 1 \quad \Rightarrow \quad \frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = \frac{1.73 - 1.414}{1.414} = 0.225$$

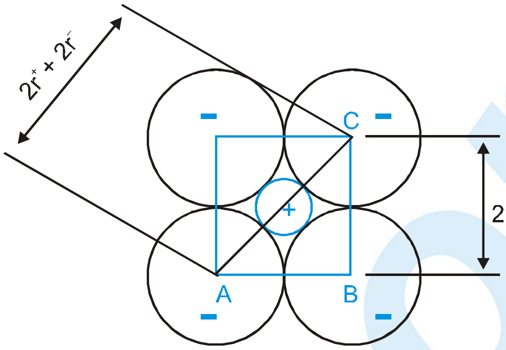
(iii) **Octahedral void :** All the anions are touch each other and co ordination number is 6.

In ΔABC $AC^2 = AB^2 + BC^2$

$= a^2 + a^2$

$AC = \sqrt{2}\ a$

$2r^+ + 2r^- = AC = \sqrt{2}\ a$



$BC = a = 2r^-$

$$\frac{2r^+ + 2r^-}{2r^-} = \frac{\sqrt{2} \times 2r^-}{2r^-}$$

$$\frac{r^+}{r^-} + 1 = \sqrt{2} \quad \Rightarrow \quad \frac{r^+}{r^-} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

(iv) **Cubic void :** All the anions are touch each other and co ordination number is 8.

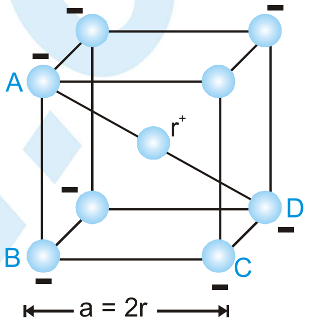
According to cube diagonal

$AD = \sqrt{3}\,a = 2r^+ + 2r^-$

$(a = 2r^- = BC)$

$\sqrt{3} \times 2r^- = 2r^+ + 2r^-$

Dividing by $2r^-$ on both sides.



$$\sqrt{3} = \frac{r^+}{r^-} + 1 \Rightarrow \frac{r^+}{r^-} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$

The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular $\xrightarrow{0.225}$ Tetrahedral $\xrightarrow{0.414}$ octahedral $\xrightarrow{0.732}$ Cubic

Limiting radius ratio for various types of sites

Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planaer	–
0.414 - 0.732	6	Octahedral	NaCl, MgO_2
0.732 - 1.000	8	Cubic	CsCl

Ex. A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

Sol. In Na^+Cl^- crystal each Na^+ ion is surrounded by 6 Cl^+ ions and vice versa. Thus Na^+ ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

or $$\frac{A^+}{B^-} = \frac{r}{R} = 0.414$$

Given that radius of anion (B^-) R = 250 pm i.e. radius of cation (A^+) $r = 0.414\,R = 0.414 \times 250$ pm

or $r = 103.5$ pm

Thus ideal radius for cation (A^+) is r = 103.5 pm.

We know that (r/R) for tetrahedral hole is 0.225.

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

or $r = 0.225\ R = 0.225 \times 250 = 56.25$ pm

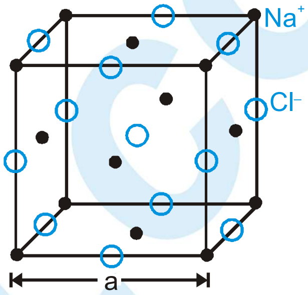
Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of C^+ is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slipped cation C^+ into the tetrahedral site.

