THE SOLID STATE

SECTION I

STRUCTURE AND CLOSE PACKING

A solid is a state of matter which possesses
i) definite shape and volume.
ii) incompressibility, rigidity and mechanical strength.
iii) the particles in solids are very closely packed in some geometric pattern with small voids and interparticle forces are very strong.
iv) particle motion is restricted to vibratory motion only.

CLASSIFICATION OF SOLIDS

The solids are of two types:

(i) Amorphous solids
Solids in which constituents do not possess the orderly arrangement over the long range are called amorphous solids. Region in an amorphous solid having an orderly arrangement are known as crystallite. They may have only short range order and do not posses sharp melting points. They undergo irregular cleavage (cut). Structures of amorphous solids are similar to that of liquid. Amorphous solids soften over range of temperature and can be molded and blown in to various shapes. On heating they become crystalline at some temperature. Therefore some time they are called as pseudo solids or super cooled liquids. Glass become milky some times on heating is due to this property. Due to lack of long range arrangement of particles or irregular arrangement of particles, amorphous solids are isotropic in nature. It is physical properties like resistivity. Refractive index is independent of direction
Examples: Glass rubber and plastics are typical examples of amorphous solids. Structure of quartz is crystal while quartz glass is amorphous. Amorphous silicon is one of the best photovoltaic materials available for conversion of sunlight to electricity

(ii) CRYSTALLINE SOLIDS
Solids in which various constituents unit like atoms, ions or molecules are arranged in an orderly manner which repeats itself over long distance are called crystalline solids. They exhibit very sharp melting points and undergo clean cleavage (cut). Crystalline solids are anisotropic in nature, that is, some physical property like electrical resistance, refractive index shows different values when measured along different direction in the same crystal. Reason for such behavior is particles are arranged differently along different direction.
Examples: all metallic elements, non-metallic elements like sulphur, phosphorous and ionic compound like sodium chloride, zinc sulphide and naphthalene
CLASSIFICATION OF CRYSTALLINE SOLIDS

Crystalline solids can be classified on the basis of nature of intermolecular forces operating between them into following four categories

i) Molecular  ii) Ionic  iii) metallic  iv) covalent

(i) Molecular solids:
Further divided into three categories

a) Non-polar molecular solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Bonding force</th>
<th>Binding energy in (kJ/mol)</th>
<th>Melting point</th>
<th>Physical nature</th>
<th>Electrical conductivity</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Non-polar molecules</td>
<td>Dispersion forces or London forces</td>
<td>0.05-40</td>
<td>Very low about 84</td>
<td>Soft</td>
<td>Insulator</td>
<td>H₂, N₂, O₂, He, NA Ar, Kr</td>
</tr>
</tbody>
</table>

b) Polar molecular solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Bonding force</th>
<th>Binding energy in (kJ/mol)</th>
<th>Melting point</th>
<th>Physical nature</th>
<th>Electrical conductivity</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Polar molecules</td>
<td>Dipole -dipole interaction</td>
<td>5-25</td>
<td>low about 158</td>
<td>Soft</td>
<td>Insulator</td>
<td>HCl, HBr, SO₂, SO₃ etc</td>
</tr>
</tbody>
</table>

c) H-bonded molecular solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Bonding force</th>
<th>Binding energy in (kJ/mol)</th>
<th>Melting point</th>
<th>Physical nature</th>
<th>Electrical conductivity</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Polar molecules containing O, N F and H</td>
<td>Hydrogen bonding and Dipole -dipole interaction</td>
<td>10-40</td>
<td>low about 273</td>
<td>Hard</td>
<td>Insulator</td>
<td>H₂O (ice)</td>
</tr>
</tbody>
</table>

(ii) Ionic solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Bonding force</th>
<th>Binding energy in (kJ/mol)</th>
<th>Melting point</th>
<th>Physical nature</th>
<th>Electrical conductivity</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Ions</td>
<td>Electrostatic force of attraction</td>
<td>400-4000</td>
<td>High 1500</td>
<td>Hard but brittle</td>
<td>Insulator in solid state but conductor in molten and in aqueous state</td>
<td>NaCl, KCl, CuSO₄, CaF₂, CsCl etc</td>
</tr>
</tbody>
</table>
iii) Metallic solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Positively charged ions (kernels) in a sea of mobile electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Bonding force</td>
<td>Metallic bonding</td>
</tr>
<tr>
<td>ii</td>
<td>Binding energy in (kJ/mol)</td>
<td>70-1000</td>
</tr>
<tr>
<td>iii</td>
<td>Melting point</td>
<td>800-1000</td>
</tr>
<tr>
<td>iv</td>
<td>Physical nature</td>
<td>Hard but malleable and ductile except Na, K, Li etc</td>
</tr>
<tr>
<td>v</td>
<td>Electrical conductivity</td>
<td>conductor</td>
</tr>
<tr>
<td>vi</td>
<td>Examples</td>
<td>Fr, Cu, Zn, Ni, Co, Al, Au, Pt etc</td>
</tr>
</tbody>
</table>

iv) Covalent or Network solids:

<table>
<thead>
<tr>
<th></th>
<th>Constituent particles</th>
<th>Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Bonding force</td>
<td>Covalent bonds</td>
</tr>
<tr>
<td>ii</td>
<td>Binding energy in (kJ/mol)</td>
<td>150-500</td>
</tr>
<tr>
<td>iii</td>
<td>Melting point</td>
<td>High 4000</td>
</tr>
<tr>
<td>iv</td>
<td>Physical nature</td>
<td>Hard</td>
</tr>
<tr>
<td>v</td>
<td>Electrical conductivity</td>
<td>Insulator except graphite</td>
</tr>
<tr>
<td>vi</td>
<td>Examples</td>
<td>SiO₂, diamond, graphite, SiC (carborundum)</td>
</tr>
</tbody>
</table>

CRYSTAL LATTICE AND UNIT CELL

Crystal lattice:
The regular arrangement of an infinite set of points which describes the three dimensional arrangement of constituent particles (atom, ions, molecules) in space is called a **crystal lattice or space lattice**. The space lattice may be one, two or three dimensional depending upon the number of parameters required to define it.

