1. We know solids are the substances which have a definite volume and definite shape. A solid is nearly incompressible state of matter with definite shape, rigidty and definite volume.

2. **Classification of Solids:**

    Solids can be broadly classification into two types :

    (1) Crystalline   (2) Amorphous

Difference Between Crystalline and Amorphous Solids

| S.No.	Property	Crystalline solids	Amorphous solids
1.	Geometry	These have definite regular geometry which extends throughout the crystals i.e., these solids have long range order.	These do not have definite orderly arrangment.
2.	Melting Points	These have sharp m.p.	These do not have sharp m.p.
3.	Symmetry	These possess symmetry.	These do not possess any symmetry.
4.	Heat of Fusion	These have definite heat of fusion	These do not have definite heat of fusion.
5.	Interfacial angles	Crystals are always guarded by planes so that a definite angle exists between two planes called interfacial angle.	These do not possess interfacial angle.
6.	Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
7.	Isotropy and Anisotropy	These are anisotropes i.e., their physical properties such as refractive index, conductivity etc. have definite values in different directions.	They are isotropic i.e., their physical properties such as refractive index conductivity etc. have same value in all the directions.

3. **Types of Crystalline solids:**

    On the basis of the nature of the constituent particles, and the interparticle forces, Crystalline solids may be divided into four classes

    (a) Covalent network solids

    (b) Ionic solids

    (c) Metallic solids

    (d) Molecular solids

Characteristics of Various Types of Solids

Characteristics	Molecular Solids	Covalent Network	Metallic Solids	Ionic Solids
1. Units that occupy Lattice points	Atoms or molecules	Atoms	Positive ions in a 'sea of electrons'	Positive and negative ions
2. Binding forces	Van der Waal's forces (weak intermolecular forces) of following two types (*i*) London (dispersion) forces (*ii*)Dipole-dipole forces	Covalent bonding (shared pair of electrons)	Metallic bonding (extreme deloc-alised bond)– positively charged atomic cores surrounded by 'sea' of deloc-alised electrons	Ionic bonding (electrostatic attraction between positive and negative ions)
3. Physical Properties	(*i*) Very soft. (*ii*) Low melting points (*iii*) Non conductors	(*i*) Very hard (*ii*) Very high melting points (*iii*) Non conductors	(*i*) Hard or soft (*ii*) Moderate to high melting points (*iii*) Good conductors	(*i*)Quite hard and brittle (*ii*)Fairly high melting points
4. Examples	Solid Ne, Solid NH_3, Ice (solid H_2O), Dry ice (solid CO_2)	Diamond, Carborundum(SiC), Quartz(SiO_2)	Cu, Fe, Ag	NaCl, KNO_3 Na_2SO_4

4. **Space Lattice :** It may be defined as a three dimensional arrangement of points that shows how the atoms or ions are arranged in 3D-space. Each point is individually called as lattic point.


Space Lattice

Representation of dimension of unit cell
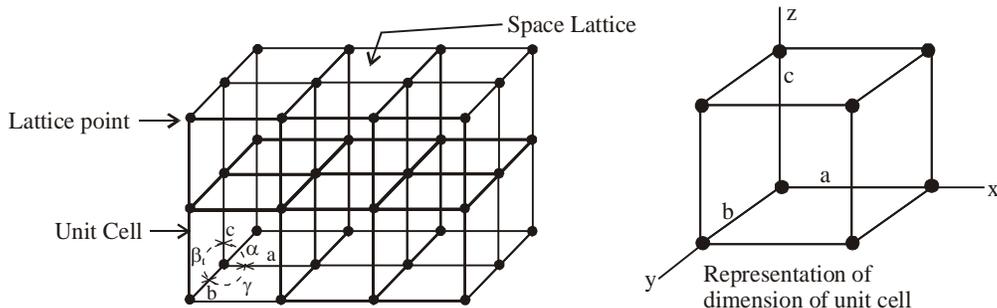
5. **Crystal Lattice :** When the lattice points in the space are replaced by actual atoms or ions then the space lattice is called crystal lattice.

Unit Cell : The smallest repeating pattern in space lattice is called as unit cell.

Close Packing in Two Dimension

Let us consider the packing of hard spheres of equal size

(*i*) The spheres can be arranged side by side in a row (horizontal alignment) as shown below
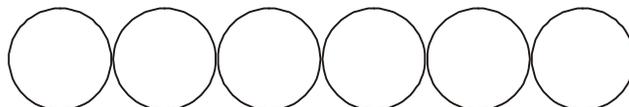
Close Packing of Spheres in one dimension

(*ii*) The spheres are packed in such a way that the rows have both horizontal as well as vertical alignment. In this arrangement the spheres are found to form a square. This packing is called square close packing.
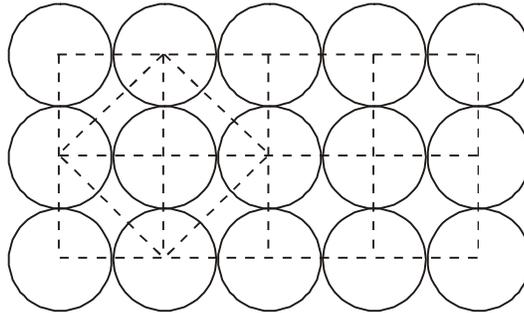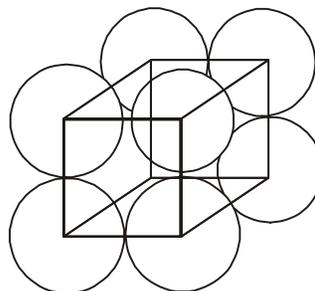

Square Closed Packing Layer

(*iii*) The spheres may also be packed in such a way that the second row are placed in the depression between spheres of first row. Similarly the spheres in the third row are placed in the depression between the spheres of second row and so on. This gives rise to a hexagonal closed packing of spheres.
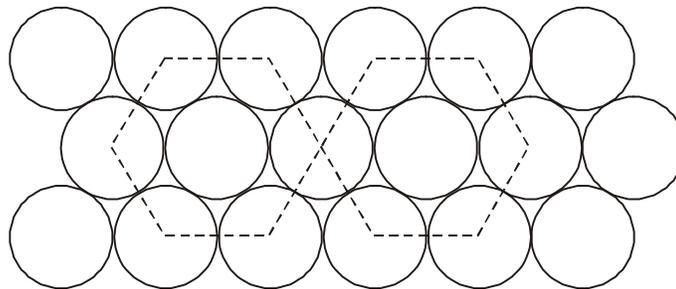

Hexagonal Closed Packed Layer

Closed Packing in Three Dimension

1. If in a square arrangement of layers with spheres touching each other, the second layer is placed right above the first layer of spheres then the repetition of layers become AAAA......