NaCl type :

For NaCl : Distance between two nearest ions ($r^+ + r^-$) :-

$$2r^+ + 2r^- = a$$

i.e. $$r^+ + r^- = \frac{a}{2}$$

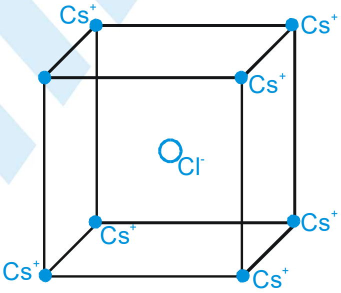


CsCl type :

For CsCl : Distance between nearest ions ($r^+ + r^-$) :-

$$2r^+ + 2r^- = \sqrt{3}\,a$$

$$r^+ + r^- = \frac{\sqrt{3}a}{2}$$



Ex. How many 'nearest' and 'next nearest' neighbours respectively does potassium have in b.c.c. lattice

(A) 8, 8 **(B)** 8, 6 **(C)** 6, 8 **(D)** 8, 2

Ans. **(B)**

Ex. If a metal has a bcc crystal structure, the coordination number is 8, because :

(A) each atom touches four atoms in the layer above it, four in the layer below it and none in its own layer.

(B) each atom touches four atoms in the layer above it, four in the layer below it and one in its own layer.

(C) two atoms touch four atoms in the layer above them, four in the layer below them, and none in their own layer.

(D) each atom touches eight atoms in the layer above it, eight in the layer below it and none in its own layer.

Ans. **(A)**

Ex. Potassium crystallizes in body centered cubic lattice with a unit cell length a = 5.2 Å

(A) What is the distance between nearest neighbours

(B) What is the distance between next nearest neighbours

(C) How many nearest neighbours does each K atom have

(D) How many next nearest neighbours does each K have

(E) What is calculated density of crystalline K.

Sol. **(A)** 4.5 Å, **(B)** 5.2, **(C)** 8 **(D)** 6 (E) 0.92 g/mL

(A) $2r = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 5.2}{2} = 4.5$ Å **(B)** distance = a = 5.2 Å

(C) 8 **(D)** 6

(E) $d = \frac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92$ g/ml

Ex. A metal crystallizes in two cubic phases i.e., FCC and BCC whose unit cell lengths are 3.5Å and 3.0 Å respectively. The ratio of their densities is :

(A) 3.12 **(B)** 2.04 **(C)** 1.26 **(D)** 0.72

Ans. **(C)**

Sol. $d = \frac{ZM}{a^3 N_A}$ $\frac{d_1}{d_2} = \frac{4}{(3.5)^3} \times \frac{(3)^3}{2} = 1.26.$

Ex. In a ccp structure, the :

(A) first and third layers are repeated
(B) first and fourth layers are repeated
(C) second and fourth layers are repeated
(D) first, third and sixth layers are repeated.

Ans. **(B)**

Ex. Lithium borohydride crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are a = 6.8 Å, b = 4.4 Å and c=7.2 Å. If the molar mass is 21.76, then the density of crystals is :

(A) 0.6708 g cm^{-2} **(B)** 1.6708 g cm^{-3} **(C)** 2.6708 g cm^{-3} **(D)** None of these.

Ans. **(A)**

Sol. $d = \frac{ZM}{a^3 N_A} = \frac{4 \times 21.76}{6.8 \times 10^{-8} \times 4.4 \times 10^{-8} \times 7.2 \times 10^{-8} \times 6.023 \times 10^{23}} = 0.6708$ g cm^{2-}.

Ex. An fcc lattice has lattice parameter a = 400 pm. Calculate the molar volume of the lattice including all the empty space:

(A) 10.8 mL **(B)** 96 mL **(C)** 8.6 mL **(D)** 9.6 mL

Ans. **(D)**

Sol. Volume of 4 atoms = $a^3 = (4 \times 10^{-8})^3$ cm^3

volume of N_A atoms $= \frac{(4 \times 10^{-8})}{4} \times 6.023 \times 10^{23} = 9.6$ ml.

Ex. **(a)** In a face centred cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?