There are only 14 possible three dimensional lattices. They are called **Bravais Lattice**.

Following are the characteristics of a crystal lattice:
(i) Each point in a lattice is called lattice point or lattice site
(ii) Each point in a crystal lattice represents one constituent particle which may be atom, ion or molecule
(iii) Lattice points are joined by straight line to bring out the geometry of the lattice

The smallest repeating units of space lattice which when repeated over and over again in three dimensions, result into whole of the space lattice of crystal is called **unit cell**. The crystal may, therefore be considered to consists of infinite number of unit cells.

A unit cell is characterized by:
(i) its dimensions along the three edges a, b, c. These edges may or may not be perpendicular to each other
(ii) angle between edges α (between b and c); β (between a and c) and γ (between a and b).

Thus unit cell is characterized by six parameters.
Types of unit cells:
(i) Simple or primitive
The unit cells in which, particles (i.e. atoms, ions, or molecules) are present only at the corners of the unit cell are called simple or primitive cells

(ii) Face-centered
In this type of unit cells, points are represented at the corners as well as centers of each six faces

(iii) Body-centered
These are the unit cells in which points are present at the corners and an additional point is present at the centre of the unit cell

(iv) End centered
The unit cell in which points are present at the corners and at the centre of the two ends faces

Number of atoms in unit cell
It should be noted that
(i) An atom present at the corner is equally shared by eight unit cells. Therefore contribution of an atom present at the corner to each unit cell is $\frac{1}{8}$
(ii) An atom present at the face centre is equally shared between two unit cells. Therefore, contribution of an atom present at the face centre towards each unit cell is $\frac{1}{2}$
(iii) An atom present within the body of the unit cell (body centre) is shared by no other unit cell. Hence, contribution of an atom present within body of unit cell is 1.
(iv) An atom present at the edge centre of unit cell is equally shared by four unit cells. Therefore, contribution of an atom present at the edge centre towards each unit cell is $\frac{1}{4}$
The point representing the atoms, molecules or ions in a unit cells are known as *lattice point* and is denoted by $Z$. Also called as *Rank of a crystal*.

The number of lattice points (or number of atoms) per unit cell in the above four types of unit cells may be calculated as follows -

<table>
<thead>
<tr>
<th>Type</th>
<th>Simple or Primitive</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Simple or Primitive</td>
<td>$8 \times \frac{1}{8}$ ($from$ corners) $= 1$</td>
<td></td>
</tr>
<tr>
<td>b Face-centered</td>
<td>$8 \times \frac{1}{8}$ ($from$ corners) $+ 6 \times \frac{1}{2}$ ($from$ face centre) $= 4$</td>
<td></td>
</tr>
<tr>
<td>c Body-centered</td>
<td>$8 \times \frac{1}{8}$ ($from$ corners) $= 1 1$ ($from$ body centre) $= 2$</td>
<td></td>
</tr>
<tr>
<td>d End-centered</td>
<td>$8 \times \frac{1}{8}$ ($from$ corners) $+ 2 \times \frac{1}{2}$ ($from$ end faces) $= 2$</td>
<td></td>
</tr>
</tbody>
</table>

**Unit cells of 14 types of Bravais Lattices**

<table>
<thead>
<tr>
<th>System</th>
<th>Axial Ratio</th>
<th>Axial angles</th>
<th>Unit cells</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Cubic regular</td>
<td>a = b = c</td>
<td>$\alpha = \beta = \gamma$ all $90^\circ$</td>
<td>1) simple  2) face centered  3) body centered</td>
<td>NaCl, KCl, ZnS, Cu$_2$O, Pb,Ag, Au, Hg, diamond, Alums</td>
</tr>
<tr>
<td>2 Tetragonal</td>
<td>a = b $\neq$ c</td>
<td>$\alpha = \beta = \gamma$ all $90^\circ$</td>
<td>4) simple  5) Body centered</td>
<td>SnO$_2$, ZnO$_2$, TiO$_2$, NiSO$_4$, ZrSiO$_4$, PbWO$_4$, White Sn</td>
</tr>
<tr>
<td>3 Hexagonal</td>
<td>a = b $\neq$ c</td>
<td>$\alpha = \beta = 90^\circ$ $\gamma = 120$</td>
<td>6) simple</td>
<td>ZnO, PbI$_2$, CdS, HgS, Graphite, Ice, Beryl, Mg, Zn, Cd</td>
</tr>
<tr>
<td>4 Trigonal or Rhombohedral</td>
<td>a = b = c</td>
<td>$\alpha = \beta = \gamma$ $\neq 90$</td>
<td>7) simple</td>
<td>NaNO$_3$, CaSO$_4$, Calcite, Quarts, As, Sb, Bi</td>
</tr>
<tr>
<td>5 Orthorhombic (Rhombic)</td>
<td>a $\neq$ b $\neq$ c</td>
<td>$\alpha = \beta = \gamma$ all $90^\circ$</td>
<td>8) Simple  9) face centered  10) Body centered  11) end centered</td>
<td>KNO$_3$, K$_2$SO$_4$, Calcite, BaSO$_4$, Rhombic sulphure, MgSO$_4$.7H$_2$O</td>
</tr>
<tr>
<td>6 Monoclinic</td>
<td>a $\neq$ b $\neq$ c</td>
<td>$\alpha = \gamma = 90^\circ$ $\beta \neq 90$</td>
<td>12) Simple  13) End centered</td>
<td>Na$_2$SO$_4$.10H$_2$O, Na$_2$B$_2$O$_7$.10H$_2$O CaSO$_4$.2H$_2$O. Monoclinic sulphur</td>
</tr>
<tr>
<td>7 Triclinic</td>
<td>a $\neq$ b $\neq$ c</td>
<td>$\alpha \neq \beta \neq \gamma$ $\neq 90$</td>
<td>14) Simple</td>
<td>CuSO$_4$.5H$_2$O, K$_2$Cr$_2$O$_7$, H$_3$BO$_3$</td>
</tr>
</tbody>
</table>

**Solved example**:  
Q) A compound formed by the element X and Y crystallizes in cubic structure in which X atoms are at the corners of the cube with Y atoms are at the centre of the face. What is the formula of the compound.
Solution:
The number of X–atoms per unit cell \(8 \times \frac{1}{8}\) (from corners) = 1
Number of Y atoms per unit cell = \(6 \times \frac{1}{2}\) (from face centre) = 3
Thus chemical formula = \(XY_3\)

CLOSE PACKING OF CRYSTALLINE SOLIDS

*Close packing* refers to tight arrangement of spheres in a given space in such a way that they occupy the maximum available space and hence the crystal has maximum density.