Such a 3-D packing gives rise to a simple cubic closed packing structure.
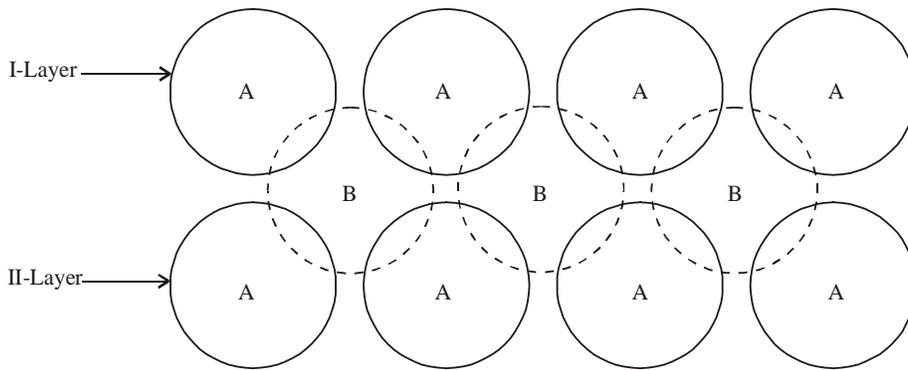

Simple Cubic Closed Packing

2. Where in the square packing of layers we have spheres not touching each other i.e.
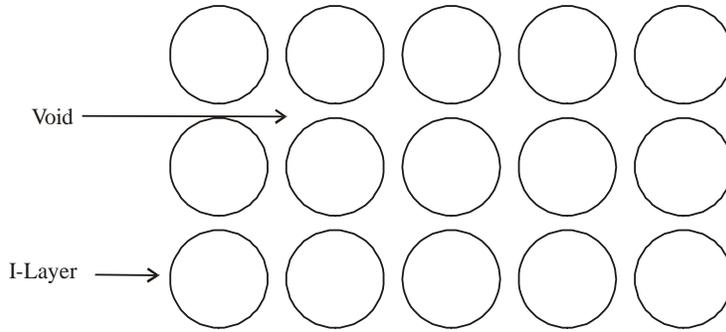
If the second layer spheres are placed in the voids of the first layers spheres and the third layer spheres are placed in the voids of the second layer spheres then the repetition becomes AB AB.....
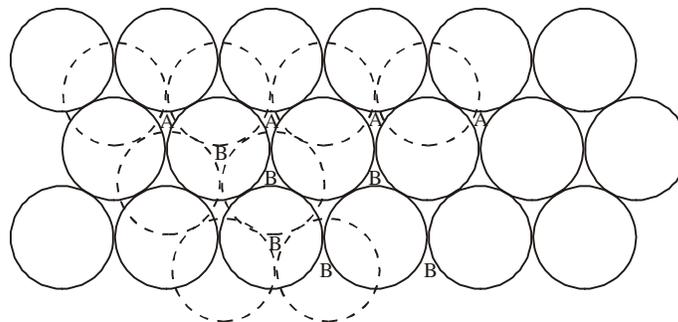

Such a 3-D arrangement leads to Body centred cubic closed packing.


(a)　　　　　　　(b)
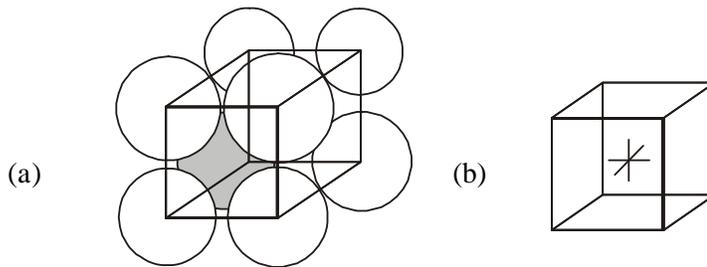
3. If in the hexagonal arrangement of layers, the second layer is placed in the voids of the first layer then we come across two types of voids
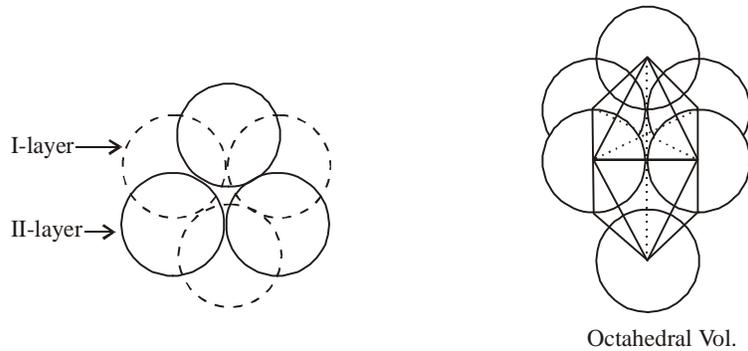
Voids - A –   Octahedral Voids

Voids - B –   Terahedral Voids

Tetrahedral void : When the sphere of one layer is covered by the sphere of other layer then such a void is called as tetrahedral voids. e.g.

After sliding ≡ slightly the black sphere

After sliding ≡ slightly the black sphere
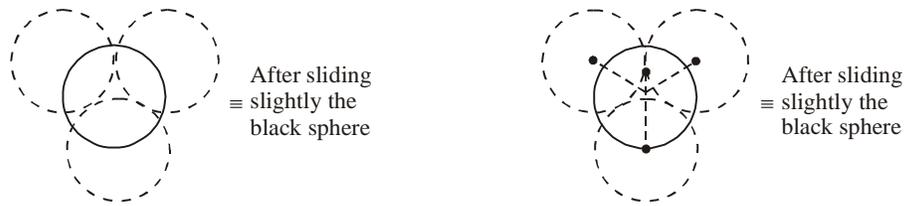
Octahedral Void : When the voids of two layers mix together, such voids are called octahedral voids.

I-layer→

II-layer→

Octahedral Vol.