(A) 0.543 **(B)** 0.732 **(C)** 0.414 **(D)** 0.637

Ans. **(A)**

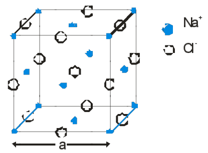
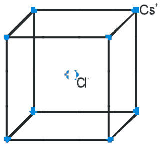
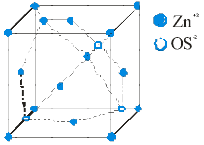
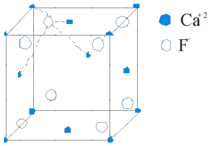
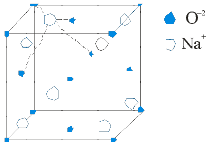
Sol. $\frac{r_{\text{tetrahedral}}}{r_{\text{octahedral}}} = \frac{0.225R}{0.414R} = 0.543.$

(b) The numbers of tetrahedral and octahedral holes in a ccp array of 100 atoms are respectively

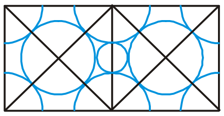
(A) 200 and 100 **(B)** 100 and 200 **(C)** 200 and 200 **(D)** 100 and 100

Ans. **(A)**

TYPES OF IONIC CRYSTAL

S.No.	Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples	
1	NaCl (1 : 1) (Rock Salt Type)	C.C.P. $\langle$ $Na^{+} \rightarrow$ Every element of C.C.P. $Cl^{-} \rightarrow$ At every OHV	6:6	$4Na^{+} + 4Cl^{-}$ 4NaCl	Halides of (Li, Na, K, Rb) Oxides and sulphides of ………………………. ………………………4X	
2	CsCl Type (1 : 1)	B.C.C. $\langle$ $Cs^{+} \rightarrow$ at every corner $Cl^{-} \rightarrow$ at Body centre or at cubic void	8 : 8	$1Cs^{+} + 1Cl^{-}$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS	
3	Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. $\langle$ $Zn^{+2} \rightarrow$ Every element of C.C.P. $S^{-2} \rightarrow$ At 50% of T.H.V. or at alternate tetrahedral voild	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI	
4	CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P. $\langle$ $Ca^{+2} \rightarrow$ Every element of C.C.P. $F^{-} \rightarrow$ At every T.H.V.	$4Ca^{+2} : 8F^{-}$ 8 : 4	$4Ca^{+2} + 8F^{-}$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2 $CaCl_2$, CaF_2	
5	Na_2O Type (2 : 1) (Antiflourine)	C.C.P. $\langle$ $Na^{+} \rightarrow$ At every T.H.V. $O^{-2} \rightarrow$ Every element of C.C.P.	$8Na^{+} : 4O^{-2}$ 4 : 8	$8Na^{+} + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S	
6	ZnS Type (1 : 1) (Wurtzite) another geometry of Zns	H.C.P. $\langle$ $Zn^{+2} \rightarrow$ Every element of H.C.P. $S^{-2} \rightarrow$ 50% of T.H.V. or (at alternate T.H.V.)	4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite	

Ex. Copper has a face-centred cubic structure with a unit-cell edge length of 3.61Å. What is the size of the largest atom which could fit into the interstices of the copper lattice without distorting it?



Figure

(**Hint. :** Calculate the radius of the smallest circle in the figure)

Ans. 0.53Å

Sol. $r_{octahedral} = 0.414\,R$

for FCC $4R = \sqrt{2}\,a$

$$R = \frac{\sqrt{2}\,a}{4}$$

$$r = \frac{0.414\sqrt{2}\,a}{4} = \frac{0.414\sqrt{2}\times 3.61}{4} = 0.53\ \text{Å}$$

Ex. A mineral having formula AB_2 crystallize in the cubic close packed lattice, with the A atoms occupying the lattice points. What is the co-ordination no. of A atoms? of the B atoms? What fraction of tetrahedral sites is occupied by B atoms.

Ans. 8, 4, 100%.

It has fluorite (CaF_2) structure.

Ex. CsBr has b.c.c. structure with edge length 4.3 A. The shortest inter ionic distance in between Cs^+ and Br^- is:

(A) 3.72 **(B)** 1.86 **(C)** 7.44 **(D)** 4.3

Ans. **(A)**

Sol. $r_+ + r_- = \frac{\sqrt{3}\,a}{2} = \frac{\sqrt{3}\times 4.3}{2} = 3.72\ \text{Å}$.

DEFECTS OR IMPERFECTIONS IN SOLIDS

IDEALCRYSTAL

The crystal in which all the lattice points are occupied by the component particles or groups of particles is called an ideal crystal.

