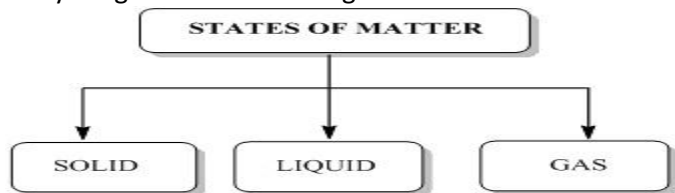# Class 12 Chemistry: The Solid State (By Mohd Sharif)

Introduction

Everything in our surroundings is known as matter that can be categorized into three states.

STATES OF MATTER

SOLID   LIQUID   GAS

In our day to day life solids plays a crucial role to pursue different purposes. Different types of solids with different properties are required for different purposes. The constituent particles and the type of bonds between the particles determine the nature of a specific solid. For eg. Bucket or a container used to carry water, utensils used for cooking food, computer, vehicles, electronic gadgets, notebooks, pencils, papers etc. are all solid substances used in our day to day life.

Daily Use Items

Liquids and gases on the other hand are another state of matter and are also known as *fluids* due to their ability to flow. They attain the ability to flow due to the free movement of molecules.

VAPOUR

LIQUID

Fig. Particles of liquid (water) are loosely packed than solid and have space between them whereas particles of gas are loosely packed and have excess space between the particles

Characteristics of solid state

o   They have definite shape due to strong Intermolecular forces of attraction.
o   They have distinct boundaries.
o   They have a fixed volume.
o   They cannot flow.
o   They have negligible compressibility due to negligible distance between the neighbouring molecules.
o   They possess a tendency to uphold their shape when exposed to external force.
o   They break under force but it is difficult to change their shape so they are rigid.
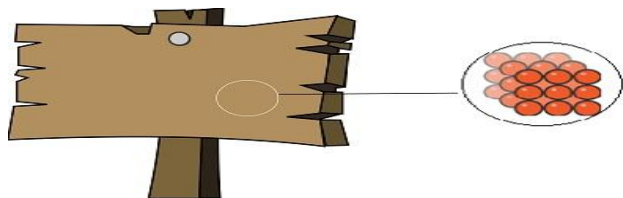o   They have high density and do not diffuse at all.

Fig. Particles of solid (Wooden plank) are compact together and have less space between them

Amorphous Solids

o The term amorphous solid is derived form a Greek word *amorphous* meaning *no form*.
o The constituent particles are arranged in a *short range order* with a regular and periodically repeating pattern over short distances.
o These solids get softened at a certain temperature and hence can be moulded and drawn into various desired shapes. Solids may also acquire crystalline form at some temperature when heated.
o These solids have the ability to flow very slowly due to which they are also termed as pseudo solids or super cooled liquids.
o These solids are isotropic in nature due to the absence of long range order and irregular arrangement of the constituent particles in all direction. This leads to same value of physical property along all the direction.

Fig. Irregular arrangement of particles in an amorphous solid
o Glass, rubber, amorphous silicon and plastics are typical examples of amorphous solids.
o Amorphous silicon is a photovoltaic material widely used for conversion of sunlight into electricity.
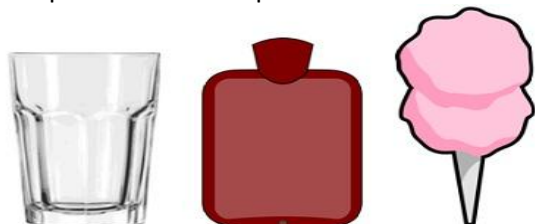

Fig. The glass used in making glassware, rubber used in making hot water bags and cotton candy are amorphous solids

Crystalline Solids

o This range of solids consists of a broad range of small crystals having a definite characteristic geometrical shape.

Fig. Crystals are crystalline solids
o The constituent particles are arranged in a long range order (symmetry and regularity of arrangement of constituent particles that repeat at any distance from a given atom due to the interaction between the particles) with a regular and periodically repeating pattern over the entire crystal.

o Crystalline solids possess a sharp melting point.
o Crystalline solids are *anisotropic* in nature due to different arrangement of particles in different directions. This leads to different value of physical property along different directions in the same crystals.
o Metallic elements including iron, copper and silver are typical examples of crystalline solids.
o On the other hand non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene and quartz are typical examples of crystalline solids.
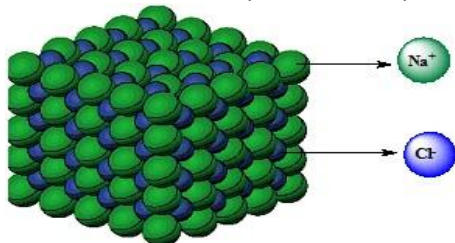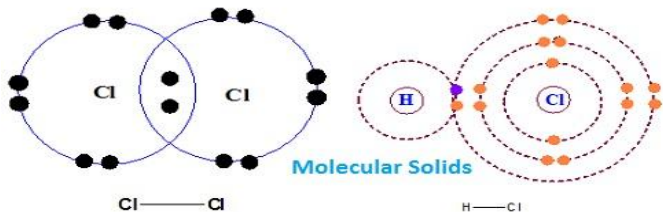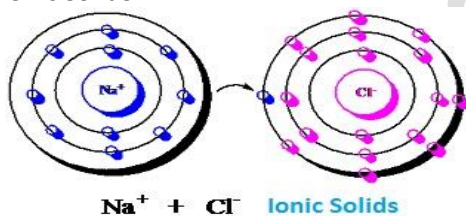

Fig. Crystalline form of Sodium Chloride

o These solids can be further be into four categories the basis of the nature of intermolecular forces acting over them
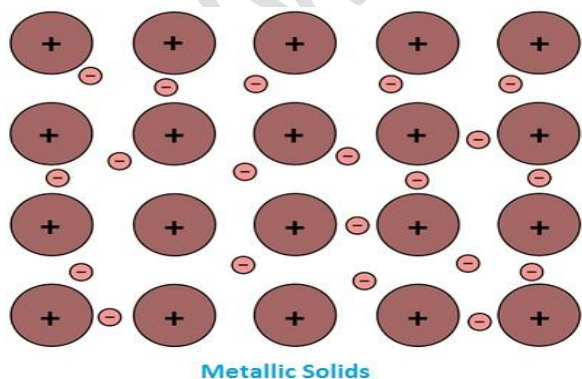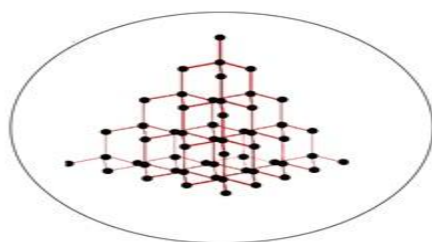
Molecular solids

Ionic solids

*Metallic solids*

Covalent solids

Covalent Solids

Molecular Solids

Solid composed of molecules as constituent particles. These solids can further be categorized into following types:
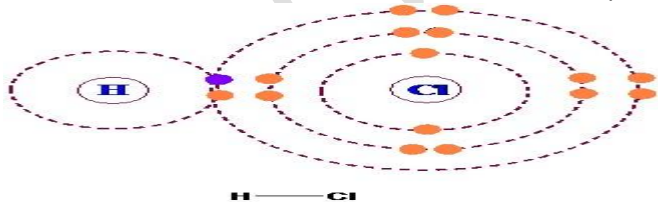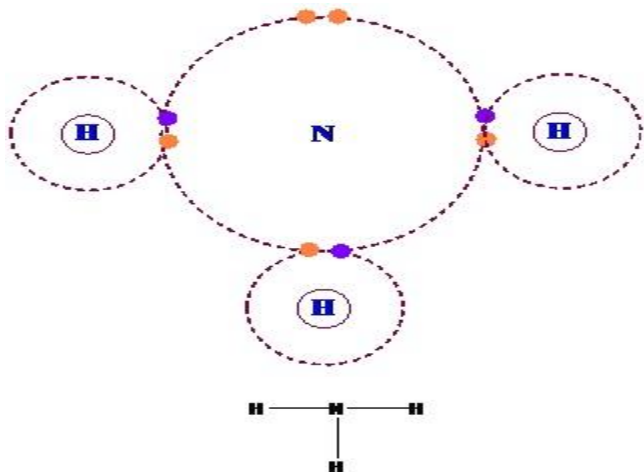
o **Non polar Molecular Solids**:
o They are composed of either atom.
o H_2, Cl_2 and I_2.are some of the typical example.
o In non-polar Molecular solids the comprised atoms or molecules are held together by weak dispersion forces or London forces.
o They are soft and non-conductors of electricity.
o They have low melting points and usually exist in liquid or gaseous state at room temperature and pressure.
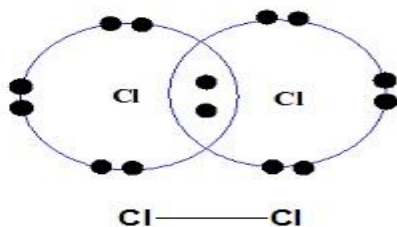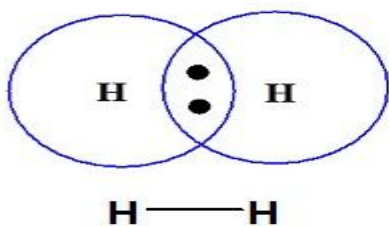
(ii) **Polar Molecular Solids:**
o The molecules like HCl, SO_2, are formed by polar covalent bonds.
o In polar Molecular solids the comprised atoms or molecules are held together by stronger dipole-dipole interactions.
o They are soft and non-conductors of electricity.
o The melting points of these solids are higher than those of non-polar molecular solids and usually exist in liquid or gaseous state at room temperature and pressure.
o Molecules like SO_2 and solid NH_3 are some examples of such solids.
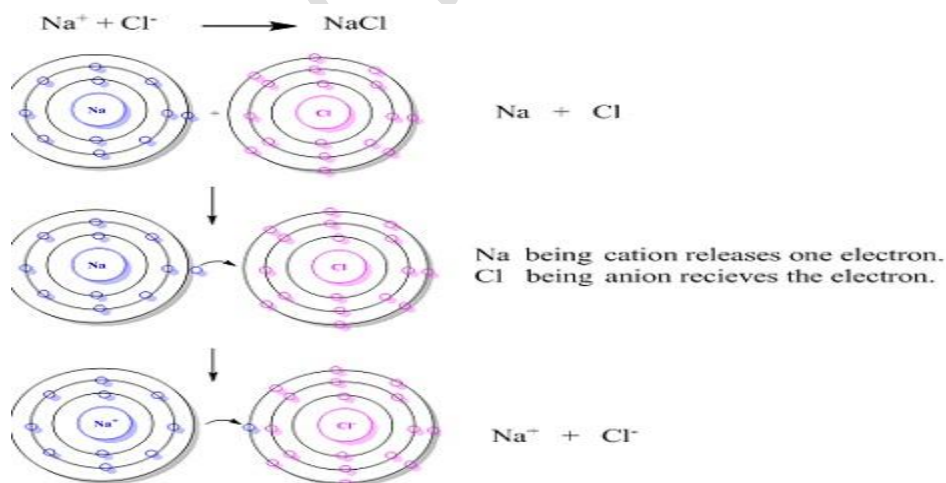
H——N——H
     |
     H