4.   When the third layer is placed on the tetrahedral voids of the first layer then the repetition become ABAB because the third layer will be right above the first layer. Such a 3-D arrangement is called Hexagonal Closest Packing as in fig (a)

A

B

Hexagonal Closed Packing

(a)

A

(b)

A

B

A
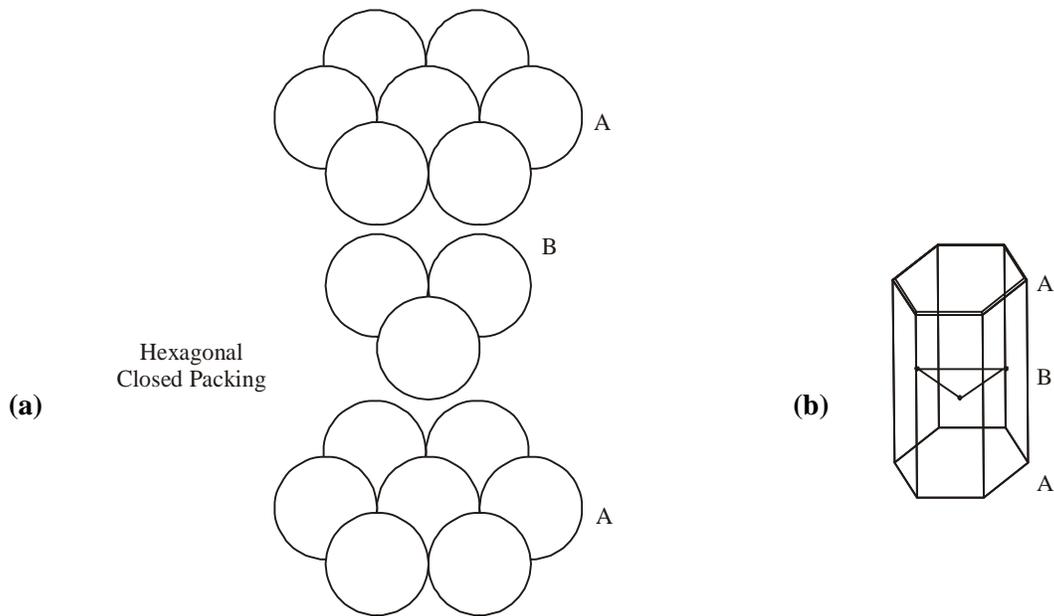
5.   When the third layer is placed on the octahedral voids of the second layer then the repetition becomes ABC....... Such a 3-D arrangement is called Cubic Closed Packing or Face Centred Cubic closed packing.

Face centred
Cubic Close parking
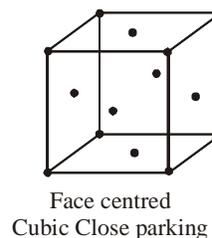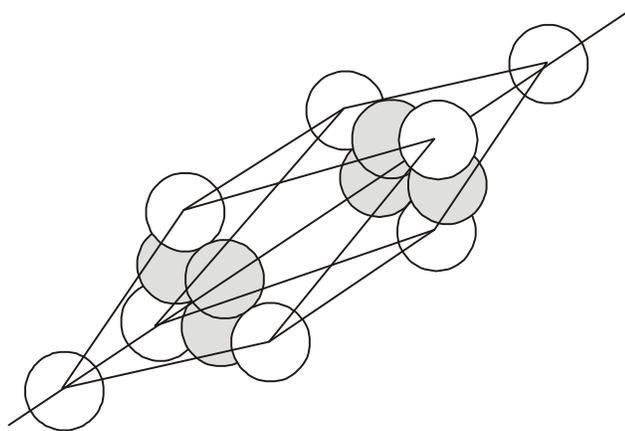
Crystal System : The unit cell in a 3-dimensional lattice is characterized by the length a, b, c and their angles α, β, γ. These are known as unit cell parameters.

BRAVAIS LATTICES : An arrangement of spheres as given above leads to simple or primitive unit cell, when there are points only at the corner of the unit lattice. However certain unit cells have lattice points at other sides in additions to the corners. Such unit cell are called non-primitive unit cells. Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points (spheres) can be arranged.

These fourteen types of lattices are known as Bravais lattices. They can be divided into seven crystal systems as shown below :
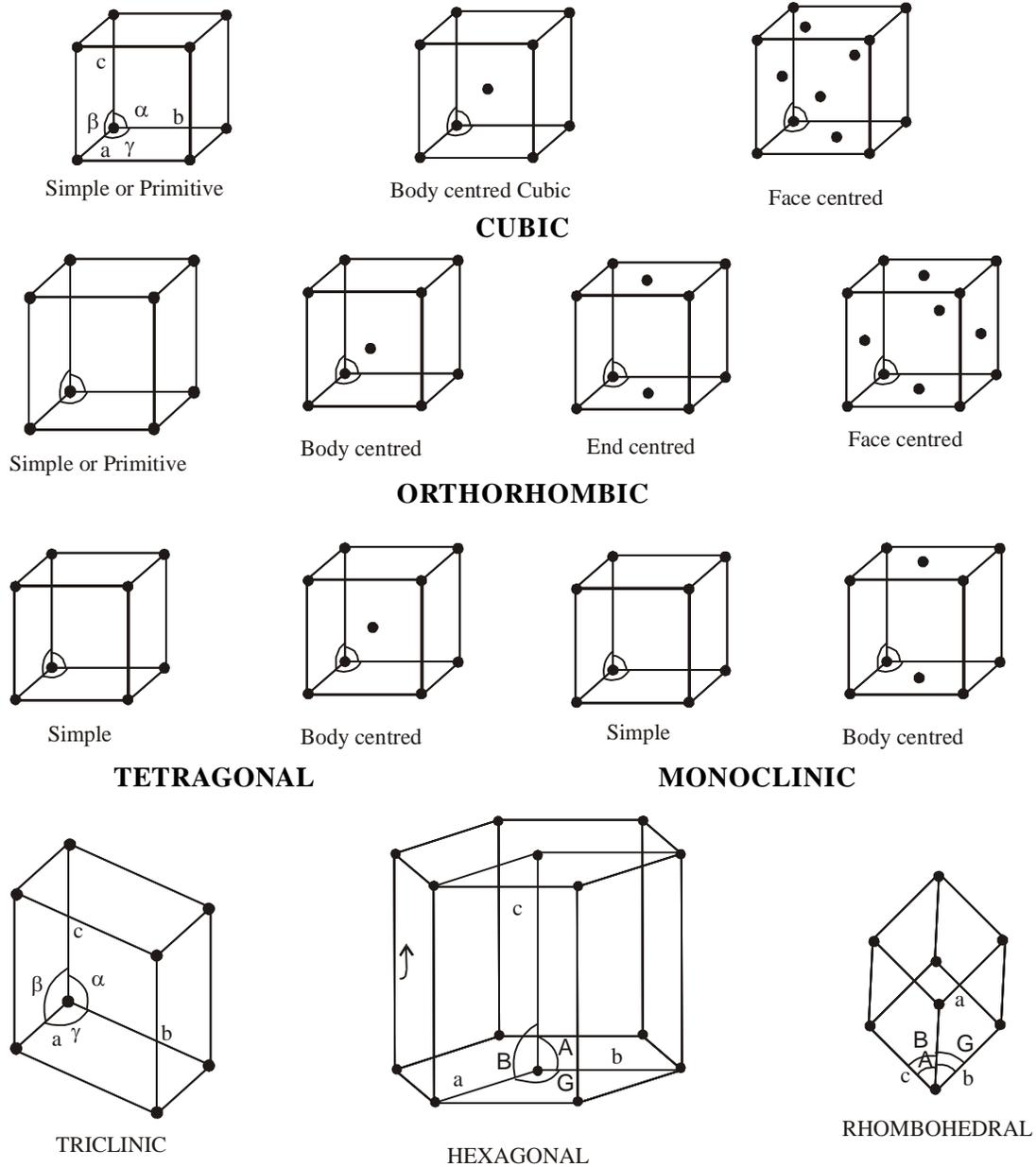
Crystal Systems Table