Solid state is characterised by vibratory motion about the mean position of constituent particles. At absolute zero, all the types of motions cease, and therefore crystals tend to have a perfectly ordered arrangement. As the temperature increases, molecular motions (vibratory amplitudes) increase and therefore the ions may lose their usual sites and either get missed or occupy interstitial positions in the crystal, ie., deviations from ordered arrangement take place. Any deviation from the perfectly ordered arrangement gives rise to a defect or imperfection in the crystal. Defect in crystals are produced either due to thermal effects or by adding certain impurities in the pure crystals (doping). Defects in crystals may be discussed under two titles :

A. Stoichiometric defects

B. Non-stoichiometric defects

[A] Defects in stoichiometric compounds :

Stoichiometric compounds are those in which the number of positive and negative ions are exactly in the ratio as shown by their chemical formulae. Two types of defects are observed in these compounds.

(i) Schottky defect,

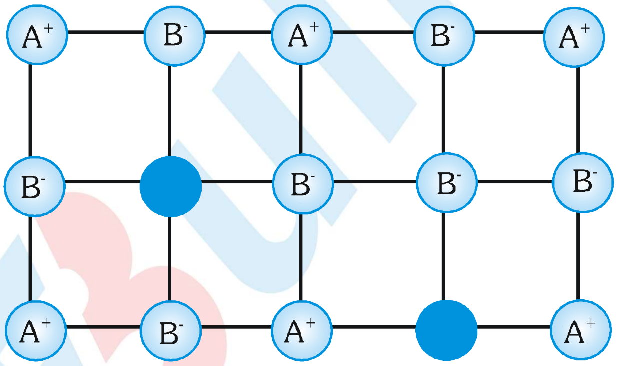
(ii) Frenkel defect

(i) Schottky defect :

This type of defect is produced when one cation and anion are missing from their respective positions leaving behind a pair of holes. The crystal as a whole remains neutral because the number of missing positive ions (cations) and negative ions (anions) is the same

- Schottky defect appears generally in ionic compounds in which radius ratio $[r^+/r^-]$ is not far below unity. For this defect, the cations and anion should not differ much in size.
- For schottky defect, co-ordination numbers of the ions should be high, Examples of ionic solids showing this defect are NaCl, CsCl, KCI, KBr etc.

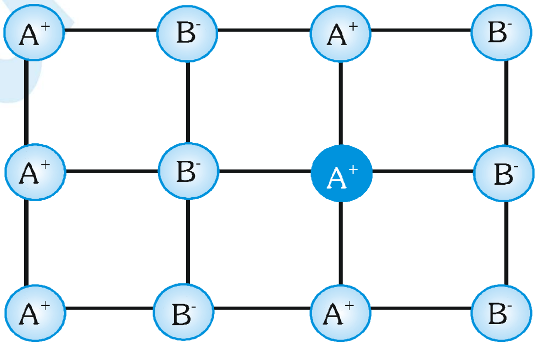
  Consequences of schottky defect :
- Density of the crystal decreases
- The crystal begins to conduct electricity to small extenet by ionic mechanism.
- The presence of too many 'voids' lowers lattice energy or the stability of the crystal.



Schottky defect

(ii) Frenkel defect :

This type of defect is created when an ion leaves its appropriate site in the lattice and occupies an interstitial site. A hole or vacancy is thus produced in the lattice.



Frenkel defect

The electroneutrality of the crystal is maintained since the number of positive and negative ions is the same. Since positive ions are small, in size, they usually leave their positions in the lattice and occupy interstitial positions.

Frenkel defect is exhibited in ionic compounds in which the radius ratio $[r^+/r^-]$ is low. The cations and anions differ much in their sizes and the ions have low co-ordination numbers. Examples are ZnS, AgBr, AgI, AgCl.

CONSEQUENCES OF FRENKEL DEFECT :

- The closeness of like charges tends to increase the dielectric constant of the crystal.
- The crystal showing a frenkel defect conducts electricity to a small extent by ionic mechanism.
- The density of the crystal remains the same.