(iii) **Hydrogen Bonded Molecular Solids:**

- o Hydrogen Bonded Molecular Solids contain polar covalent bonds between H and F, O or N atoms.
- o Strong hydrogen bonding binds molecules of such solids like H_2O (ice).
- o They are non-conductors of electricity and are volatile liquids or soft solids under room temperature and pressure.


H————O————H
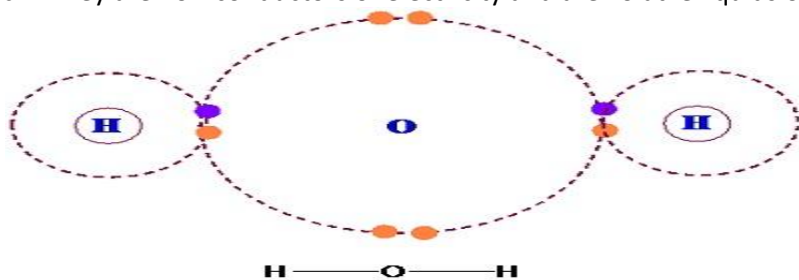
Ionic Solids

- o The constituent particles of these solids are ions.
- o The solid is composed of three dimensional arrangements of cations and anions that are bonded by strong coulombic (electrostatic) forces.
- o These solids are hard and brittle in nature and have high melting and boiling points.
- o They are electrical insulators in solid state due to the absence of movement of free electrons but are good conductors in molten state due to the movement of ions.

$Na^+ + Cl^- \longrightarrow NaCl$

Na + Cl

Na being cation releases one electron.
Cl being anion recieves the electron.

$Na^+ + Cl^-$

Metallic Solids

o In these solids positive ions is surrounded by mobile free electrons and are evenly spread all over the crystal.
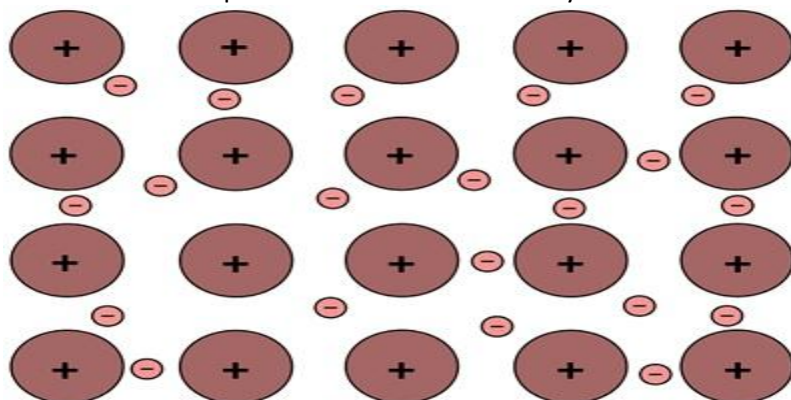
Metallic Solids

o Each metal atom donates one or more electrons to the group of mobile electrons which increases the electrical and thermal conductivity of the metallic elements.
o Application of electric field makes these electrons flow through the linkage of positive ions.
o Whereas application of heat to one portion of a metal makes the thermal energy spread uniformly throughout by free electrons.
o Presence of free electrons in metals makes them lustrous, malleable and ductile. For example, Cr, Fe etc.

Covalent solids

o Crystalline solids of non-metals comprises of covalent bonds between adjacent atoms that are strong and directional in nature due to which atoms are held very strongly at their positions all over the crystal.
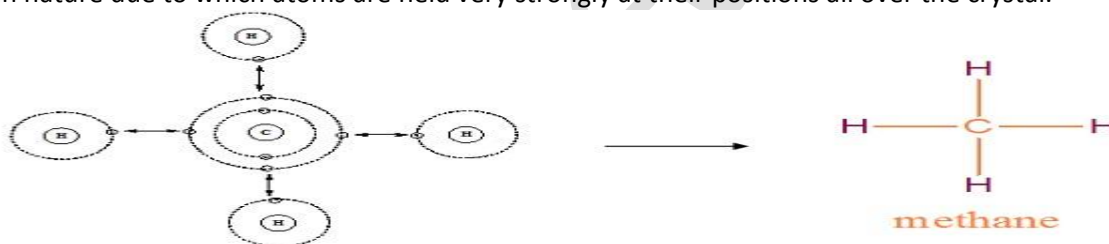

methane

Fig. Covalent bonding between Carbon and hydrogen
o They are also called **giant molecules**.
o These solids are very hard and brittle.
o They have extremely high melting points and may decompose before melting.
o They are insulators and do not conduct electricity.
o Diamond and silicon carbide are typical examples of such solids but Graphite is an exception as it is soft and a good conductor of electricity.
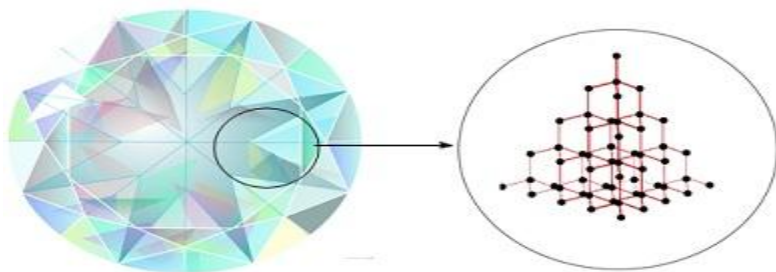
What makes graphite soft and a good conductor of electricity?

- Graphite is a covalent solid that act as a good conductor of electricity and is soft.
- The carbon atoms of graphite are prescribed in different layers and are covalently bonded to three of its surrounding atoms in the same layer.
- The fourth valence electron of each atom is present between different layers and is free to move which makes graphite a good conductor of electricity.
- The characteristic of sliding between different layers makes graphite a soft solid and a good solid lubricant.
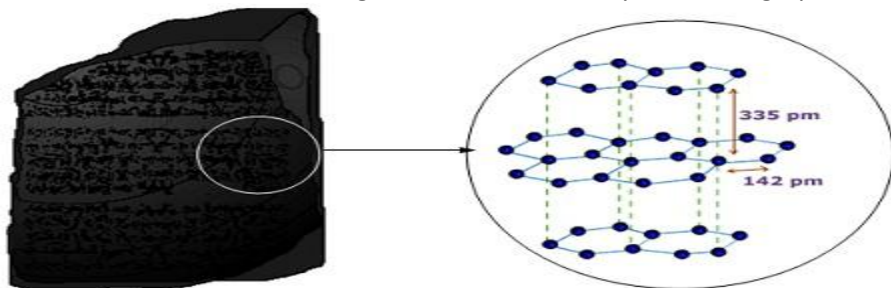

Crystal Lattices
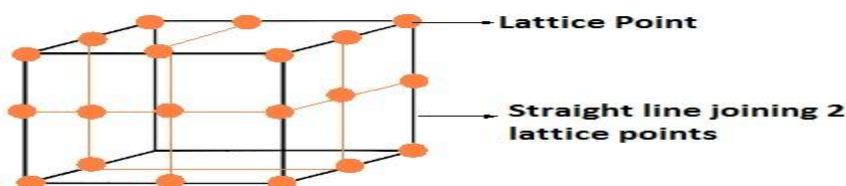
- Crystalline solids have a regular and periodically repeating pattern of constituent particles.
- The diagrammatical representation of three dimensional arrangements of constituent particles of a crystal in space with each particle depicted as a point is called *crystal lattice*.
- There are only 14 possible three dimensional lattices and are known **Bravais Lattices.**
- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice signifies one constituent particle which can be an atom, a molecule or an ion.
- Lattice points are joined together using straight lines to identify the geometry of the lattice.