The number of nearest neighbors of a particle is called **coordination number**

a) Close packing in one dimension:
There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange in row and touching each other. Coordination number is 2

b) Two dimensional close packing

(1) Square close packing
Here spheres are arranged in such a way that every sphere is in contact with four other spheres coordination number 4 since second row exactly below first such arrangement is called AAA type arrangement

(2) Hexagonal close packing:
In this kind of packing, spheres are arranged in such a way that every sphere is in contact with six other spheres. Coordination number 6

The second row may be placed above the first in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of first row is called A type, the one in second row is different type and may be called B type. When third row is placed are line with first row then this row is also A. And arrangement is known as ABAB type

c) Three dimensional close packing
Two types of three dimensional close packing are obtained from hexagonal close packing layers a) Hexagonal close packing (hcp) b) Cubic close packing (ccp)
While other two types of three dimensional close packing are obtained from square close packed layers. c) Body Centered cubic arrangement (bcc) and d) simple cubic arrangement
a) Hexagonal Close –packing (hcp)
In this arrangement, atoms are located at the corners and centre of two hexagonal placed parallel to each other, three more atoms are placed in a parallel to midway between these two planes:

Characteristic features of hcp
(i) This type of packing is ABAB... type of arrangement of the layers which indicates that every alternate layers are alike
(ii) It has a 6-fold axis of symmetry
(iii) Each atom is surrounded by 12 another atoms, 6 in own layer and 3 above and 3 blow layers. Coordination number 12
(iv) In hcp arrangement, the atom occupy 74% of the available space and thus 26% of space is empty
(v) It has only one set of parallel close –packed layers. Hence, the chances for slipping of one layer over the other is less..
Example : BE, Cd, Li, Ca, Cr, Mo, V, Mg, Zn, Ce, Zr, OS, Ru, He

b) Cubic closed packing (ccp) or face centered cubic (fcc)
In this type of close packing, atoms are arranged at the corners and at the centers of all six faces of a cube.
If we start with hexagonal layers of spheres as shown in figure and second layer of spheres is arranged placing the spheres over the holes in first layer, one half of the holes can be filled by these spheres. Suppose that spheres in third layers are so arranged that they cover holes in second layer, the third layer neither resembles first layer or second layer. The fourth layer resembles first, fifth resembles second and sixth resembles third layer, then this type of arrangement is known as cubic closed-packed (ccp) arrangement or face centered cubic (fcc) arrangement. The percentage of free space is 26% and coordination number is 12.
Characteristic features of ccp:
(i) This type of packing has ABCABC... type of arrangement of the layer i.e. the first three layers are quite different from each other but this set of layer is repeated over and again the addition of more layers
(ii) It has cubic symmetry, the whole structure has four 3-fold axis of symmetry
(iii) As in hcp, each atom in ccp arrangement has 12 nearest has 12 nearest neighbors i.e. the coordinate number of each atom is 12
(iv) The ccp arrangement of atoms occupies 74% of the available space and thus 26% of the space remains empty.
(v) It has four sets of parallel close packed layers. Hence, the chances for slipping of one layer over the other are more in the ccp arrangement than in the hcp arrangement. Hence, metals having ccp structure
(vi) Example : Cu, Ag, Au, Pt, Al, Cr, Co, Cu, Ag, Fe, PB, Mn, Ni, Ca, Sr, Pt all noble gases except He are found to possess cubic close packed structure. Nearly 60% of the metals have been found to possess either hcp or ccp structure.

c) Body – Centered cubic structure (bcc)
Characteristic feature of body centered cubic arrangement:
i) In a body centered cubic arrangement, the atoms occupy corners of a cube with an atom at its centre.
(ii) Each atom is in contact with eight other atoms (four atoms in the layer just above and four atoms in the layer just below) and hence the coordination number in this type of arrangement is only eight
(iii) This arrangement of atoms occupies only 68% of the total volume, so this arrangement is found in Na, K, Cs, Rb, W, V, Mo, and Ba. Only 20% of the metallic elements found to posses bcc arrangement.
d) Simple cubic arrangement
The particles in the adjacent rows may show a horizontal as well as a vertical alignment forming cubic. A central sphere is surrounded by four other spheres in two dimension and in three dimension surrounded by 6 spheres

VOIDES OR HOLES
A crystal is formed as result of close packing of its constituting particles which are supposed to have spherical shape. Since they are touching each other only at one point, there must remain some empty spaces are called voids or holes or interstitial site

a) Tetrahedral voids
The voids, which are surrounded by four spheres which lie at the vertices of a regular tetrahedron are called tetrahedral void. There are 8 tetrahedral voids around each sphere. If N are the number of close packed sphere than tetrahedra voids are 2N. coordination number of tetrahedral void is 4
If r = radius of the spherical tetrahedral site
R = radius of closely packed sphere
Size of the tetrahedral void = 0.225R

b) Octahedral voids
The void, which are surrounded by six sphere which lie at the vertices of a regular octahedron, is known as octahedral void. There are six octahedron void around each sphere. There is one void per atom in a crystal. If N are the number of close packed sphere than octahedral voids are N. coordination number of octahedral void = 6
If r = radius of the spherical octahedral site
R = radius of closely packed sphere
Size of the tetrahedral void = 0.414R

c) Trigonal void
The void, enclosed by three sphere in contact is called a Trigonal void. This void and the spheres surrounding it are in same plane. There are 24 void around each sphere. There are 8 Trigonal voids per atom in a crystal.
If r = radius of the spherical Trigonal site
R = radius of closely packed sphere
Size of the tetrahedral void = 0.155R

d) Cubic void
This type of void is formed between 8 closely packed spheres which occupy all eight corners of cube. This site is surrounded by eight spheres which touches each other. Size of the cubical void is given as
If r = radius of the spherical cubical site
R = radius of closely packed sphere
R = 0.732R