[B] Non-stoichiometric defect :

These types of defects are observed in the compounds of transitional elements. These defects arise either due to the presence of excess metal ions or excess non-metal ions.

(i) Metal excess defect due to anion vacancies :

A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron.

Ionic crystal which are likely to posses schottky defect, may also develop this type of metal excess defect.

When alkali metal halides are heated in a atmosphere of vapours of the alkali metal, anion vacancies are created. The anions (halide ions) diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cations. The e^- lost by the metal atom diffuse through the crystal are known as F-centres. The main consequence of metal excess defect is the development of colour in the crystal. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow.

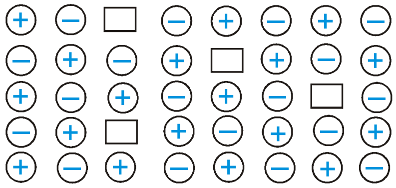
Similarly, KCI crystal when heated in an atmosphere of potassium vapours, it appear violet.

(ii) Metal excess defect due to interstitial cations :

This type of defect is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial site. To maintain electrical neutrality, an electron is present in the intrestitial site. An example showing this type of defect is ZnO. When ZnO is heated, it loses oxygen reversibly. The excess Zn^{++} ions are accommodated in the interstitial sites, the, electrons are enclosed in the neightbouring interstitials. The yellow colour of ZnO when hot is due to these trapped electrons. These electrons also explain electrical conductivity of the ZnO crystal.

Doping : The addition of small amount of foreign impurity in the host crystal is called as doping. It results in an increase in the electrical conductivity of the crystal. Doping of group 14 elements (such as Si, Ge, etc.) with elements of group 15 (such as As) produces an excess of electrons in the crystals, thus giving n-types semiconductors. Doping of groups 14 elements with group 13 elements (such as Indium) produces holes (electron deficiency) in the crystals. Thus p-type semiconductors are produced. Then symbol 'p' indicates flow of positive charge.

Ex. Which of the following is incorrect



(A) The defect is known as schottky defect

(B) Density of compound in the defect decreases

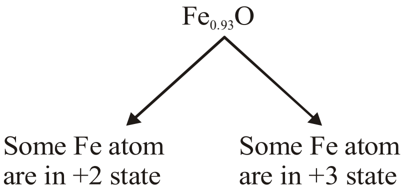
(C) NaCl(s) is example which generally shows this defect

(D) Stoichiometry of compound will change slightly.

Ans. **(D)**

Ex. Ferrous oxide (FeO) is experimentally found to have the formula Fe0.93O. Find the %age of Fe ions in +3 state.

Sol.



Let there is xFe atom in +3 state

$3x + 2(93 - x) = 200$

$x = 14$

$$\% \, Fe^{3+} = \frac{14}{93} \times 100\% = \frac{1400}{93}\%$$

$\approx 15.54\%$

PROPERTIES OF SOLIDS

(i) Electrical Properties

(ii) Magnetic Properties

(i) **Electrical Properties:** Solids exhibit an amazing range of electrical conductivities, the range of electrical conductivities from 10^{-20} to 10^{7} ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(1) **Conductors :** Metals are goods conductors and have conductivities in the order 10^{7} $(\Omega m)^{-1}$.

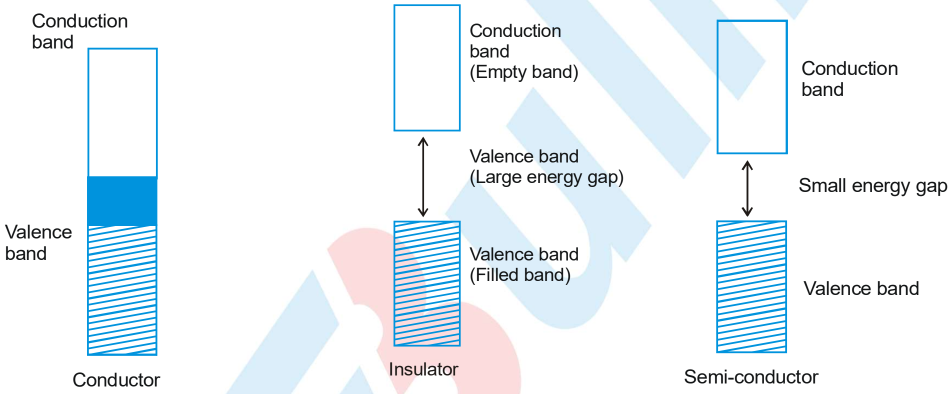
(2) **Insulators :** Those solids which have very low conductivities ranging from 10^{-20} to 10^{-10} $(\Omega m)^{-1}$ are electrical insulators e.g.; MnO, CoO; NiO, CuO, Fe_2O_3, TiO_2.