Unit Cells
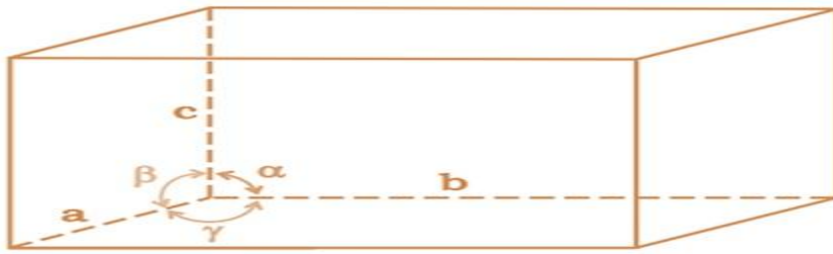
Unit cell can be described as the smallest portion of a crystal lattice.
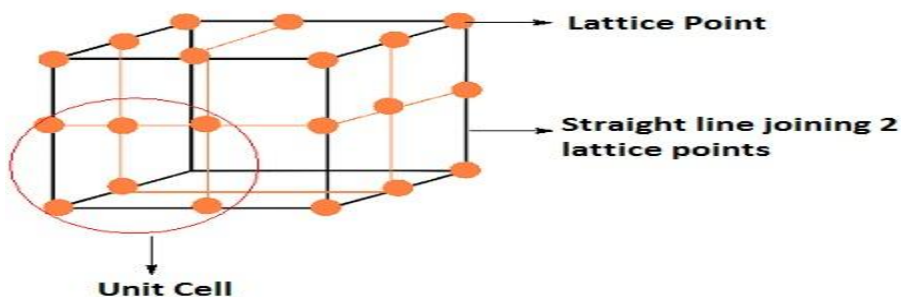

A unit cell is characterized by:

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

o   Angles between the edges, α (between b and c) β (between and c) and γ (between a and b). Thus, a unit cell is characterized by six parameters a, b, c, α, β and γ.

Primitive Unit Cells

If the constituent particles of a crystal lattice are present only on the corner positions of a unit cell, it is known as **primitive unit cell**.
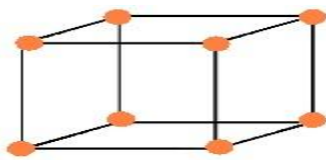
Primitive Unit Cell

Centered Unit Cells

o   If the constituent particles of a crystal lattice are present at positions other than corners in addition to those at corners, it is known as **centered unit cell**.
o   Centered unit cells are of three types:
   o   *Body-Centred Unit Cells:*
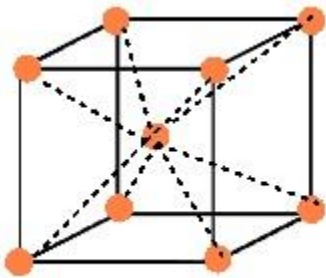
Body Centered Unit Cell

If the constituent particles of a unit cell are present at its body-centre besides the ones that are at its corners.
o   *Face-Centred Unit Cells:*
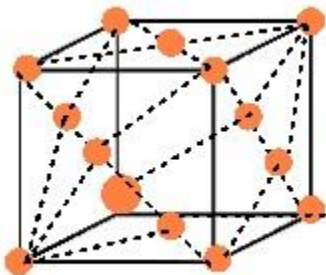
Face Centered Unit Cell

If the constituent particles of a unit cell are present at the center of each face, besides the ones that are at its corners.

o   *End-Centred Unit Cells:*

End Centered Unit Cell

If the constituent particles of a unit cell are present the center of any two opposite faces besides the ones present at its corners.

Number of atoms per unit cell : Primitive Cubic Unit Cell

Each cubic unit cell has 8 atoms on its corners.

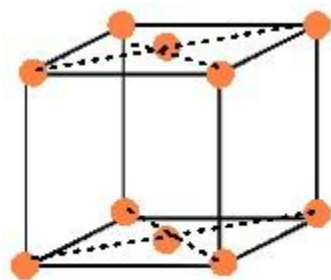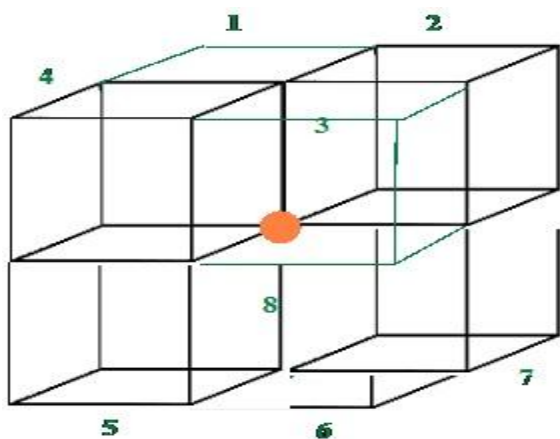Therefore total number of atoms in one unit cell = 8 * 1/8 = 1 atom

Number of atoms per unit cell : Body Centered Cubic Unit Cell

In a body-centered cubic (*bcc*) unit cell, the atoms are present in the body-center besides the ones that are at its corners that wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

8 corners X 1/8 per corner atom = 8 * 1/8   = 1 atom

1 body center atom = 1 X 1   = 1 atom

Total number of atoms per unit cell   = 2 atoms

Question: Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm-3, calculate atomic radius of niobium using its atomic mass 93 u.

Answer: Density = 8.55 gcm^{-3}

Consider length of the edge = a cm

Number of atoms per unit cell, Z = 2

M = 93 u

Using the formula

$$d = \frac{zM}{(a^3 N_A)}$$

$8.55 = 2 \times 93/a^3 \times 6.022 \times 10^{23} = 36.12 \times 10^{-24}$ cm3

$a = (36.12 \times 10^{-24})1/3 = 3.306 \times 10^{-8}$ cm
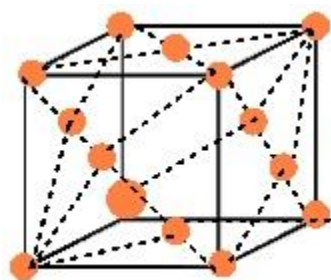
Radius in body centered cubic, $r = \sqrt{3}/4\ a$

Putting the value of a,

.$r = 1.431 \times 10^{-10}$ m

Number of atoms per unit cell : Face Centered Cubic Unit Cell
o   In a face-centered cubic (*fcc*) unit cell the atoms are present in the corners and at the center of all the faces of the cube.

Face Centered Unit Cell

o   Each atom present at the face-center is shared between two adjacent unit cells and only a ½ of each atom belongs to a unit cell.
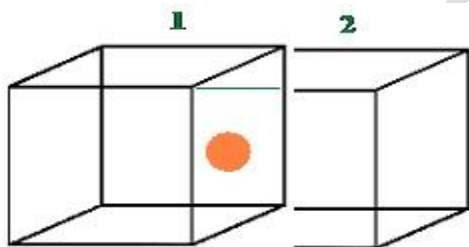
Thus, in a face-centered cubic (*fcc*) unit cell:
8 corners X 1/8 per corner atom =   8 * 1/8   = 1 atom
6 face-centered atoms X 1/2 per unit cell = 6 X 1/2   = 3 atoms
Total number of atoms per unit cell   = 4 atoms
In solids, these constituent particles are closely-packed that leaves minimum vacant space.

Question : An element with molar mass 2.7×10^{-2}kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3kg^{-3}, what is the nature of the cubic unit cell?
Answer : d = 2.7×10^3kg^{-3}
M = 2.7×10^{-2} kg mol^{-1}
a= 405 pm = 405 X 10^{-12}
N$_A$= 6.023 X 10^{23}

Using the formula

$$d = \frac{zM}{(a^3 N_A)}$$

$$2.7 \times 10^3\, kg^{-3} = \frac{z\, 2.7 \times 10^{-2}\, kg\, mol^{-1}}{[(405\ X10^{-12})^3\ X\, 6.023\ X\ 10^{23}]}$$

Z=4

Unit cell is fcc unit cell.

Volume of 54 g of the element = $0.054/(2.7 X 10^3)$ = $2\ X\ 10^{-6}$

Number of unit cell in this volume = volume of 554 g of element/volume of each unit cell = $2\ X\ 10^{-6}/(405\ X\ 10^{-12})^3$ = 3.012 X 10^{22}

Question: Copper crystallises into a fcc lattice with edge length 3.61 x 10^{-8}cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}

Answer: Given that Copper crystallises into a fcc lattice

Hence Z= 4

M = 63.5

a = $3.61 x 10^{-8}$

N_o = 6.023 x 10^{23}

Using the formula

$$d = \frac{zM}{(a^3 N_o)}$$

$$Density = \frac{4 \times 63.5}{[(3.61 x 10^{-8})^3\ X\, 6.023\ X\ 10^{23}]} = 8.96\ gcm^{-3}.$$

Therefore, approximately the value is equal to 8.92.

Close Packing in One Dimension

o   The only way to arrange spheres in a one dimensional close packed structure is to arrange the spheres in a single row and touching each other.

o   Each sphere is in contact with two of its surrounding atom.

o   The number of nearest surrounding particles is called its **coordination number**. Therefore in one dimensional close packed arrangement, the coordination number is 2.

Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres.
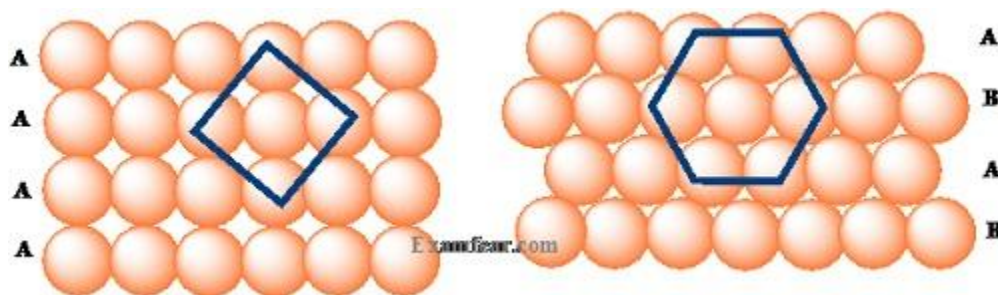
The second row can be placed in contact with the first row in such a way that the spheres of second row are exactly above the first row.

o The spheres of the two rows are aligned horizontally as well as vertically.
o Let the first row be 'A' type row and the second row is also of 'A' type due to its similarity with the first one.
o Similarly, we may place more rows to obtain AAA type of arrangement.
o Each sphere is in contact with four of its surrounding atom. Thus, the two dimensional coordination numbers is 4.
o If the centers of these 4 immediate surrounding spheres are joined, a square is formed. Due to which this packing is known as square close packing in two dimensions.
o The second row can be placed above the first row in a staggered manner in such a way that the spheres fit in the depressions of the first row.
o Let the first row be 'A' type row, and the second row be 'B' type row.
o When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type.
o The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type.
o This arrangement provides less free space and is more efficient than the square close packing.
o Each sphere in this arrangement is in contact with six of surrounding spheres and the two dimensional coordination numbers is 6.
o The centers of these six spheres are at the corners of a regular hexagon due to which this packing is also known as two dimensional hexagonal close packing**.
o These are triangular in shape. In one row, the apex of the triangles is pointing upwards and in the next layer the apex of the triangles is pointing downwards.

Close Packing in Three Dimensions
All real structures are three dimensional structures that are obtained by stacking two dimensional layers one above the other in a square close-packed and hexagonal close-packed manner. It can be categorized into two types:
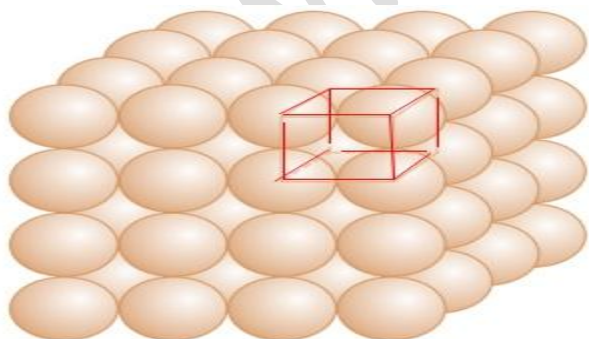
**Three dimensional close packing from two dimensional square close-packed layers:**
o The second layer is placed over the first layer in such a way that the spheres of the upper layer are exactly above those of the first layer.

- o In this arrangement of spheres, both the layers are perfectly aligned horizontally as well as vertically.
- o Let the first row be 'A' type row, and the second row be 'B' type row.
- o Thus this lattice has AAA.... type pattern.
- o The lattice therefore generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell.
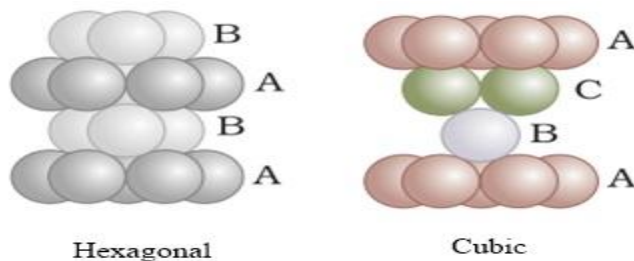
Three dimensional close packing from two dimensional hexagonal close packed layers:

 Three dimensional close packed structure can be generated by placing layers one over the other.
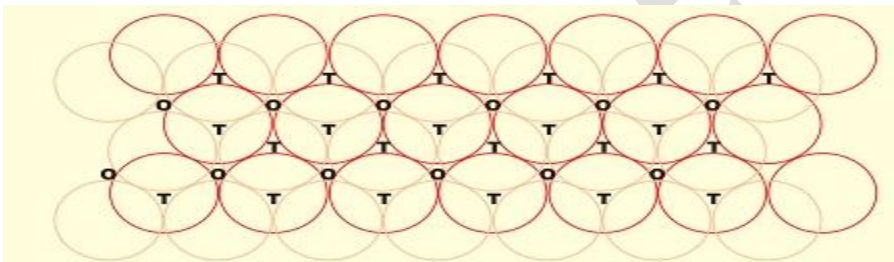- o Placing second layer over the first layer
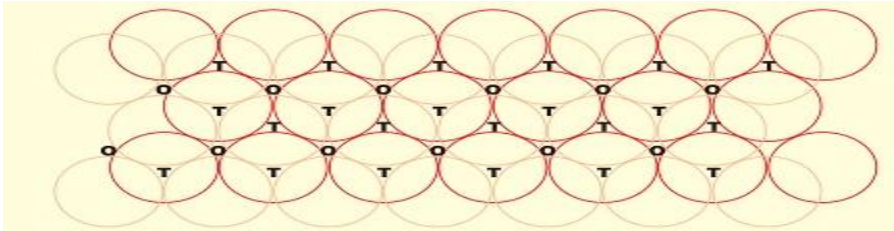
- o Placing third layer over the second layer

Hexagonal   Cubic

Placing second layer over the first layer

- o Consider a two dimensional hexagonal close packed layer of type 'A' and place a similar layer above it in such a way that the spheres of the second layer lies in the depressions of the first layer.
- o Let the second layer be of type 'B' due to its different alignment.
- o All the triangular voids of the first layer are not covered by the spheres of the second layer which gives rise to a different arrangement.
- o The area where a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed.
- o These voids are called tetrahedral voids because a joining of the centers of four spheres gives rise to *tetrahedron*.
- o There are areas where the triangular voids in the second layer lies above the triangular voids of the first layer, and the triangular shapes of these do not overlap.
- o One of them has the apex of the triangle pointing upwards and the other downwards.

Tetrahedral Hole
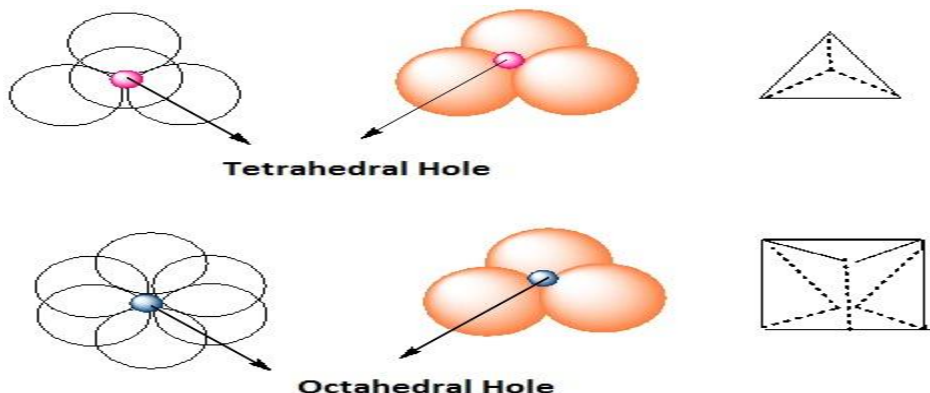
Octahedral Hole

o   Such voids are surrounded by six spheres and are called **octahedral voids (O).**

Let the number of close packed spheres be *N*, then:

The number of octahedral voids generated in the structure = *N.*

The number of tetrahedral voids generated in the structure = *2N.*

Question : If the radius of the octachedral void is r and radius of the atoms in close packing is R, derive relation between r and R.