S.No.	Crystal System	Axial Characteristics	Examples
1.	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	NaCl, KCl, CsCl, Zinc blende, Cu, Ag, Diamond
2.	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2
3.	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Rhombic Sulphur, KNO_3, $PbCO_3$, $PbSO_4$
4.	Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	Monoclinic Sulphur, $CaSO_4, 2H_2O$, $Na_2SO_4, 10H_2O$
5.	Rhombohedral or trigonal	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$	Calcite, Quartz, As, Sb, $NaNO_3$, ICl
6.	Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, H_3BO_3, $CuSO_4. 5H_2O$
7.	Hexagonal	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	Graphite

In case of cubic system which is the simplest crystal system, there are three types of lattices depending upon the unit cell. These are :

(*i*) **Simple Cubic Lattice**. In this type of lattice, there are lattice points only at corners of each unit cell.

(*ii*) **Face Centred Lattice (fcc) :-** In this type of lattice, there are points at the corners of the cube with additional points at the centre of each face.

(*iii*) **Body Centred Cubic Lattice (bcc) :-** This type of lattice has points at the corners of a cube with an additional point in the centre of the cube.

The Bravais lattice associated with the seven crystal systems are shown below.

Simple or Primitive   Body centred Cubic   Face centred

CUBIC

Simple or Primitive   Body centred   End centred   Face centred

ORTHORHOMBIC

Simple   Body centred   Simple   Body centred

TETRAGONAL   **MONOCLINIC**

TRICLINIC   HEXAGONAL   RHOMBOHEDRAL

Bravais lattices corresponding to different crystal systemsTable

S.No.	System	Number of Bravais lattices	Description of the lattices
1.	Cubic	3	Simple, Face-centred, Body centred.
2.	Tetragonal	2	Simple, Body-centred
3.	Orthorhombic or Rhombic	4	Simple, Face-centred, End centred Body - centred
4.	Monoclinic	2	Simple, End-centred
5.	Triclinic	1	Simple
6.	Rhombohedral or trigonal	1	Simple
7.	Hexagonal	1	Simple

Types of symmetry in a crystal

1. Centre of Symmetry :- Centre of symmetry of a crystal may be defined as an imaginary point within a crystal such that any line through it intersects the crystal at equal distances in both directions e.g. <u>staggered</u> form of ethane possesses a centre of symmetry.

The centre of symmetry is also called the centre of inversion because if the crystal is inverted through the centre of symmetry, it is distinguishable from the original.
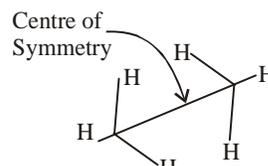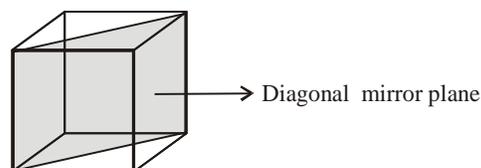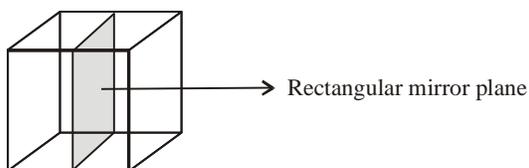
Every Crystal Possesses Only One Centre of Symmetry

2. Plane Of Symmetry :

It is an imaginary plane passing through the crystal which can divide crystal into two equal parts such that one part is exact mirror image of the other . These are therefore also called as mirror planes.

There are two types of mirror planes :

(a) Rectangular mirror plane

(b) Diagonal mirror plane

Axis of Symmetry or Axis of Rotation

An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete rotation. i.e. through 360°.

When the same appearance of crystal is repeated, on rotating through an angle of $\dfrac{360º}{n}$ around an imaginary axis it is called n-fold axis of symmetry where n– is known as order of axis.

Two-Fold Axis :

If a similar appearance occurs two times in one complete rotation i.e. after a rotation through 180º, the axis is called two fold axis of symmetry or diad axis.

Three-Fold Axis :

If the original appearance occurs thrice it is called three fold axis of symmetry.

(a)   (b)   (c)

(d)   (e)   (f)

Diagonal plane -1 CBGF   Diagonal plane - 4 CDEF
Diagonal plane -2 ADEH   Diagonal plane - 5 CAFH
Diagonal plane -3 ABGH   Diagonal plane - 6 EGDB

Total Elements of Symmetry in a Cubic Crystal

Total Planes of Symmetry $= 3 + 6 \ = 9$

     Axis of Symmetry $= 4$ (3-Fold axis)

                           3 (Four Fold axis)

                           6 (Two Fold axis) $= 13$ Axis of Symmetry

     Centre of Symmetry $= 1$

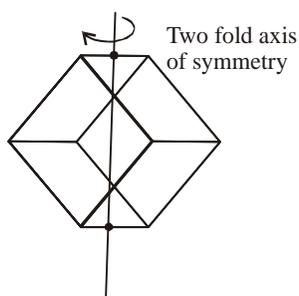Hence a cube has 23 elements of symmetry

Nearest Neighbouring Distance In Case of Identical Spheres :

Nearest neighbouring distance is the distance between the centres of any two touching spheres.

1.   In case of SCC (Simple Cubic Lattice)

In a simple cubic lattice the edge length (a) = Nearest neighbouring distance

       $a = d = 2r$

$\Rightarrow$ $r = a/2$

2. **Body Centred**

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

$\Rightarrow$ $(\text{Body Diagonal})^2 = (\text{Face Diagonal})^2 + (\text{edge})^2$

                    $= 2 \ (\text{edge})^2 + (\text{edge})^2$

                    $= 3 \ (\text{edge})^2$

$\Rightarrow$ $\boxed{(\text{Body diagonal})^2 = 3\,(\text{edge})^2}$

Also Body Diagonal $= r + 2r + r = 4r$

$\Rightarrow$ $(4r)^2 = 3a^2 \Rightarrow 4r = \sqrt{3}\ a$

$\Rightarrow$ $\boxed{r = \dfrac{\sqrt{3}}{4}\,a}$

$d = 2r \quad \Rightarrow \quad \boxed{d = \dfrac{\sqrt{3}}{2}\,a}$ $=$ nearest neighbouring distance

3. **Face Centred Cubic Lattice**

   Here $(\text{Face diagonal})^2 = (\text{edge})^2 + (\text{edge})^2$.