(3) **Semiconductors :** Those solids which have intermediate conductivities generally from 10^{-6} to 10^{4} $(\Omega m)^{-1}$ are termed as semiconductors.

Intrinsic Semiconductors : The conduction by pure substances such as silicon and germanium is called intrinsic conduction and these pure substances exhibiting electrical conductivity are called intrinsic semiconductors.

CAUSES OF CONDUCTANCE IN SOLIDS

1. In most of the solids, conduction is through electron movement under an electric field.
2. In ionic solids conduction is by movement of ions in molten state.
3. The magnitude of electrical conductivity strongly depends upon the number of electrons available to take part in conduction process.
4. In metals, conductivity strongly depends upon the number of electrons available per atom. The atomic orbitals form molecular orbitals which are too close in energy to each other so as to form a band.
5. If conduction band is not completely filled or it lies very close to a higher unoccupied band, then electrons can flow easily under an electric field thereby showing conductivity.
6. In case of insulators, the gap between valence band conduction band is too large, so electrons cannot jump from valence band to conduction band and very small conductivity is observed.
7. In case of semiconductors, the gap between valence band and conduction band is small and therefore some of the electrons may jump from valence band to conduction and some conductivity is observed.
8. Electrical conductivity of semiconductors increases, with increase in temperature. This is due to the fact that with increase in temperature, large number of valence electrons from the valence band can jump to conduction band. Pure substances like silicon and germanium that exhibit this type of conducting behaviour are called intrinsic semiconductors.
9. For particle purpose, the conductivity of pure silicon and germanium is too low at room temperature, therefore, there is need to increase the conductance by doping.



Figure

Doping : The conductivity of silicon and germanium can be increases by adding appropriate amount of suitable impurity. The process is called doping.

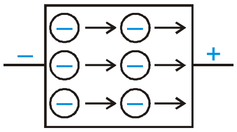
Type of Semiconductors

(1) **n-Type Semiconductors :** Metal excess compounds conduct electricity through normal electron conduction mechanism and are therefore n-type semiconductors.

Creation n-Type Semiconductor

1. When silicon is doped with small amount of group -15 elements such as P, As or Sb, its electrical condcutivity increases sharply.
2. In pure silicon each silicon atom uses its four valence electrons for the formation of four covalent bonds with the neighbouring silicon atoms.
3. When silicon is doped with some group-15 element, the some of the positions in the lattice are substituted by atoms of groups -15 elements have five valence electrons. After forming the four covalent bonds with silicon (or anyother group-14 element such as germanium). One excess electron is left on them.

4. Since this electron is not involved in bonding it becomes delocalized and contribute to electrical conduction. Silicon doped with group 15 element behaves as a n-type semiconductor.

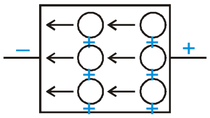


n-type semiconductor

(2) p-Type Semiconductors : Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore p-type semiconductors.

Creation p-Type Semiconductor

1. Electrical conductivity of silicon or germanium can also be increases by doping with some group-13 element such as B, Al or Ga.
2. Goup-13 elements have only three valence electrons. The combine with group-14 elements to form an electron deficient bond or electron vacancy or a hole. These holes can move though the crystal like a positive charge giving rise to electrical condcutivity.
3. Gorup-14 elements doped with group-13 elements behave as p-type semiconductors. In the presence of electrical field the holes move in direction opposite to that of electrons.



p-type semiconductor

Application of n-type and p-type semiconductors

1. Diode is a combination of n-type and p-type semiconductors used as rectifier.
2. They are used for making transistors which contains n-p-n and p-n-p junctions to amplify radio and audio signals.
3. The solar cell is photo-diode used to convert light energy into electrical energy.