Answer: Given that

Radius of octahedral void in close packing = r

Radius of atom in close packing = R

Using Pythagoras theorem,

$2R^2 = (R+ r)^2 + (R+ r)^2$

$4R^2 = 2(R +r)^2$

$2R^2 = (R+ r)^2$

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

$R\sqrt{2} - R = r$

$r = R\sqrt{2} - R$

Putting the value of √2, we derive

r = R (1.414-1)

r = 0.414R

Placing third layer over the second layer : **Covering Tetrahedral Voids**

o   Tetrahedral voids of the second layer can get covered by the spheres of the third layer.

o   Here the spheres of the third layer get exactly aligned with the spheres of the first layer.

o   Therefore it can be observed that the pattern of spheres is repeated in alternate layers.

o   This pattern is often written as ABAB .... pattern and the structure is called hexagonal close packed (*hcp*) structure found in many metals like magnesium and zinc.
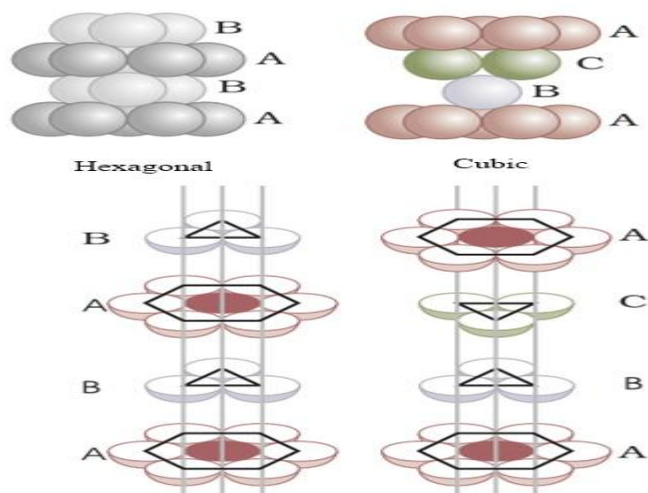
Hexagonal   Cubic

Question : A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Answer: Number of particles in 1 mol of compound = 6.022×10^{23}
Number of particles in 0.5 mol = $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$
Number of octahedral voids = number of atoms or particles.
Number of tetrahedral voids = 2 X number of particles
Therefore number of octahedral in the given compound = 3.011×10^{23}
Number of tetrahedral voids = $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$
The total number of voids = $3.011 \times 10^{23} + 6.022 \times 10^{23}$
= 9.033×10^{23}
Number of tetrahedral voids = 6.022×10^{23}

Question. Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?
**Answer**: Number of tetrahedral voids = 2 X number of particles of atom B
Number of atoms of A is equal to of the number of atoms of B.
Hence the ratio A:B = (4/3):1 or 4:3
Therefore, the formula of the compound is A_4B_3.

Placing third layer over the second layer : **Covering Octahedral Voids**
o   The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.
o   When placed in this manner, the spheres of the third layer are not aligned with
     those of either the first or the second layer. This arrangement is called "C'
o   Only when fourth layer is placed, its spheres are aligned with those of the first layer.
o   This pattern of layers is often written as ABCABC........... This structure is called cubic close packed (*ccp*) or face-centered cubic (*fcc*) structure.
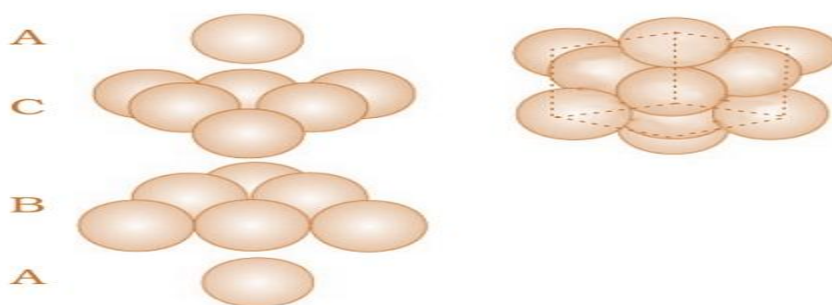
o Metals such as copper and silver crystallize in this structure. Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

Question: A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Answer: The ccp lattice is made by the atoms of the element N.
Here, the Number of tetrahedral voids = 2 X number of particles of the elements N.
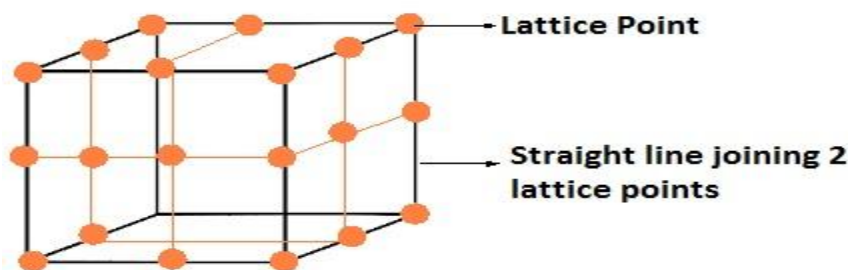According to the question, the atoms of element M occupy = $1/3^{rd}$ of the tetrahedral voids.
Therefore, the number of atoms of M is equal to
2 x 1/3 = 2/3rd of the number of atoms of N.
Therefore, the ratio M:N = 2/3 :1   = 2:3
Hence formula of the compound is M_2N_3.

Formula of a Compound and Number of Voids Filled

o The number of octahedral voids present in a lattice = The number of close packed particles.
o The number of tetrahedral voids produced is twice this number.
o In ionic solids, the bigger ions i.e. anions forms close packed structure and the smaller ions i.e. cations occupy the voids.
o If the latter ion is small then tetrahedral voids are occupied, if bigger, then octahedral voids are occupied.
o In a compound, the fraction of octahedral or tetrahedral voids that are occupied depends upon the chemical formula of the compound.
o Close packed structures have both tetrahedral and octahedral voids.

Locating Tetrahedral Voids
o Take a unit cell of ccp or fcc lattice divide into eight small cubes with each small cube having atoms at alternate corners.
o Thus, each small cube has 4 atoms that on joining to each other make a regular tetrahedron.

- o Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total.
- o Each of the eight small cubes have one void in one unit cell of *ccp*
- o *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.
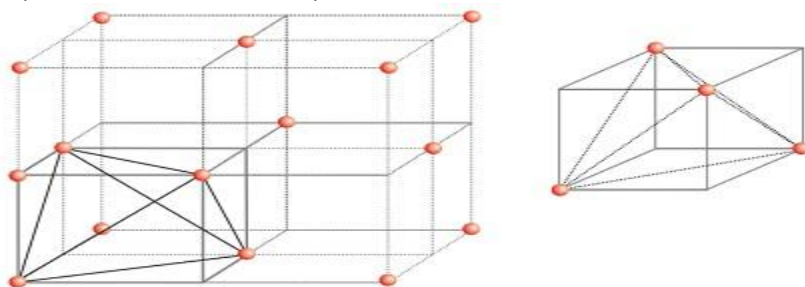
Locating Octahedral Voids
- o Take a unit cell of ccp or fcc.
- o The body center of the cube, C is not occupied but surrounded by six atoms on face centers.
- o Joining the face centers creates a octahedron.
- o Thus, this unit cell has one octahedral void at the body centre of the cube.
- o There is one octahedral void at the centre of each of the 12 edges.
- o It is surrounded by six atoms, three belonging to the same unit cell and three belonging to two adjacent unit cells.
- o Each edge of the cube and octahedral void are shared between four adjacent unit cells.
- o Only ¼ of each void belongs to a particular unit cell
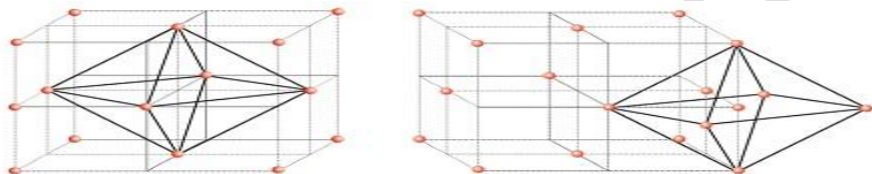
In *cubic close packed structure* octahedral void at the body-center of the cube = 1

12 octahedral voids positioned at each edge and shared between four unit cells =12 x 1/4 =3

Total number of octahedral voids = 4

In ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

Packing Efficiency in hcp and ccp Structures
let the unit cell edge length be 'a' and face diagonal AC = b.
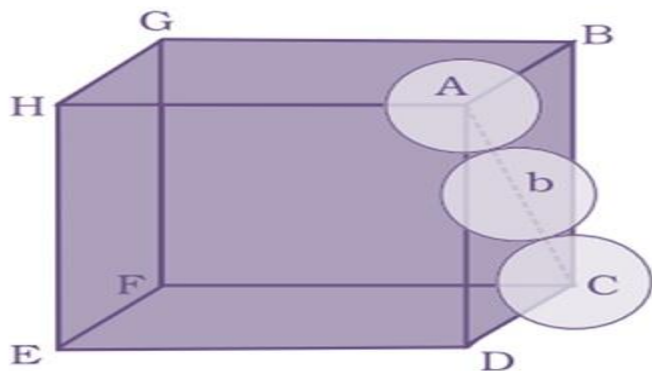
ΔABC

$$AC^2 = b^2 = BC^2 + AB^2$$
$$= a^2 + a^2 = 2a^2$$
$$b = \sqrt{2}a$$

Let r be the radius of the sphere. So we get

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

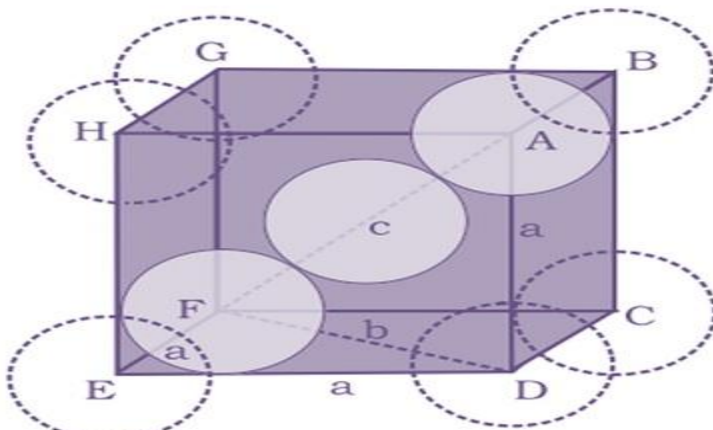Each unit cell in ccp structure has effectively 4 spheres.
Hence total volume of four spheres is equal to 4 X (4/3)Π r³ and volume of the cube is a³ or (2√2r)³.
Therefore, Packing efficiency = (Volume occupied by four spheres in the unit cell X 100)/(Total volume of the unit cell)