Decreasing order of the size of the various voids:
Cubic > Octahedral > Tetrahedral > Trigonal

Number of tetrahedral void = 2 (Number of atoms or octahedral voids)
PACKING EFFICIENCY OF ccp AND hcp STRUCTURE

Packing efficiency is the percentage of total space filled by the particles.

a) Packing efficiency of ccp and hcp structure

In figure, let cell edge length be ‘a’ and face diagonal $AC = b$

In $\Delta ABC$

$AC^2 = BC^2 + AB^2$

$b^2 = a^2 + a^2$ Thus $b = \sqrt{2} a - (i)$

If radius of sphere is $r$, we find $b = 4r$

From eq(i) $\sqrt{2} a = 4r$ Thus $r = \frac{a}{2\sqrt{2}}$

There are four spheres per unit cell in ccp structure.

Volume of four spheres = $4 \times \frac{4}{3} \pi r^3$

Volume of the cube = $a^3 = \left(2\sqrt{2}r \right)^3 = 16\sqrt{2}r^3$

Percentage of packing efficiency =

\[
\frac{\text{Volume occupied by four spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\%
\]

\[
= \frac{4 \times \frac{4}{3} \pi r^3 \times 100}{16\sqrt{2}r^3} \times 100\%
\]

\[
= \frac{\pi \sqrt{2}}{3\sqrt{2}} \times 100\%
\]

Thus efficiency = 72%

OR Packing factor = $\frac{\pi \sqrt{2}}{6} = 0.72$
b) Packing efficiency of Body Centered Cubic Structure

In figure, let cell edge length be ‘a’ and face diagonal $FD = b$, diagonal $FD = c$

From $\Delta EFD$ $b^2 = a^2 + a^2$ Thus $b = \sqrt{2} a$ – (i)

From $\Delta AFD$ $c^2 = a^2 + b^2$

From eq(i) $c^2 = a^2 + 2a^2 = 3a^2$

$c = \sqrt{3} a$ – (ii)

The length of the body diagonal $c$ is equal to $4r$. Here $r$ is the radius of the sphere (atom)

From eq(ii) we get $\sqrt{3} a = 4r$

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

There are two spheres per unit cell in bcc

Volume of two sphere = $2 \times \frac{4}{3} \pi r^3$

Volume of cube = $a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3$

Percentage of packing efficiency =

$$\frac{\text{Volume occupied by two spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\%$$

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

$$= \frac{\sqrt{3} \pi}{8} \times 100\% = 68\%$$

Thus efficiency = 68%

OR Packing factor = $\frac{\pi \sqrt{3}}{6} = 0.68$

c) Packing efficiency in simple cubic lattice

In simple cubic lattice, 8 lattice points are on the corners of the cube. Since a simple cubic has only one atom. Let edge length be a then $a = 2r$, here $r$ is the radius of sphere
Percentage of packing efficiency =

\[
\frac{\text{Volume occupied by one spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\%
\]

\[
= \frac{\frac{4}{3} \pi r^3 \times 100}{(2r)^3} \times 100\%
\]

\[
= \frac{\pi}{6} \times 100\% = 52.4\%
\]

**Density of cubic crystal**

Density of unit cell \((\rho)\)

\[
\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}
\]

Mass of unit cell = number atoms in a unit cell \(\times\) mass of one atom

\[
\text{mass of unit cell} = Z \times \frac{M}{N_0}
\]

where \(N_0\) = Avogadro’s number and \(M\) = Molar mass

If length of edge = \(a\) then volume = \(a^3\)

\[
\rho = \frac{M \times Z}{N_0 a^3}
\]

**SUMMARY OF STRUCTURE OF METALS**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Property</th>
<th>Hexagonal close packed (hcp)</th>
<th>Cubic close packed (ccp or fcc)</th>
<th>Body centered cubic (bcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arrangement of packing</td>
<td>Closed pack</td>
<td>Closed pack</td>
<td>Not closed pack</td>
</tr>
<tr>
<td>2</td>
<td>Type of packing</td>
<td>AB AB AB A…</td>
<td>ABC ABC AB…</td>
<td>AB AB AB A…</td>
</tr>
<tr>
<td>3</td>
<td>Packing efficiency</td>
<td>74%</td>
<td>74%</td>
<td>68%</td>
</tr>
<tr>
<td>4</td>
<td>Coordination number</td>
<td>12</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>Malleability and ductility</td>
<td>Less malleable, hard and brittle</td>
<td>malleable and ductile</td>
<td>------</td>
</tr>
<tr>
<td>6</td>
<td>Examples</td>
<td>BE, Mg, Ca, Cr, MO, V, Zn</td>
<td>Cu, Ag, Au, Pt</td>
<td>Alkali metals, Fe</td>
</tr>
</tbody>
</table>
Radius ratio

In ionic compounds, the geometrical shape of ionic crystals as well as the coordinate number depends on the relative size of the ions. Positive ions are small in size thus occupy positions in voids. And negative ions are larger in size occupy positions in corners. The ratio of the radii of the cation to the anion in crystal lattice is called radius ratio

\[ \text{Radius ratio} = \frac{r_+}{r_-} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} \]

<table>
<thead>
<tr>
<th>Radius ratio</th>
<th>Coordination number</th>
<th>Structural arrangement</th>
<th>Structure type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.155 – 0.225</td>
<td>3</td>
<td>Planer triangular</td>
<td>--</td>
<td>B₂O₃</td>
</tr>
<tr>
<td>0.225-0.414</td>
<td>4</td>
<td>Tetrahedral</td>
<td>ZnS</td>
<td>CuCl, CuBr, CuI, BaS, HgS</td>
</tr>
<tr>
<td>0.414 – 0.732</td>
<td>6</td>
<td>Octahedral</td>
<td>Sodium chloride</td>
<td>NaBr, KBr, MgO, MnO,CaO,CaS</td>
</tr>
<tr>
<td>0.732 -1</td>
<td>8</td>
<td>Body- centred cubic</td>
<td>cesium chloride</td>
<td>CsI, CsBr, NH₄Br</td>
</tr>
</tbody>
</table>

Solved examples

Example 1: Potassium metal crystallises in face-centred cubic arrangement with edge length 574pm. What is the shortest separation of any two potassium nuclei

Solution: For fcc arrangement distance of neighbour = 2r = 2 \times \frac{a}{\sqrt{2}} = \frac{a}{\sqrt{2}} = 0.707a

=0.707 \times 574 = 46pm

Example 2: The cubic unit cell of aluminium ( molar mass 27.0 g/mole) has an edge length of 405 pm and density 2.70 g/cm³. What type of unit cell is?