   Also face diagonal $= r + 2r + r = 4r$

   $\qquad\qquad\qquad (4r)^2 = 2\,(\text{edge})^2$

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

   $\boxed{r = \dfrac{\sqrt{2}}{4}\,a} \Rightarrow \boxed{r = \dfrac{1}{2\sqrt{2}}\,a}$

   $\Rightarrow$ $\boxed{d = \dfrac{\sqrt{2}}{2}\,a = \dfrac{1}{\sqrt{2}}\,a}$
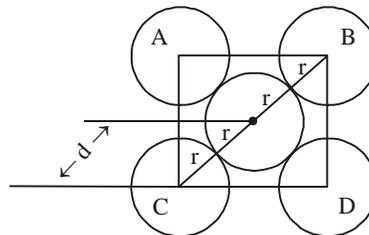
   Hence we can say

Unit Cell	Distance between nearest neighbour	Radius
Simple cubic	a	$a/2$
Face Centred Cubic	$a/\sqrt{2} = \dfrac{\sqrt{2}a}{2}$	$\dfrac{a}{2\sqrt{2}} = \dfrac{\sqrt{2}}{4}\,a$
Body Centred Cubic	$\dfrac{\sqrt{3}}{2}\,a$	$\dfrac{\sqrt{3}}{4}\,a$

4. **Packing Fraction in Case of Identical Spheres**

   Packing fraction is the ratio of volume occupied by spheres to the total volume of the cube.

   Packing Fraction $= \dfrac{\text{Volume occupied by sphere}}{\text{Total volume of cube}}$

   $\qquad\qquad\qquad = \dfrac{\dfrac{4}{3}\pi r^3 \times z}{a^3}$

   where a = edge of cube

   $\qquad\quad z$ = number of spheres per unit cell

Packing fraction for SCC

$$r = \frac{a}{2} \qquad\qquad z = 1$$

$$PF = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \times z}{a^3} \;=\; \frac{4\pi}{8\times 3} \;=\; \frac{\pi}{6}$$

$$\Rightarrow \quad PF = \frac{\pi}{6}$$

$$\Rightarrow \quad \% \text{ volume occupied by spheres} = \frac{\pi}{6} \times 100 = 53.4\%$$

$$\Rightarrow \quad \% \text{ Free space} = 100 \left[1 - \frac{\pi}{6}\right] = 47.6\%$$

Packing fraction for BCC

$$r = \frac{\sqrt{3}}{4} \qquad\qquad z = 2$$

$$PF \;=\; \frac{\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3 \times 2}{a^3} \;=\; \frac{4}{3}\times \frac{\pi\times 3\sqrt{3}\times 2}{64}$$

$$PF \;=\; \frac{\sqrt{3}\,\pi}{8}$$

$\Rightarrow \quad \%$ volume occupied = 68.04%

$\quad \%$ Free space = 100 – 68.04 = 31.96%

Packing Fraction for FCC

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

$$\Rightarrow \quad PF \;=\; \frac{\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3 \times 4}{a^3} \;=\; \frac{4}{3}\times \frac{\pi\times 2\sqrt{2}}{64}\times 4$$

$$=\; \frac{\sqrt{2}}{6}\pi \;=\; 0.7407$$

$$PF = \frac{\sqrt{2}}{6}\pi$$

$\%$ Volume occupied = 74.07%

$\%$ Free space = 25.93%

Calculation of Density of a Crystal System

Cubic Crystal

Let number of atom per unit lattice $= n$

$$\text{Mass of unit cell} = \text{number of atom per unit cell (z)} \times \text{Mass of one atom}$$

$$\text{Mass of each atom} = \frac{\text{Atomic Mass of Atom}}{\text{Avogadro's number } N_A}$$

$$\text{Mass of unit cell} = \frac{z \times M_0}{N_A} \quad \text{or} \quad \frac{n \times A_0}{N_A}$$

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

$$\text{Length of edge} = a \text{ pm}$$

$$\text{Volume of cube} = a^3 \text{ pm}^3 = a^3 \times 10^{-30} \text{cm}^3$$

$$\text{Density} = \frac{nM}{N_o \times a^3 \times 10^{-30}} \text{ gm/cc}$$

$$\text{Density} = \frac{zM \times 10^{30}}{N_o \times a^3}$$

$$= \frac{zM \times 10^7}{6.023 \times a^3}$$

CRYSTAL STRUCTURES OF AB TYPE OF IONIC COMPOUNDS

The three basic structure of this type are NaCl, CsCl and Zinc sulphide. The ionic compound of type AB have one of these three of structure

IONIC RADIUS AND RADIUS RATIO

Ionic radius of an ion is the distance from the nucleus of that ion upto which it has its influence in an ionic bond.

Co-ordination number. It is the number of oppositely charged ions surrounding a particular ion in the ionic crystal.

Radius ratio. In an ionic solid, the central cation can touch only that number of anions which should lead to maximum electrostatic attraction and minimum electrostastic repulsions. These interactions depend upon the sizes of the cation and anion. Thus, the arrangement of ions in a crystal is greatly influenced by the ratio of radius of the cation and the anion.

Thus, Radius ratio is defined as the ratio of the radius of the cation to that of the anion.

$$\text{Radius ratio} = \frac{\text{Radius of the cation } (r_+)}{\text{Radius of the anion } (r_-)}$$

Larger the cation, greater will be the number of anions surrounding it and greater will be its co-ordination number.

Significance. Radius ratio helps to predict co-ordination number and the structure of the ionic crystal as follows :

Radius ratio	Co-ordiation number	Structure	Example
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1	8	Cubic	CsCl

(a) **Rock Salt NaCl type**

(i) $r_{Na^+} = +96$ pm $r_{Cl^-} = 181$ pm

$\Rightarrow \dfrac{r_{Na^+}}{r_{Cl^-}} = \dfrac{96}{181} = 0.524$ this ratio lies between 0.414 and 0.732 and coordination number is

thus 6.