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

$$= \frac{\frac{16}{3}\pi r^3 X 100}{16\sqrt{2}r^3}\% = 74\%$$

Efficiency of Packing in Body Centered Cubic Structures

ΔEFD

$$b^2 = a^2 + a^2 = 2a^2$$

ΔAFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

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

The length of the body diagonal c = 4r, where r is the radius of the sphere as all the spheres along the diagonal touch each other. Therefore,

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

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

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

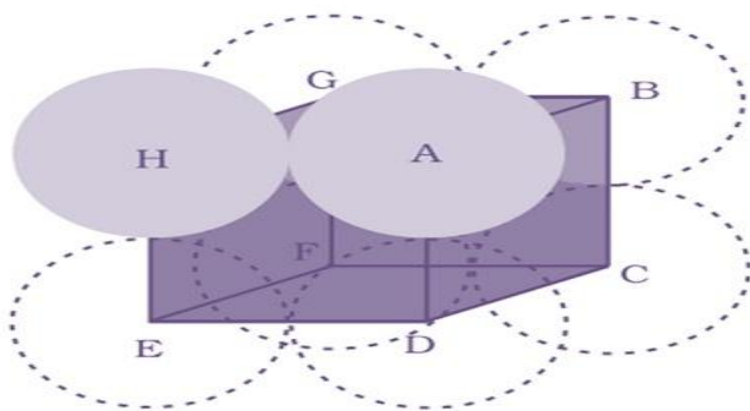This type of structure has 2 atoms and their volume is $2 \times (\frac{4}{3})\pi r^3$.

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

Packing efficiency = (Volume occupied by two spheres in the unit cell X 100)/(Total volume of the unit cell)

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

$$= \frac{\frac{8}{3}\pi r^3 X 100}{64/(3\sqrt{3})r^3}\% = 68\%$$

Packing Efficiency in Simple Cubic Lattice

a = 2r

Where a = Edge length or side of the cube

r = radius of each particle,

The volume of the cubic unit cell = a3 = $(2r)^3$ = $8r^3$

A simple cubic unit cell contains only 1 atom. The volume of the occupied space =4/3 Π r^3

Packing efficiency = (Volume of one atom X 100)/(Volume of cubic unit cell)

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} X100 = \frac{\pi}{6} X100 = 52.4\%$$

Therefore it can be concluded that ccp and hcp has maximum packing efficiency.

Calculations Involving Unit Cell Dimensions

Edge length of a unit cell of a cubic crystal = *a,*

Density of the solid substance = *d*

Molar mass = M

Volume of a unit cell = *a3*

Mass of the unit cell = number of atoms in unit cell × mass of each atom = number of atoms present in one unit cell (*z)* × mass of a single atom *(m)*

$$m = \frac{M}{N_A}$$

Density of the unit cell

$$m = \frac{M}{N_A}$$

Density of the unit cell = (Mass of unit cell)/(Volume of unit cell)

$$\frac{z.m}{a^3} = \frac{z.m}{a^3 N_A}$$

$$d = \frac{z.m}{a^3 N_A}$$

Imperfections in Solids

o   Constituent particles in crystalline solids are arranged in a short range as well as long range
     order yet crystals are not perfect.
o   They possess small crystals have defects that are irregularities in the arrangement of constituent
     particles in them when crystallization process occurs at fast or moderate rate.
o   These defects are of two types- point defects and line defects.
o   The irregularities or deviations from ideal arrangement around a point or an atom in a
     crystalline substance.
o   The irregularities or deviations from ideal arrangement in entire rows of lattice points are known as line defects.
o   These irregularities are called *crystal defects*.
o   Point defects can be classified into three types: (i) stoichiometric defects
     (ii) impurity defects and (iii) non-stoichiometric defects

Stoichiometric Defects

o   These ranges of point defects do not disturb the stoichiometry of
     the solid.
o   They are also called *intrinsic* or **thermodynamic defects.**
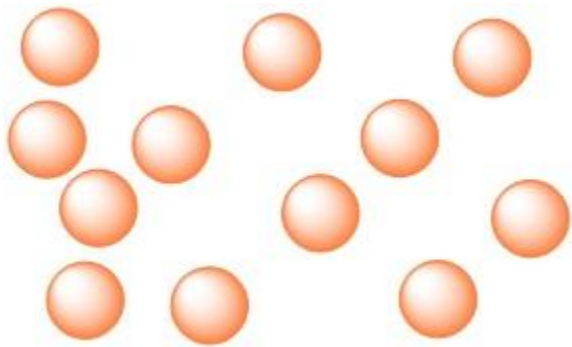o   Non-ionic solids exhibit their defects as vacancy defects and interstitial defects.

*Vacancy Defect***:**
A crystal containing vacant lattice sites is said to have **vacancy defect.** This defect can also develop due to heating up of
     a substance.
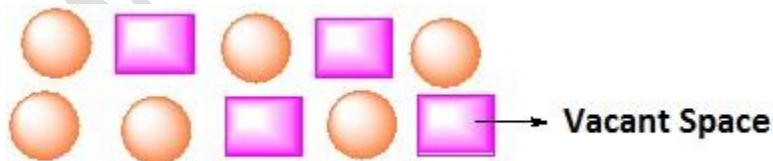
*Interstitial Defect***:**
A crystal in which some constituent particles occupy an **interstitial** site,
     are said to have **interstitial defect** which increases the density of the substance.

Ionic solids exhibit their defects as **Frenkel and Schottky defects.**

Frenkel Defect:
o   This defect is exhibited by the ionic substances due to the large difference in size of ions.
o   The smaller ion (cation) is displaced from its normal site to an interstitial site which creates a vacancy defect at its original site and an interstitial defect at the new location.
o   It is also called dislocation defect.
o   It does not alter the density of the solid.
o   For example, ZnS, AgCl, AgBr and AgI due to small size of Zn2+ and Ag+ ions.
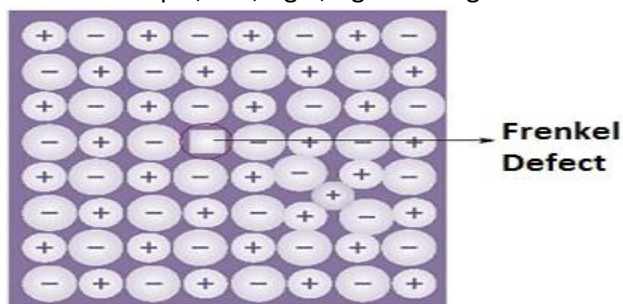

Schottky Defect:
o   This defect in ionic solids is equivalent to the vacancy defect in non-ionic solids.
o   In order to maintain electrical neutrality, the number of missing cations and anions are equal
o   Schottky defect also decreases the density of the substance.
o   This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
o   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 Schottky defect per 10^{16} ions.
o   For example, NaCl, KCl, CsCl and AgBr.
o   Out of these AgBr shows both, Frenkel as well as Schottky defects.

Schottky Defect
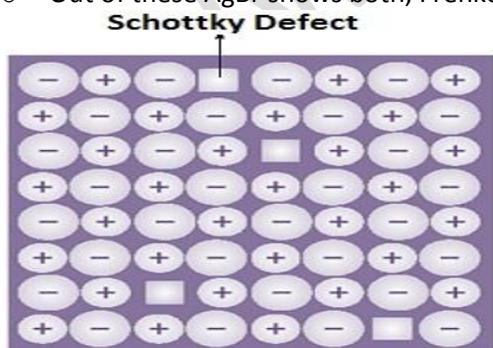

Impurity defect
o   Crystallization of molten NaCl with little amount of $SrCl_2$ results in Sr^{2+} occupying some of the sites of Na^+