13-15 Compounds : The solid state materials are produced by combination of elements of groups 13 and 15 the compounds thus obtained are called 13-15 compounds e.g. In Sb, AlP GaAs.

12-16 Compounds : The solid state compounds are obtained by combination of elements for groups 12 and 16 the compounds are called 12-16 compounds e.g. ZnS, CdS, CdSe and HgTe.

Super Conductivity : The electrical resistance of metals is found to depend on temperature. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero. Materials in this state are said to possess. Superconductivity. The phenomenon of superconductivity was first discovered by kamerlingh Onners in 1913 when he found that mercury becomes superconducting at 4.0 K temperature.

Transition Temperature : The temperature at which a substance starts behaving as super-conductor is called transition temperature.

(ii) Magnetic Properties of Solids

Solids can be divided into different classes. Depending on their response to magnetic fields.

(a) Paramagnetic (weakly magnetic) : Such materials contain permanent magnetic dipoles due to the presence of atoms, ion or molecules with unpaired electrons e.g. O_2, Cu^{+2}, Fe^{+3} and they are attracted by the magnetic field. They however lose their magnetism in the absence of a magnetic field.

(b) Diamagnetic : They are weakly repelled by magnetic fields. Diamagnetism arises due to the absence of unpaired electrons e.g. H^-, Li^+, Be^{+2}, (2 electron type), O^{-2}, F^-, Na^+, Mg^{+2} (8 electron type), Ag^+, Zn^{+2}, Cd^{+2} (18 electron type).

(c) Ferromagnetic : It is caused by spontaneous alignment of magnetic moments in the same direction.

(d) Ferrimagnetism : It occurs when the moments are aligned in parallel and antiparallel direction in unequal number resulting in a net moment e.g. Fe_3O_4.

(e) Antiferromagnetism : It occurs if the alignment of moments is in a compensatory way so as to give zero net moment e.g. MnO.

All magnetically ordered solids (ferromagnetic and antiferromagnetic solids) transform to the paramagnetic state at some elevated temperatures. This is most probably due to the randomisation of spins.

↑ ↑ ↑ ↑ ↑↑

Ferromagnetic character

↑ ↓ ↑ ↓ ↑↓

Antiferromagnetic character

↑↑ ↓↑ ↑↓

Ferrimagnetic character

Effect of Temperature on Metal (Conductor) Semiconductor or Insulator

1. The conductivity of semiconductors and insulators increases with increase in temperature
2. The conductivity of metal (conductors) decreases with increase in temperature.

Ex. What is a semiconductor? Name the two main types of semiconductors.

Ans. Substances whose conductance lies in between that of metals (conductors) and insulators are called semiconductors. Two main types of semiconductors are n-type and p-type.

Ex. Explain the following with suitable examples:

(i) Ferromagnetism (ii) Paramagnetism (iii) 12-16 and 13-15 group compounds.

Ans. (i) **Ferromagnetism :** When substances show permanent magnetism even in the absence of the magnetic field this phenomenon is called as Ferromagnetism and such substances as called as Ferromagnetic substances e.g. Fe Ni Co and CrO_2.

This type of magnetism arise due to the spontaneous alignment of magnetic moments due to unpaired electron in the same direction.

(ii) **Paramagnetism :** When substances which are attracted by the external magnetic field are called paramagnetic substances and the phenomenon is called as paramagnetism. Atoms ion or molecules containing unpaired electron show this property, eg. O_2 Cu^{2+}, Fe^{3+} etc. these substances lost their magnetism in the absence of magnetic field.

(iii) **13-15 Compounds :** The solid state materials are produced by combination of elements of groups 13 and 15 the compounds thus obtained are called 13-15 compounds e.g. InSb, AlP GaAs.

12-16 Compounds : The solid state compounds are obtained by combination of elements for groups 12 and 16 the compounds are called 12-16 compounds e.g. ZnS, CdS, CdSe and HgTe.