(ii) Cl^- forms FCC type packing

(iii) Na^+ ions occupy all octahedral voids

(iv) Coordination number for $Na^+ = 6$

coordination number for $Cl^- = 6$

(v) Number of Na^+ ions per unit lattice = 4

number of Cl^- ions per unit lattice = 4

Hence total number of ions = 8

Hence for each Na^+ ion there is only one Cl^- ion (A unit lattice consists of 4 formula units of NaCl or vice versa if $Na^{\oplus}$ ion forms unit lattice

(vi) Number of Cl^- ions used = 14

Number of Na^+ ions used = 13

Other examples of this type are halides of Li, Na, K, Rb, fluoride of Cs oxides and sulphides of Mg, Ca, Sr, Ba, AgCl, AlBr, AgF

(b) **Cesium Chloride CsCl Type**

(i) $r_{Cs^+} = 169$ $r_{Cl^-} = 181$

$\dfrac{r_{Cs^+}}{r_{Cl^-}} = \dfrac{169}{181} = 0.93$ Hence $\dfrac{r_+}{r_-}$ lies between
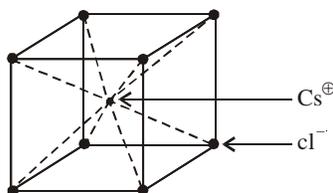
0.732 to 1.0 thus coordination number = 8

CsCl has BCC type structure

(ii) Cl^- form SCC packing

(iii) Cs^+ ions occupy the body centred void

(iv) Each Cs^+ ion is surrounded by 8 Cl^- ions and

each Cl^- ion is surrounded by 8 Cs^+ ions

(v) Number of Cl⁻ ions

per unit lattice = 1

Number of Cs^+ ions per unit lattice = 1

(vi) A unit cell of Cesium chloride has one formula unit of CsCl i.e. one Cs^+ and one Cl⁻ ion.

Other examples of this type is CsBr, CsI, NH_4Br, NH_4I, Thallous cyanide, Thallous chloride.

(c) **Zinc Blende, ZnS**

(i) $r_{zn^{2+}} = 74$ $r_{s^{--}} = 184$

$\dfrac{r_{zn^{2+}}}{r_{s^{--}}} = 0.4$ this value lies between 0.225 and 0.411

hence a tetrahedral void is occupied, co-ordination number = 4

(ii) S^{2-} ions are arranged in FCC types structure

(iii) Zn^{2+} ions occupy half the tetrahedral void

(iv) Number of Zn^{2+} ions = 4

Number of S^{2-} ions = 4

The $\dfrac{r^+}{r^-}$ should have been 0.225 but the value is 0.40. The close packed arrangement of S^{2-} ion opens up and accumulates the larger S^{2-} ions

(v) Coordination number of Zn^{2+} = 4

Coordination number of S^{2-} = 4

(vi) The formula unit for ZnS type lattice = 4. Other examples are :

CuCl, CuBr, CuI, in which cations is smaller than anion.

AgI, Beryllium oxides all have Zinc blende structure.

Crystal Lattice of the Type AB_2 & A_2B

1. *Calcium Fluoride CaF_2 (Fluorite Type)*

(i) Ca^{2+} is arranged in FCC type structure

(ii) F⁻ occupy all tetrahedral voids

(iii) Each Ca^{2+} ion surrounded by 8 F⁻ ions and

Each F⁻ ion is surrounded by 4 Ca^{2+} ions. This gives a 8 : 4 coordination number. CaF_2 type unit cells are : SrF_2, CdF_2

2. *Sodium oxide Na_2O (Anti Fluorite Type)*

(i) O^{2-} form FCC

(ii) Na^+ ion occupies tetrahedral voids

(iii) Coordination number of O^{2-} = 8; Coordination number of Na^+ = 4

Imperfections in Solids

The crystal structures of ionic compounds of the type AB and AB_2 discussed earlier represent ideal structures in which there is a completely ordered arrangement of constituent particles. However, in *real* crystals the arrangement of constituent particles is not regular and thus crystals have imperfect structures. Such **imperfections** are from the perfectly ordered arrangement of atoms. Thus *any deviation from the completely ordered arrangement in a crystal constitutes disorder. The disorder in a crystal of an element depends upon :*

(i) *Temperature and* (ii) *Presence of impurities*

Electronic Imperfections

In a perfectly covalent or ionic crystal such as **Silicon** or **Germanium** or **Sodium chloride,** the electrons are present in the fully occupied lowest energy states at 0K. The valence electrons are mainly concentrated around the electronegative component in ionic crystals. As the temperature is raised above 0K, some of the electrons gain energy and move to higher energy states. The electron-deficient bond produced as a result of the removal of an electron is called **hole.** As the electrons have moved away from their normal positions creating *holes,* the *electrons* and *holes in solids* are considered **electronic imperfections** or **defects.** *Electrons and holes are generally designated by the symbols 'e' and 'h' respectively and their concentrations by 'n' and 'p' respectively. So* **Si and Ge behave as semiconductors or intrinisic semiconductors.**

Thus the promotion of electrons cause holes which results in increased electrical conductivity. The electrical conductivity of silicon increases with increasing temperature (this behaviour is opposite to that of metals).

The electrons and holes can also be produced by adding certain impurities to a covalent crystal. For example, electrical conductivity of Silicon or Germanium can be greatly enhanced by adding traces of Aluminium or Arsenic as an impurity.

Atomic Imperfections

These can be classified into two categories **Lattice imperfections and point defects.**

Lattice Imperfections

These arise due to a deviation from periodic repetition of the lattice points over a large section of the crystal. Lattice imperfections may extend along lines known as *line defects or dislocations or these may extend along surface known as plane defects.* Two common types of dislocation are **edge dislocation** and **screw dislocation.** Edge dislocation is formed when a layer of particles discontinues within the crystals.

Points Defects

These are caused by a departure from the periodic arrangement in the vicinity of an atom or a group of atoms. Point defects in crystals may be classified as :

(a) *Defects in stoichiometric solids also called stoichiometric defects.*

(b) *Defects in non-stoichiometric solids also called non-stoichiometric defects.*

(c) *Impurity defects*

Defects in Stoichiometric Solids

Stoichiometric solids are those in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formulae. The causes give rise to two types of defects as :
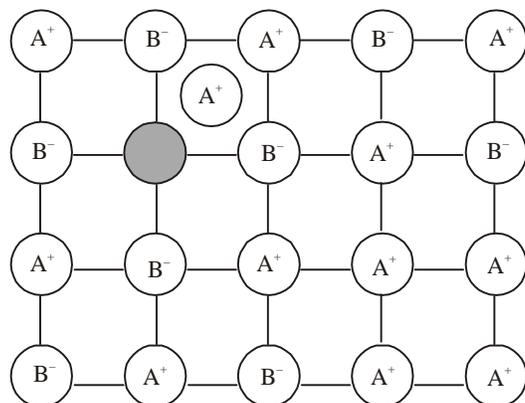
(i) *Schottky defect*

(ii) *Frenkel defect*

(i) Schottky defect : A pair of '*holes*' or vacancies exists in the crystal lattice due to one cation and one anion missing from the normal lattice sites. The crystal as a whole remains neutral because the number of missing cations and anions remains the same. *This sort of defect occurs in highly ionic compounds with a high coordination number and where the ions (both cations and anions) are of similar size.* Alkali metal halides such as NaCl, KCl, KBr, and CsCl show this defect. In NaCl crystal, at room temperature, there will be one Schottky defect per 10^{16} ions.
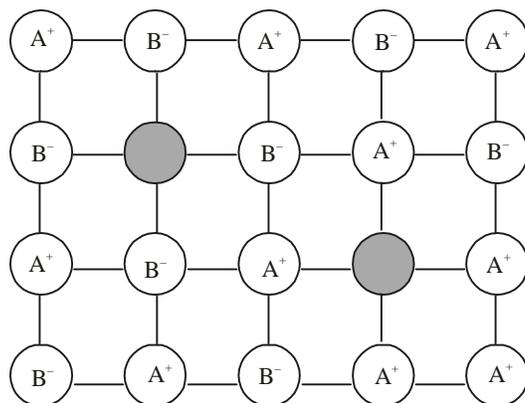
Since the presence of a large number of Schottky defects in a crystal leads to decrease in the number of ions in the lattice, this results in lowering the density of the solid markedly.