- o Each Sr^{2+} replaces two Na+ ions.
- o It occupies the site of one ion and the other site remains vacant.
- o The cationic vacancies thereby produced are equal in number to that of Sr^{2+}
- o Solid solution of $CdCl_2$ and AgCl.
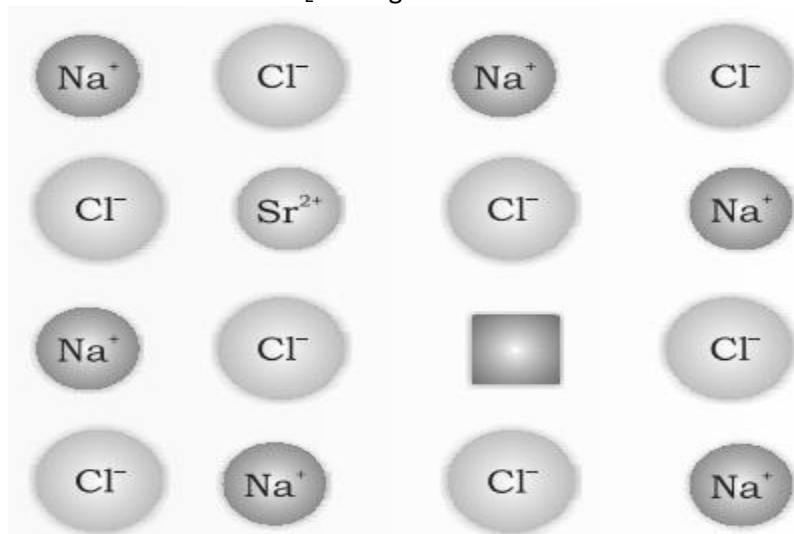
Non-Stoichiometric Defects
- o Nonstoichiometric inorganic solids contain the constituent elements in a non-stoichiometric ratio due to defects in their crystal structures.
- o These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect.
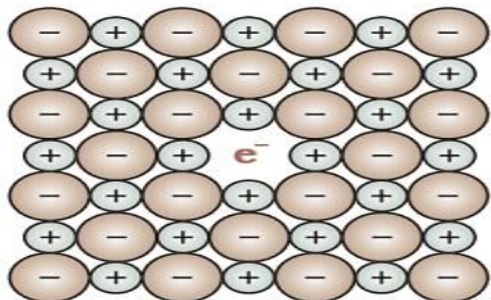
- o Metal excess defect due to anionic vacancies:
- o This type of defect is exhibited by alkali halides like NaCl and KCl.
- o Application of heat to NaCl in an atmosphere of sodium vapour results in deposition of the sodium atoms on the surface of the crystal.
- o The sodium atoms lose electron to form Na^+
- o The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.
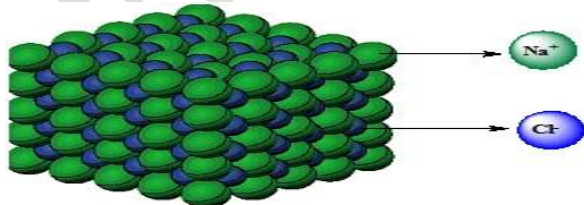
- o The released electrons diffuse into the crystal and occupy anionic sites.
- o The anionic sites occupied by unpaired electrons are called F-centres that imparts yellow colour to the crystals of NaCl due to the excitation of the electrons on absorption of energy from the visible light falling on the crystals.

- Excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet.
- Metal excess defect due to the presence of extra cations at interstitial sites:
- Heating Zinc oxide that exists in white colour at room temperature loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + 1/2\ O_2 + 2e^-$$
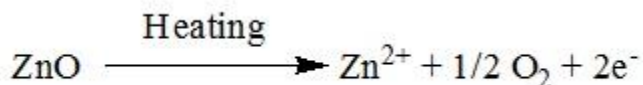
- This results in excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$.
- The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.
- Metal Deficiency Defect:
- Many solids possess less amount of the metal as compared to the stoichiometric proportion.
- For example, FeO is mostly found with a composition ranging from $Fe_{93}O$ to $Fe_{0.96}O$.
- In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+}

Electrical Properties of soilds
Solids exhibit electrical conductivities that extend from 27 orders of magnitude ranging from 10^{-20} to 10^7 $ohm^{-1}\ m^{-1}$.
Conductors:
- Solids with conductivities ranging between 10^4 to 10^7 $ohm^{-1}m^{-1}$ are conductors.
- Metals have conductivities in the order of 10^7 $ohm^{-1}m^{-1}$ are good conductors.
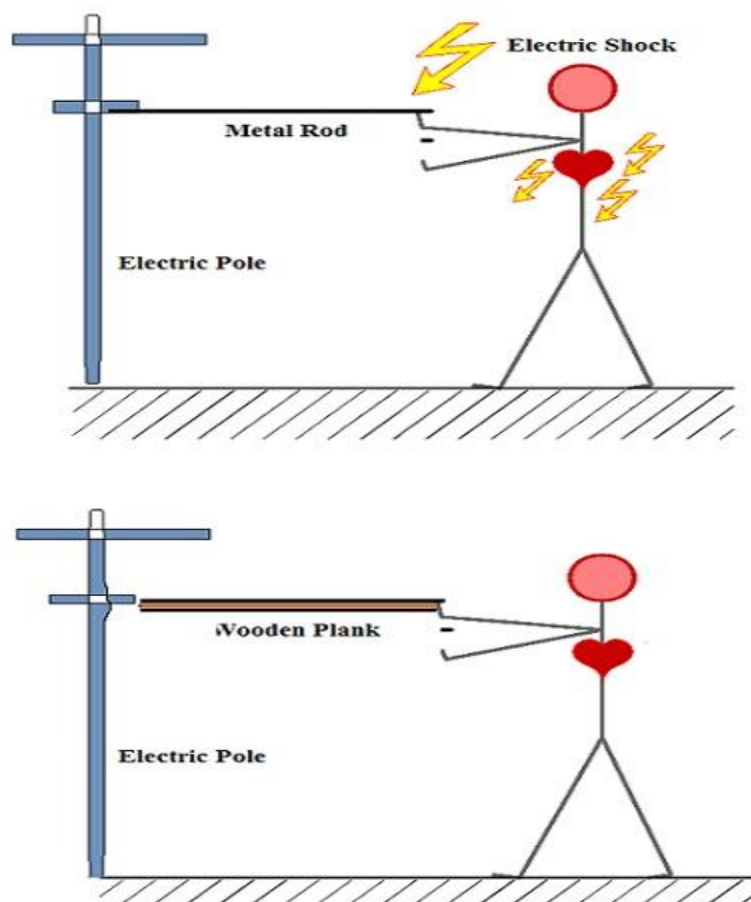- For example, Iron, Copper, Aluminum.

Fig. Metal is used at the tip of the plug that is inserted into the socket

Insulators:
- Solids with very low conductivities ranging between 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$.
- For example, Wood, plastic, cloth, glass.

**Fig.** Wood and plastics are also solids but are insulators

A man touching the electric pole with a metal rod will get an electric shock because metal rod is a conductor whereas a man touching the same with a wooden plank will be safe because wood is an insulator.

o Semiconductors:
o Solids with conductivities in the intermediate range from 10–6 to 104 ohm^{-1} m^{-1}.
o For example, Gallium, Germanium, Silicon

Conduction of Electricity in Metals
o A conductor conducts electricity due to the movement of electrons or ions.
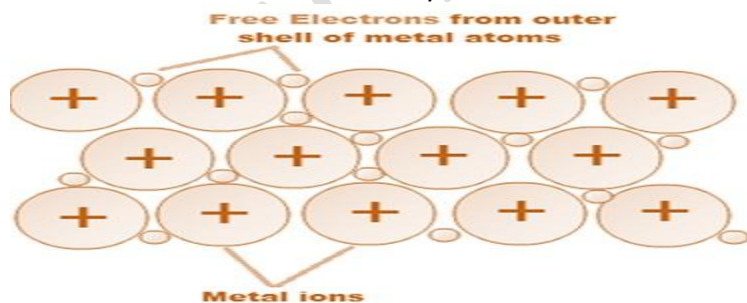
o Metals conduct electricity both in solid state as well as molten state.
o The conductivity of metals depends upon the number of valence electrons available per atom.
o The atomic orbitals of metal atoms form molecular orbitals that are close in energy to each other as to form a band.
o Partial filling or overlapping with a higher energy unoccupied conduction band enables the electrons to flow easily under an applied electric field.
o This results in conductivity of metals.

If the gap between valence band and the conduction band is large, electrons cannot jump to it and such a substance has very low conductivity that makes it behave like an insulator

Conduction of Electricity in Semiconductors
In semiconductors, the gap between the valence band and conduction band is small.
This enables some electrons to jump to conduction band and exhibit their conductivity.
Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump to the conduction band due to small gap between the valence band and conduction band.
Silicon and germanium exhibit this behavior and are called intrinsic semiconductors.
The conductivity of these intrinsic semiconductors is too low to be practically used.
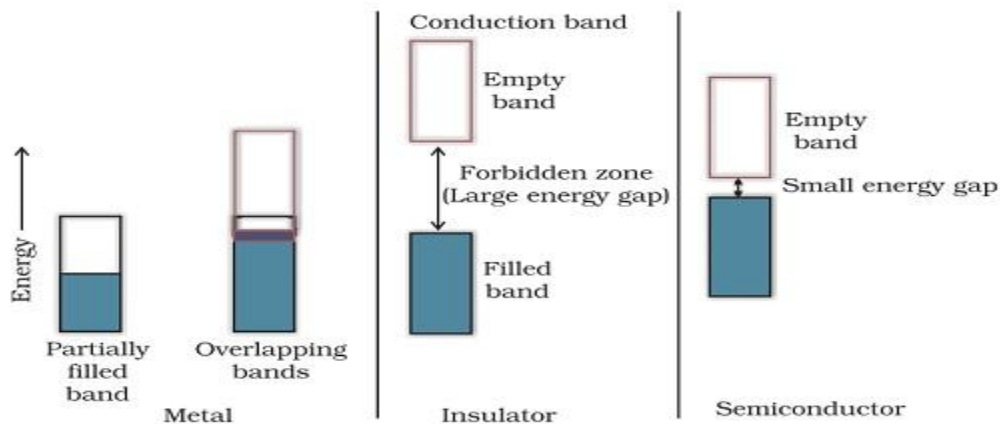
Doping
o   The conductivity of metal is increased by adding an appropriate amount of suitable impurity.
o   This process is known as doping.
o   It can be performed with an impurity which is electron rich or electron deficient than the intrinsic semiconductor silicon or germanium.
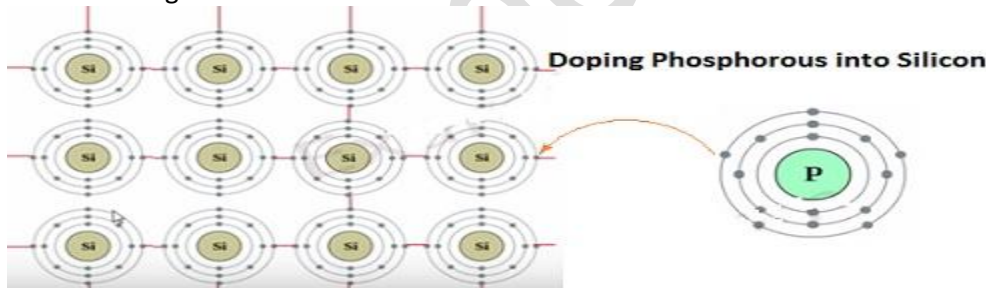