Solution : from formula for density \( \rho = \frac{M \times Z}{N_0 a^3} \)

\[ Z = \frac{\rho N_0 a^3}{M} \]

\[ Z = \frac{2.7 \times 6.023 \times 10^{23} \times (405 \times 10^{-10})^3}{27.0} = 4 \]

i.e number of atoms per unit cell is 4. Hence, unit cell is face centred type

Example 3: Crystalline CsCl has density 3.988 g/cc. Calculate the volume occupied by single CsCl ion pair in the crystal ( CsCl = 168.4)

Solution: CsCl has simple cubic arrangement hence Z=1

Thus volume of unit cell = volume of single CsCl ion pair

From formula for density \( \rho = \frac{M \times Z}{N_0 a^3} \)

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\[ a^3 = \frac{M \times Z}{N_0 \rho} = \frac{168.41}{6.023 \times 10^{23} \times 3.998} = 7.014 \times 10^{-23} \text{ cc} \]

Example 4: A metal is found to have a specific gravity of 10.2 at 25°C. It crystallises in a body-centred cubic lattice with a unit cell edge length of 3.0 Å. Calculate the atomic weight

Solution: From formula for density \( \rho = \frac{M \times Z}{N_0 a^3} \), for body centred \( Z=1 \)

\[
M = \frac{\rho N_0 a^3}{Z} = \frac{10.2 \times 6.023 \times 10^{23} \times (3 \times 10^{-8})^3}{2} = 82.9 \text{ u}
\]

Example 5: If the anions (B0 form hexagonal close packing and cation (A) occupy only 2/3 octahedral sites in it, then what would be the general formula of the compound

Solution: Number of anions (B) per unit cell = 6 (for hcp arrangement)

Total number of octahedral sites = 6

Number of cations per unit cell = 6 \times (2/3) = 4

A:B = 4 :6 or A:B = 2:3

Hence formula of compound is \( A_2B_3 \)

Example 6: A metallic element has cubic lattice. Each edge of unit cell is 3 Å. the density of the metal is 8.5 g/cc. How many unit cells will be present in 50g of metal?

Solution: Volume of unit cell = \( a^3 = (3 \times 10^{-8})^3 \) cm³

Mass of unit cell = density \( \times \) volume = 8.5 \( \times \) \( 3 \times 10^{-8} \)^3

Number of unit cell = Mass of sample \( \div \) mass of unit cell

Number of unit cell = \( \frac{50}{8.5 \times 27 \times 10^{-24}} = 2.178 \times 10^{23} \)

Example 7: Tungsten is arranged in face-centred cube having unit cell volume of 31.699 Å³. Calculate the radius and atomic volume of tungsten.

Solution: \( \text{Volume (}a^3\text{)} = 31.699 \text{ Å}^3 \)

Edege length \( a = 3.165 \text{ Å} \).

For fcc arrangement

\[
\text{Radius } r = \frac{\sqrt{2}a}{4} = \frac{1.414 \times 3.165}{4} = 1.1188 \text{ Å}
\]

Example 8: A substance has a face centred cubic crystal with density of 1.984g/cm³ and edgelenlength 630 pm. Calulate the molar mass of the substance.

Solution:

From the formula of density \( \rho = \frac{M \times Z}{N_0 a^3} \) for fcc \( Z = 4 \)

\[
M = \frac{\rho N_0 a^3}{Z} = \frac{1.984 \times 6.023 \times 10^{23} \times (630 \times 10^{-10})^3}{4} = 74.70
\]
Example 9: Analysis shows that nickel oxide has formula $\text{Ni}_{0.98} \text{O}_{1.0}$. What fraction of the nickel exists as $\text{Ni}^{2+}$ and $\text{Ni}^{3+}$ ions?

**Solution:** If there are 100 oxygen then $\text{Ni} = 98$.

Let $\text{Ni}^{2+}$ ions = $x$
then $\text{Ni}^{3+}$ ions = $98 - x$

Since electric neutrality is maintained

Charge on $\text{Ni}$ ions = Change on oxygen

$2(x) + 3(98 - x) = 2(100)$

$-x + 294 = 200$

$x = 94$

Thus $\text{Ni}^{2+}$ = 94% and $\text{Ni}^{3+}$ = 6%

Example 10: A mineral having the formula $\text{AB}_2$ crystallises in the cubic closed lattice, with the A atoms occupying the lattice points. What are the co-ordination number of the A and B

**Solution:** In ccp of $\text{AB}_2$, A- atom occupy the lattice points, aand number of B are twice the A thus must be occupying terahedral void. Thus A must have Coordination number 8 and B coordination number 4.