(ii) Frenkel defect : When a *'hole'* or *'vacancy'* exists in the crystal lattice because an ion occupies an interstitial lattice site, it gives rise to Frenkel defect. The crystal remains neutral. *The defect occurs more frequently in solids which have low coordination number and possess ions (cations and anions) of different sizes. Since cations are generally smaller than anions, it is more common to find the cations occupying the interstitial sites.* For example, in AgBr and ZnS crystals, Ag^+ ions and Zn^{2+} ions are missing from their normal lattice sites and are present in the interstitial positions. **AgBr, AgCl and AgI contains Schottky defects also.**

Since the presence of Frenkel defects does not change the number of ions in the lattice, the density of the solid remains the same. *The defect causes increase in dielectric constant of the crystals as similar charges come closer.*

Difference between Frenkel and Schottky Defects

| Frenkel defect		Schottky defect	
1.	The ion occupies an interstitial position than its actual lattice positions.	1.	Both cations and anions are missing from their lattice positions in the crystal.
2.	There is no change in the density of the crystal	2.	The defect decreases the density of the crystal
3.	It occurs in ionic compounds with low coordination number and with a large difference in the size of cations and anions	3.	It occurs in compounds with high coordination number and with ions of similar sizes.

Defects in Non-Stoichiometric Solids

Non-Stoichiometric solids are those in which the ratio of positive and negative ions present differs from that indicated by the ideal chemical formula. In compounds such as FeO, FeS, CuO, TiO, ZrO, VO and Cu_2S the real composition of the constituent ions can vary. Curprous sulphide, for example, may contain anything between $Cu_{1.96}$ S and Cu_2S. Similarly, in vanadium oxide, VOx, x can be anywhere between 0.6 and 1.3. The balance of positive and negative charge is maintained either by having extra electron or extra positive charges present.

Metal Excess Defects

These defects may arise in two ways:

(*i*) **Metal excess due to anionic vacancies.** A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron which was associated with the negative ion and remains trapped in the vacancy thereby maintaining the electrical neutrality. When NaCl is treated with sodium vapours, **a yellow coloured** non-stoichiometric form of NaCl is obtained in which there is an excess of sodium ions. Sodium atom removes chlorine atom from the anionic lattice site leaving its electron trapped in the vacancy and makes the lattice excess of Na^+ ions. Similarly excess of Potassium in KCl makes the crystal to appear violet and excess of Lethium in LiCl makes it **pink.** The electrons trapped in anion vacancies are referred to as 'F'-**centres** (F = Farben in German means colour).
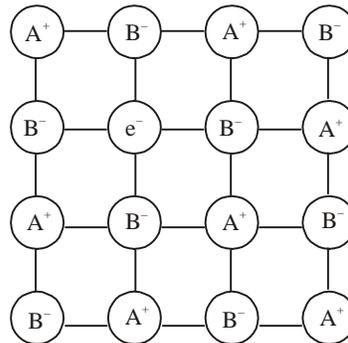

These electrons absorb energy of the white light, giving *yellow colour to NaCl, pink colour to LiCl and violet colour to KCl.*

(*ii*) **Metal excess due to extra cations.** In this case, the excess metal occurs when an extra positive ion occupies an interstitial position in the lattice. The free electron is trapped in another interstitial site close to the vicinity of the interstitial cation. This electron helps to maintain the electrical neutrality.
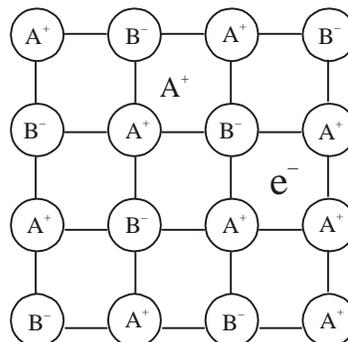
When zinc oxide is heated at high temperatures, it loses oxygen reversibly and turns yellow in colour. The excess metal ion is accommodated in the interstitial sites giving rise to electrons trapped in the neighborhood. The higher electrical conductivity of the non-stoichiometric ZnO is due to these electrons.

$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$
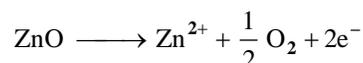
ZnO is yellow when hot and white when cold.

Metal Deficiency Defects

These defects occur in metals with variable oxidation states, i.e., the transition metals. A cation may be missing from its lattice site but the electrical neutrality is maintained when the adjacent metal ion acqires higher oxidation state (fig.) Examples include FeO, FeS and NiO. Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore **p-type semi-conductors**
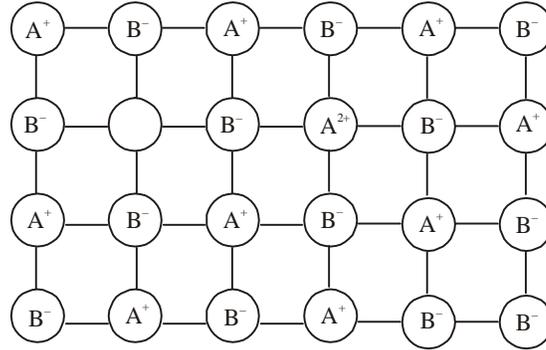
Impurity Defects

These defects aries due to the presence of foreign atoms or ions at the lattice sites. Thus depending upon the nature of impurity, two types of impurity defects are possible.

(i) **Impurity defect due to neutral atoms :** Foreign atoms can occupy interstitial or substitutional sites in a crystal. The electronic structure of impurity is of importance in the case of substitutional solid solutions while the size of the impurity atom determines the formation of interstitial or substitutional solid solution. *Solid solutions of group 13 or group 15* **as impurities** *with group 14 elements such as Ge or Si* (**act as host**) are of great interest in electronic industry in making transistors. Group 13 elements such as Ga and Al and Group 15 elements such as P and As enter Ge or Si substitutionally.

    (a) **Group 15 elements such as P, As etc. have one excess valence electron** (*electron to Si or Ge)* **after forming four covalent bonds with Group 14 element. The excess electrons give rise to electronic conduction known as n-type semiconductors.** (as the current is carried by electrons in the *normal* way).