1. Various type of Criptals

Some Important Characteristics of Various types of Crystals

S.No.	Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1	Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2	Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole -dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3	Hardness	Hard	Very hard Graphite is soft	Soft	Hard or soft
4	Brittleness	Brittle	Intermediate	Low	Low
5	Melting point	High	Very high	Low	Varying from moderate to high
6	Electrical	Semi conductor due to crystal imperfections, conductor is fused state	Non-conductor Graphiteis good	Bad conductor	Good conductors
7	Solubility in	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
8	Heat of Vaporisation (kj mol^{-1})	NaCl(s) 170-75	Graphite 718-43	$NH_3(s)$ 23.55	Cu(s) 304.59
9	Heat of fusion (kj mol^{-1})	NaCl 28.45	– –	NH_3 (s) 5.65	Cu(s) 13.016
10	Example	NaCl, KNO_3 CsCl, Na_2SO_4	Diamond, graphite, Quartz, (SiO_2), SiC	$H_2O(s)$, $CO_2(s)$, Sulphur, Sugar, Iodine,noble gases	Na, Cu, Ag, Fe, Pt, alloys

The Seven Crystal Systems

S.No.	Name of System	Axes	Angles	Bravais Lattices
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred = 4
5	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive, End - centred = 2
6	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\beta \neq 120°$	Primitive = 1 Total = 14

Cubic unit cell

Unit cell	Relation between r and a	Packing fraction	Co-ordinatin number	Effective number of particle
Simple cubic	$r = \frac{a}{2}$	52.4%	6	1
Body centred cubic	$r = \frac{a\sqrt{3}}{4}$	68%	8	2
Face centred cubic	$r = \frac{a\sqrt{2}}{4}$	74%	12	4

Density : $d = \frac{ZM}{N_A \, x \, a^3}$ gm / cm^3

Where Z = effective number of particle

M= molar mass

N_A = Avogarodro's number

a = edge length (cm)

2. Three dimensional close packing

Hexagonal Close Packing (HCP)

Effective number of particle = 6

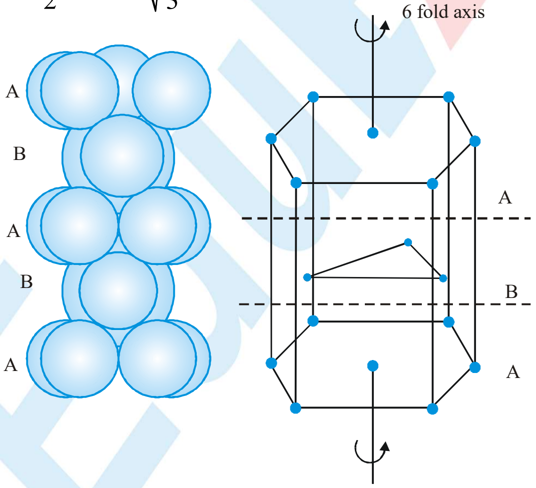
Effective number of octahedral void = 6

Effective number of tetrahedral void = 12

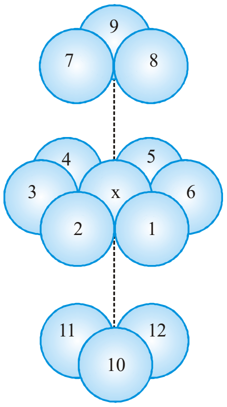
Packing fraction

= 74% ; co-ordination number = 12

$a = \frac{r}{2}$; $b = 4\sqrt{\frac{2}{3}}\,r$



ABABAB ..... or hexagonal close packing (hcp) of spheres



Coordination number of hcp and ccp structurs

Cubic Close Packing (CCP)

Effective number of particle = 4

Effective number of octahedral void = 4

Effective number of tetrahedral void = 8

Packing fraction = 74% ;

co-ordination number =12

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

3. Different Type of Voids and their Radius Ratio

Limiting radius ratio for various types of sites

Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planaer	–
0.414 - 0.732	6	Octahedral	NaCl, MgO_2
0.732 - 1.000	8	Cubic	CsCl