Example 11: An element (atomic mass = 60) having face-centred cubic unit cell has a density of 6.23 g/cm$^3$. What is the edge length of the unit cell

**Solution**

From the formula for density $\rho = \frac{ZM}{a^3N_A}$

$a = \left(\frac{ZM}{\rho N_A}\right)^{\frac{1}{3}}$ For fcc $Z = 4$,

$a = \left(\frac{4 \times 60}{6.23 \times 6.023 \times 10^{23}}\right)^{\frac{1}{3}}$

[First adject power of 10 such that we can find cube root we will make power from 23 to 24 ]

$a = \left(\frac{4 \times 60}{0.623 \times 6.023 \times 10^{24}}\right)^{\frac{1}{3}} = \left(\frac{240}{0.623 \times 6.023 \times 10^{24}}\right)^{\frac{1}{3}}$

[Take log of all the terms]

$\log(240) = 2.3802$

$\log(0.623) = \bar{1} . 7945$

$\log(6.023) = 0.7771$

[Apply log rules]

Denominatur terms are in multiplication thus log should be added

$\log(0.623) = \bar{1} . 7945$

$\log(6.023) = 0.7771$
\[
\text{Subtract (1) from } \log(240) \\
\log(240) = 2.3802 \\
\phantom{\log(240)} - 0.5716 = 0.5716
\]

1.8086 -- (2) 

[To take cube root divide (2) by three] 

\[
1.8086 / 3 = 0.6029 - (3)
\]

Now take antilog of (3) = 4.007

And cube root of \(10^{24} = 10^8\)

thus answer is \(4 \times 10^8\) cm or 400 pm

**Important formulae**

1) Density of the unit cell \(\rho = \frac{ZM}{a^3N_A}\)

\(Z\) : rank of unit cell (number of atoms per unit cell)

\(M\) : Molecular mass

\(A\) : length of edge

\(N_A\) : Avogadro’s number

2) Relationship between nearest neighbour distance\(d\) edge length of unit cell\(a\) and radius of atom\(r\)

<table>
<thead>
<tr>
<th>Simple</th>
<th>Face-centered</th>
<th>Body-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d = a)</td>
<td>(d = \frac{\sqrt{2}}{2}a = 0.707a)</td>
<td>(d = \frac{\sqrt{3}}{2}a = 0.866a)</td>
</tr>
<tr>
<td>(r = a/2)</td>
<td>(r = \frac{\sqrt{2}}{4}a = 0.3535a)</td>
<td>(r = \frac{\sqrt{3}}{4}a = 0.433a)</td>
</tr>
</tbody>
</table>

**STRUCTURE OF SIMPLE IONIC COMPOUNDS**

Ionic compounds consisting of cations and anions are of the type \(AB, AB_2\) and \(A_2B\)

A) Ionic compounds of \(AB\) type

\(AB\) type compounds may have one of the following types of structure.

1) Rock Salt (\(NaCl\)) type structure

2) Cesium Chloride (\(CsCl\)) type structure

3) Zinc blend (\(ZnS\)) type structure

(1) Rock Salt (\(NaCl\)) type structure

(i) \(NaCl\) has fcc (also called ccp) arrangement of \(Cl^-\) ions in which \(Cl^-\) is present at the corners and face centres of the cube

(ii) \(Na^+\) ions occupy all the tetrahedral site. i.e body centre and edge centres.

(iii) Each \(Na^+\) ion is surrounded octahedrally by six \(Cl^-\) ions and each \(Cl^-\) ion is surrounded octahedrally by six \(Na^+\) ions. Hence, coordination number of both \(Na^+\) ion and \(Cl^-\) ion is six
(iv) On applying pressure NaCl structure (6:6 coordination) changes to CsCl structure (8:8 coordination)
(v) edge length = 2(nearest neighbour distance)
Other examples: Halides of Li, Na, K, AgCl, AgBr, CaO etc

2) Caesium Chloride (CsCl) type structure
(i) In this type of ionic crystal, the size of Cs\(^+\) ion is quite big as compared to Cl\(^-\) ion. Therefore, it acquires the body centred cubic lattice structure
(ii) It has bcc arrangement
(iii) The Cl\(^-\) ions arranged in a simple cubic arrangement i.e. are present at the corners of the cubic unit cell
(iv) Cs\(^+\) ion is surrounded by 8 chloride ions and each Cl\(^-\) ion is surrounded by 8Cs\(^+\) ions. Therefore, the structure has 8:8 coordination
(v) Cs\(^+\) ion occupy cubic interstitial site i.e. body centre
(vi) At high temperature CsCl (8:8 coordination) changes to NaCl structure (6:6 coordination)
Other examples: CsBr, CsI, CsCn, TICl, TlBr, TlI, TlCN, CaS

3) Zinc Blend (zinc sulphide) type structure
(i) The sulphide ions (S\(^2-\)) form fcc by occupying corners and face centres of cubic unit cell.
(ii) Zinc ions(Zn\(^{2+}\)) occupy half of the total available tetrahedral voids in alternate manner
(iii) Each sulphide ion is surrounded tetrahedrally by 4 Zn\(^{2+}\) ions and each Zn\(^{2+}\) ion is surrounded tetrahedrally by 4S\(^2-\) ions. Therefore, ZnS has 4:4 coordination
Other examples having structure: ZnCl, CuCl, CuBr, CuI, CgS, AgI, BES etc.
Note: Znic sulphide ZnS exists in two forms: Znic blend and Wurtzite which differs only in terms of arrangement of S\(^2-\) ions. In case of znic blends, S\(^2-\) ions have cubic close packing (ccp) arrangement thus, 4 formula units per unit cell. Whereas in Wurtzite, S\(^2-\) ions have hexagonal close packing (hcp)

B) Ionic compounds of AB\(_2\) type Fluorite (CaF\(_2\)) type structure
(i) It has ccp arrangement of Ca\(^{2+}\) in which Ca\(^{2+}\) ions are present at the corners and face centres of unit cell
(ii) Fluoride ions(F\(^-\)) occupy all available tetrahedral voids
(iii) Each calcium atom is surrounded by eight fluoride ions i.e coordination number of calcium ion is eight. Each fluoride ion is in contact with four calcium ion it is coordination number is 4. Thus CaF\(_2\) has 8:4 coordination
Other examples: SrF\(_2\), BaF\(_2\), CdF\(_2\), HgF\(_2\), PbF\(_2\), CuF\(_2\), SrCl\(_2\) etc

C) Ionic compounds of A\(_2\) B type
Antifluorite (Na\(_2\)O) type structure
(i) In the crystal structure of Na\(_2\)O, the O\(^2-\) ions constitute a cubic close packed lattice (fcc structure) and the Na\(^+\) ions occupy all available tetrahedral voids
(ii) Each oxide ion, $O^{2-}$ ion, is in contact with 8 Na$^+$ ions and each Na$^+$ ion is surrounded by 4 oxide ions. Therefore Na$_2$O has 4:8 coordination.