Fig. Doping electron rich impurity into an intrinsic conductor
o   Such impurities introduce electronic defects in them.
1.   If NaCl is doped with 10-3mol % of $SrCl_2$, what is the concentration of cation vacancies?
2.   1 Cation of Sr^{2+} = 1 cation vacancy in NaCl.
Number of cation vacancies in lattice of NaCl = Number of divalent Sr^{2+} ions added.
Concentration of cation vacancy on doping with 10^{-3} mol% of $SrCl_2$. = 10^{-3} mol% = 10^{-3} **/** 100 = 10^{-5} mol.
Number of Sr^{2+} ion in 10^{-5} mol = 10^{-5} x 6.023 x 10^{23} = 6.023 x 10^{18}
Hence number of cationic vacancies = 6.023 x 10^{18}

Electron – rich impurities
In a periodic table Silicon and germanium belongs to group 14 with four valence electrons each. In their crystals each atom forms four covalent bonds with surrounding atom.
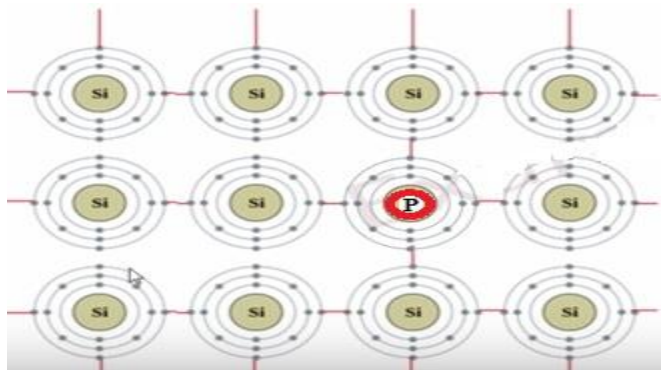
When doped with a group 15 element like P or As, which contains five valence electrons,

They occupy some of the lattice sites in silicon or germanium crystal.
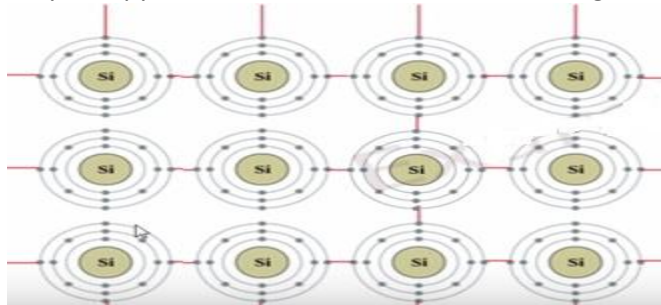
Four out of five electrons are used in the formation of four covalent bonds with the four neighboring silicon atoms. The fifth electron in P is extra and becomes delocalized.


These delocalized electrons increase the conductivity of doped silicon (or germanium).
This type of semiconductor is known as n-type semiconductor because the increase in conductivity is due to the negatively charged electron.

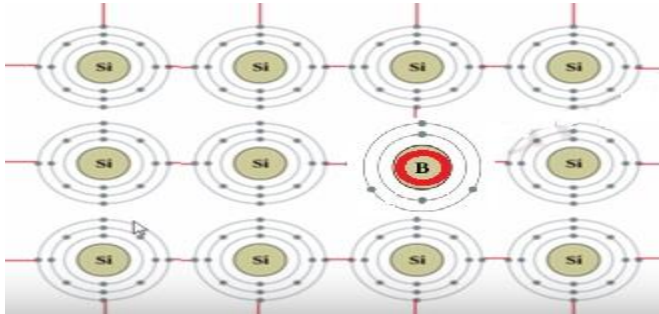**Electron – deficit impurities**
Silicon or germanium of group 14 can also be doped with elements of group 13 element like B, Al or Ga which contains only three valence electrons.
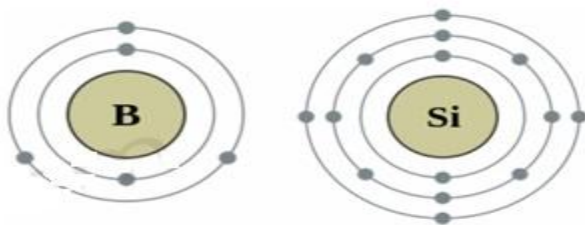
Three electrons of B form covalent bonds with three electrons of Si.
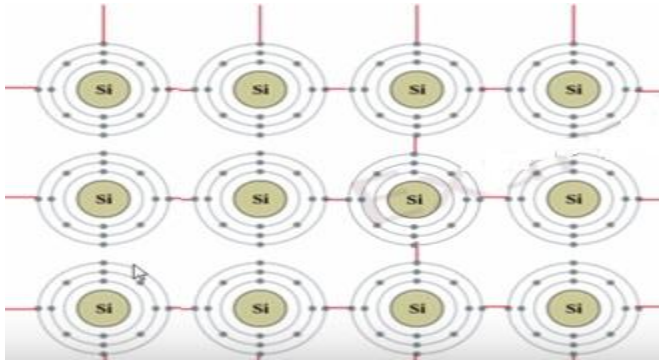
The fourth electron in Si is extra that remains isolated and creates an electron hole or electron vacancy.

An electron from a neighboring atom can come and fill the electron hole, but leave an electron hole at its original position resulting in displacement of the electron hole in the direction opposite to that of the electron that filled it.

Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate.

These types of semiconductors are called p-type semiconductors.

Applications of n-type and p-type semiconductors
o   n-type and p-type semiconductors finds a great use in manufacturing electronic components.
o   Diode is a combination of n-type and p-type semiconductors extensively used as a rectifier.
o   Transistors are manufactured by keeping a layer of one type of semiconductor between two layers of another type of semiconductor.
o   npn and pnp type of transistors are used to detect or amplify radio or audio signals.
o   The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.
o   Gallium arsenide (GaAs) semiconductors have very fast response and have transformed the design of semiconductor devices.
o   Transition metal oxides show marked differences in electrical properties.
o TiO, CrO_2 and ReO_3 behave like metals.
o   Rhenium oxide, ReO_3 resembles metallic copper in terms of its conductivity and appearance.
o   Certain other oxides like VO, VO_2, VO_3 and TiO_3 exhibit metallic or insulating properties depending on temperature.

Magnetic Properties
o   Every substance possesses magnetic properties originated from the electrons present in them.
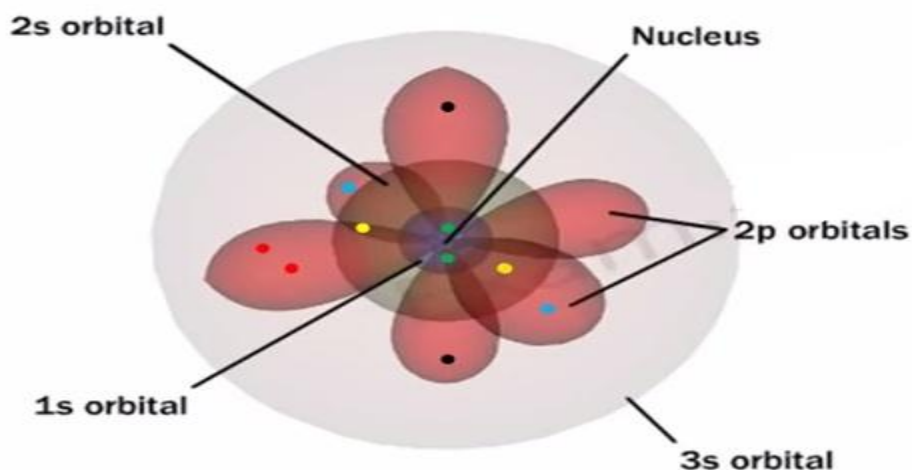
- o Each electron in an atom behaves like a tiny magnet.
- o The magnetic moment of these substances originates from two types of motions
- o its orbital motion around the nucleus and
- o its spin around its own axis.
- o Electron being a charged particle undergoes these motions and can be considered as a small loop of current possessing a magnetic moment.
- o Therefore, each electron has a permanent spin and an orbital magnetic moment associated with it.
- o Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ B and is equal to $9.27 \times 10-24$A m^2.

On the basis of their magnetic properties, substances can be classified into five categories:

- o Paramagnetic
- o Diamagnetic
- o Ferromagnetic
- o Antiferromagnetic
- o Ferrimagnetic.

Thank you
Mohd Sharif (www.free-education.in)