    (b) On the other hand a **Group 13 element such as Ga, Al or In which has only three valence electrons** (*i.e. one electron less than required for forming four covalent bonds*) **creates an electron deficient bond or a 'hole'.** Such *'holes' can move in the crystal giving rise to electrical conductivity known as* **p-type semiconductors.**

(ii) **Impurity defect due to ions :** This defect is brought about by adding impurity ions in ionic solid. If the impurity ions are in different valence state from that of the host ions, vacancies are created. For example, *addition of $CdCl_2$ to AgCl (or of $SrCl_2$ or $MgCl_2$ to NaCl) yields solid solutions where the divalent cation Cd^{2+} (or $Sr^{2+} + Mg^{2+}$) occupies the Ag^+ (or Na^+) sites and produces cation vacancies equal in number to that of the divalent ions. The $SrCl_2$ doped NaCl has much higher electrical conductivity than that of pure NaCl.*
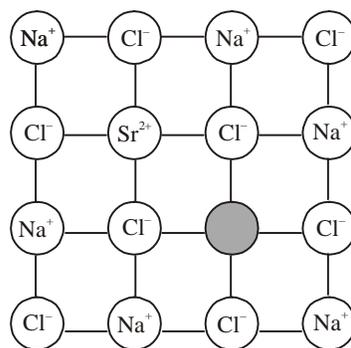
Properties of Solids

There is a close relationship between the properties of a solid and its structure and composition. Some of these properties are :

(i) *Electrical properties*

(ii) *Magnetic properties*

(iii) *Dielectric properties*

Electrical Properties (Electrical Conductivity)

Based on their electrical conductivity, solids can be broadly classified into three types :

(*i*) **Metals or conductors :** They are good conductors of electricity as the electrons can move freely without much resistance. Their conductivity value is of the order of 10^8 ohm^{-1} cm^{-1} at room temperature which decreases with rise in temperature.

Some mono oxides of transition metals (which possess NaCl structure) like TiO, VO behave like metallic conductors. CrO_2 also behaves as metal conductor.

(*ii*) **Insulators or Non-conductors:** These solids do not allow the electricity to pass through them. Non-metals like diamond, P and S, solutions of non-electrolytes like sugar and urea, substances like wood, rubber and plastics are all examples of insulators. Their conductivity value is extremely low and is of the order of less than 10^{-12} ohm^{-1} cm^{-1} at room temperature.

(*iii*) **Semi-conductors:** These solids possess conductivity values which are intermediate between those of typical metals and insulators i.e. in the range $10^2 - 10^{-9}$ ohm^{-1} cm^{-2}. The conductivity of such solids increases with temperature.

Electrical conductivity of solids may arise through the motion of electrons and holes (*electronic conductivity)* or ions (*ionic conductivity*). Substances such as pure solid alkali metal halides where the conduction is only through ions, are generally insulators as their ions cannot move. Presence of vacancies or other imperfections, however, greatly increase the conductivity of ionic solids.

Magnetic Properties

Materials can be divided into different classes depending upon the effect of magnetic fields on them.

(i) **Diamagnetic materials :** *These materials are weakly repelled by a magnetic field.* Examples are TiO_2, NaCl and Benzene.

(ii) **Paramagnetic materials :** *These materials are attracted by a magnetic field.* Examples are O_2, Cu^{2+}, Fe^{2+}. Paramagnetism is observed due to the presence of permanent magnetic dipoles as a result of unpaired electrons in atoms, ions or molecules. Paramagnetic materials, however, lose their magnetic character in the absence of a magnetic field.

Paramagnetic materials sometimes show a special type of magnetic behaviour and are classified as:

(a) **Ferromagnetic materials :** Unlike paramagnetic substances *ferromagnetic materials show permanent magnetic property even when the magnetic field is removed.* These materials exhibit unusually large paramagnetism. Examples are Fe, Co, Ni, CrO_2.

(a)   ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑   Ferromagnetic

(b) **Antiferromagnetic materials :** *These materials show much reduced paramagnetism (almost zero) than expected from their electronic structures. Examples are MnO, FeO, CoO, NiO, and many other oxides.*

(b)   ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓   Anti-Ferromagnetic
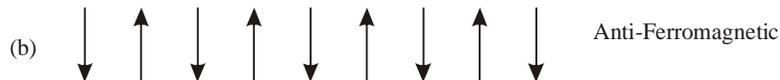
(c) **Ferrimagnetic materials :** *These materials show small paramagnetic character. Examples are Fe_3O_4 ferrites of the formula $M^{2+}Fe_2O_4$, when M = Mg, Cu, Zn. In these materials the alignment of magnetic moments are in parallel and antiparallel directions in unequal numbers.*

(c)   ↑ ↑ ↓ ↑ ↑ ↓ ↑ ↑ ↓   Ferrimagnetic

As a result the material has net magnetic moment and shows ferrimagnetism fig (c).

All magnetically ordered solids (**ferromagnetic, ferrimagnetic and anti-ferromagnetic solids) transform to the paramagnetic state at some temperature** due to the randomisation of spins. Thus ferrimagnetics, Fe_3O_4 becomes paramagnetic at 850 K.

Magnetic Properties of Typical Transition Metal Oxides

Diamagnetic	Paramagnetic	Ferromagnetic	Antiferromagnetic	Ferrimagnetic
TiO_2	TiO, Ti_2O_3	CrO_2	V_2O_3, Cr_2O_3	Fe_3O_4
V_2O_5	VO, VO_2		MnO, MnO_2	
	CuO		Mn_2O_3	
Mn_2O_3			FeO, Fe_2O_3, Co_3O_4	
			NiO, CoO	

Dielectric Properties

In insulators, electrons are closely bound to individual atoms or ions and they do not generally migrate under an applied electric field.

(*i*) These dipoles may align themselves in an ordered manner under the influence of an applied electric field such that there is net dipole moment in the crystals.

(*ii*) They may align themselves in such a manner that the dipole moments cancel each other.

(*iii*) It is also possible that there are no dipoles in the crystal, but only ions are present.

Properties of Piezoelectric Crystals :

Crystals where situation (i) is found, exhibit *piezoelectricity. When mechanical stress is applied on such crystals so as to deform them, electricity is produced due to displacement of ions.*

(a) **Electrical mechanical transducer :** *When such a crystal is deformed by mechanical stress, electricity is produced due to the displacement of ions in crystal, or conversely* if an electric field is applied to the crystal, there will be atomic displacements causing mechanical strain. Thus, a piezoelectric crystal acts as a *mechanical electrical transducer.*

(b) **Pyroelectricity :** *Some of the polar crystals, when heated, produce a small electric current called pyroelectricity.*