Other example: Li$_2$O, K$_2$O, K$_2$O and Na$_2$S etc.

**SECTION II**

**DEFECTS AND PROPERTIES OF SOLIDS**

Any deviation from regular arrangement in crystalline solids are called as *crystal defect*. Broadly defects are of two types i) Line defect ii) Point defect. The *line line defects* are the irregularities or deviations from ideal arrangement in entire rows of lattice points. *Point defects* are the irregularities or deviations from ideal arrangement around point or an atom in crystalline substance.

Various types of defects in ionic compounds are as follows:

![Diagram of point defects]

(A) Defects in stoichiometric compounds

(i) **Schottky defect**

This type of defect is characterised by missing equal number of cations and anions from their lattice sites so that the electrical neutrality of the system is maintained.

- High coordination number
- Small difference in size of the positive and negative ions i.e., $\frac{r^+}{r^-} \approx 1$

This type of defect is shown by the compound with:

- (a) High coordination number
- (b) Small difference in size of the positive and negative ions i.e., $\frac{r^+}{r^-} \approx 1$

Or cations and anions do not differ in size appreciably.
Consequences of Schottky defect
(a) Since crystal lattice have lesser number of ions, density of the crystal decreases
(b) The presence of a number of ionic vacancies lowers lattice energy or the stability of the crystal
(c) The crystal shows electrical conductivity to small extent by ionic mechanism
Examples: NaCl, CsCl, KBr, KCl
In NaCl there are approximately $10^6$ Schottky pairs per cm$^3$ at room temperature. In 1 cm$^3$ there are about $10^{22}$. Thus, there is one defect per $10^{16}$ ions.

(ii) Frenkel defect
In this defect, an ion shifts from its original lattice site to interstitial site, so that electric neutrality as well as stoichiometry of the compound is maintained. Since cations are smaller in size, so it is generally cations that shift from lattice to interstitial site.

This type of defect is shown by
(a) Compounds having low coordination number because in such compounds the attractive forces, being less, are very easy to overcome and hence the cation can easily move into the interstitial site
(b) Compound having large difference in size of cations and anions. i.e \( \frac{r^+}{r^-} \) is low
(c) Compounds having highly polarising cations and an easily polarizable anions.

Consequences of Frenkel defect
(a) Since nothing is lost from crystal as a whole, therefore density of the crystal is not effected
(b) The crystal shows electrical conductivity to a small extent by ionic mechanism
(c) The closeness of like charges tends to increase the dielectric constant of the crystal
Note: The number of these two defects in a crystal generally increases with the rise of temperature, hence they are sometimes called as \textit{thermodynamic defects}
AgBr shows both Frenkel and Schottky defect.

(B) Defects in non-stoichiometric compounds
Non-stoichiometric defects are the defects by virtue of which stoichiometry of the compound gets disturbed. Ratio of positive and negative ions becomes different from the ratio indicated by their ideal chemical formulae.
For example in FeO ratio of positive and negative ions is 0.94:1. The balance of positive or negative charge is maintained either by having extra electrons or extra positive charge which makes the structure irregular. These defects arise due to the presence of either the metal or non-metal in excess.
a) Metal excess defect
In this type of defect cations are in excess. This situation may arise either due to 1) Anion vacancies 2) Extra Cation in interstitial site

1) Anion in excess
   i) In this case, anions are missing from their lattice site leaving a hole behind and causing excess in the cation (metal) concentration
   ii) The hole formed are occupied by electrons, thus system is electrically neutral
   iii) The nonmetal atom may leave the surface in the form of gas.
   iv) The electrons trapped in anion vacancies are called $F$-centres because they impart colour to the crystal.

When an alkalihalide like NaCl is heated in an atmosphere of vapours of the sodium metal, sodium atoms deposit on surface of crystal, the chloride ions (anion) diffused to the crystal surface to combine with newly generated sodium cation, leaving behind anionic vacancy behind. The electron lost by the sodium atom diffuses through the crystal to occupy the anion vacancies. These centres are known as $F$-centres.

$Na + Cl^- \rightarrow NaCl + e^-$ (electron lost by metal atom)

Note this defect is shown by the compounds which have Schottky defects.

2) Extra Cation in interstitial site
   i) In this type of metal excess, extra positive ions are present in interstitial site
   ii) Electrical neutrality is maintained by presence of an electron, in another interstitial position.

   The common example is ZnO.

When ZnO is heated, it loses oxygen atom and turns yellow. The excess $Zn^{+2}$ are trapped in interstitial site and the electrons in the nearest neighbouring interstitials. Yellow colour of ZnO, when it is hot is due to these trapped electrons.

Note this type of defect is found in crystal having Frenkel defect.

Consequences of metal excess defects
   i) Compounds have increased conductivity due to the presence of free electrons
   ii) Compounds are usually coloured. Excess Na makes NaCl yellow in colour. Excess Li makes LiCl pink, Excess K makes KCl violet (lilac)

2) Metal deficiency defect
   Metal deficiency defect may also arise due to 1) Cation vacancies 2) Extra anion occupying the interstitial sites

1) Cation vacancies: This type of defect occurs when a positive ion is missing from its lattice site and the charge is balance by the oxidation of some of cations to higher valency state. Thus lattice remains deficient of metal atoms.

   Example: FeO which is mostly found with a composition of $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystal of FeO some $Fe^{+2}$ ions are missing and the loss of positive charge is made up by the presence of required number of $Fe^{+3}$ ions.
2) Extra anions occupying the interstitial sites: This type of defect involves the presence of an extra anion in an interstitial site, the electrical neutrality is maintained by an extra charge on cation. No example of crystal possessing this defect is known at present because anions are usually larger in size, so it is improper to expect them to fit into interstitial sites.

(C) Impurity defect: When some foreign atom is present in crystal, the defect is called impurity defect. If the foreign atom is present at lattice site, the solid is called substitutional solid solution, where as if impurity is present at vacant interstitial site, the solid is called interstitial solid solution.

Example: If molten NaCl containing a little amount of SrCl₂ is crystallize, some of the sites of Na⁺ is occupied by Sr²⁺ ions. Each Sr²⁺ replaces two Na⁺ ions. It occupy the site of one ion and other site remains vacant. the cationic vacancies are produced equal in number to that of Sr²⁺

PROPERTIES OF SOLIDS (CRYSTALS)

The properties are solid depend on their composition, lattice structure and the nature of bond. Some properties of solid are as follows

1) Electrical properties
2) Magnetic properties
3) Dielectric properties

1) Electrical properties
Solids may be classified into three categories depending upon their values of electric conductivity.

Conductors: electrical conductivity = $10^4$ to $10^7$ ohm⁻¹ cm⁻¹
Insulators: electrical conductivity = $10^{-20}$ to $10^{-10}$ ohm⁻¹ cm⁻¹
Semiconductors: electrical conductivity = $10^{-6}$ to $10^{4}$ ohm$^{-1}$ cm$^{-1}$

**Causes of conductance in solid**

(i) In most of the solids, conduction is through electron movement under an electric field
(ii) In ionic solids conduction is by movement of ions
(iii) The magnitude of electrical conductivity strongly depend upon the number of electrons available to take part in conduction process.
(iv) In metals, conductivity strongly depends upon the number of electrons available per Atom
(v) The atomic orbitals form molecular orbitals which forms band conduction band and valance band
(vi) In a case of metals conduction band and valance bands are to close or overlap and electrons flow very easily under electric file showing conductivity
(vii) gap between conduction band and valance band is known as forbidden gap
(viii) In case of insulators, the gap between valance band and conduction band is too large, so electrons cannot jump from valance band to conduction band and very small conductivity is observed.
(ix) In case of semiconductors, the gap between valance band and conduction band is small and therefore some of the electrons may jump from valance band and some conductivity is observed.
(x) 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 valance band can jump to conduction band. Pure substances like silicon and germanium that exhibit this type conducting behavior are called *intrinsic semiconductor*.

**Conduction in semiconductors**

Conductivity of semiconductors can be increased by by the introduction of impurity in semiconductors is called *doping*

**n-type semiconductors:**

When a silicon crystal is doped with a group 15 elements such as P, As, Sb, Bi, structure of crystal lattice is left unchanged but an dopent atom with five valance electrons occupy the site normally occupied by silicon atom

The foreign atom (dopent) uses four of its electrons for covalent bonding but fifth electron becomes delocalised and if thus free to contribute to electrical conduction. Silicon doped with group 15 element is called n-type semiconductor. ‘n’ stands for negative since electrons are responsible for conduction.

**p-type semiconductors**

When a silicon crystal is doped with a group 13 elements such as B, Al, Ga, In, structure of crystal lattice is left unchanged but an dopent atom with three valance electrons occupy the site normally occupied by silicon atom

The foreign atom (dopent) uses three of its electrons for covalent bonding but fourth electron is missing is called an electron vacancy or hole. Such holes can move through the crystal like positive charge giving rise to electrical conductivity. Direction of motion of
holes is opposite to that of electron. Silicon doped with group 13 element is called p-type semiconductor. ‘p’ stands for positive since electrons are responsible for conduction.

13-15 compounds: When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 12-16 compound. Example InSb, AlP, GaAs

12-16 Compound. When the solid state compounds are obtained by combination of elements of group 12 and 16, the compounds are called 12-16 compounds. Example ZnS, CdS, CdSe and HgTe

Transition metal oxides. Some transition metal oxide like TiO, CrO, ReO₃ behaves like metals. ReO₃ behaves like copper in appearance as well as conductance. VO, VO₂ VO₃ and TiO₃ also show electrical conductance depending on temperature.

2) Magnetic properties
Magnetic property of an atom is due to i) electrons orbital motion around nucleus ii) its spin around its own axis
(i) Electron is being charge particles and undergoes above mentioned motion can be considered as a small loop of current which posses a magnetic moment.
(ii) Each electron has a permanent spin and orbital magnetic moment associated with it
(iii) Magnitude of magnetic moment is small is measured in the unit called Bohr magneton \( \mu_B \). Its value is 9.27×10⁻²⁴ Am²

On the basis of their magnetic properties substances are divided in five categories
(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic (v) ferromagnetic

(i) Paramagnetic material:
Paramagnetism is due to presence of unpaired electrons. Paramagnetic materials are attracted by magnetic field. They are magnetized in a magnetic field in same direction. They lose their magnetism in absence of magnetic field.
Examples: O₂, Cu²⁺, Fe³⁺ Cr³⁺

(ii) Diamagnetic material:
Diamagnetism is shown by those substances in which all the electrons are paired and there is no unpaired electrons. Pairing cancels their magnetic moments and they lose their magnetic character.
Diamagnetic materials are repelled by magnetic field. They are weakly magnetized in a magnetic field in opposite direction.
Examples: H₂O, NaCl and C₆H₆

(iii) Ferromagnetic material:
a) Ferromagnetic substances shows permanent magnetism even when magnetic field is removed.
b) The metal ions of ferromagnetic substances are grouped together into small region called as **domain**. Each domain acts like as tiny magnet.
c) In an unmagnetised piece of a ferromagnetic substances the domain are randomly arranged and their magnetic moment gets cancelled.
d) When substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic field is produced. This ordering of domain persists even when the magnetic field is removed and ferromagnetic substance becomes permanent magnet
e) On heating ferromagnetic substance becomes paramagnetic
Examples CrO$_2$, Co, Ni, Fe

(iv) Antiferromagnetic substance.
When magnetic moments of domain are aligned in such a way that net magnetic moment is zero, then magnetism is called antiferromagnetism.
Example MnO

(v) Ferrimagnetism:
When magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in net moment then the magnetism is called ferrimagnetism
Examples Fe$_3$O$_4$, MgFe$_2$O$_4$, CuFe$_2$O$_4$, ZnFe$_2$O$_4$ etc