DON BOSCO SCHOOL, KOKAR

Sub: Chemistry
Class: 12
By: Miss Rupa

Note*: *Read the given notes carefully and answer the following questions. Kindly utilize your chemistry class work copy to write down your answers.

Ch – 1 (SOLID STATE)

GENERAL CHARACTERISTICS OF SOLID STATE:

Let us revise the general characteristics of solid:

i) Fixed mass, volume and shape

ii) Strong intermolecular force of attraction

iii) Least intermolecular space

iv) Fixed position of constituent particles

v) Incompressible and rigid

CLASSIFICATION OF SOLIDS:

Solids are classified on the basis of arrangement of their constituent particles:

1. **crystalline solid** - If the arrangement of constituent particles is same throughout the solid (long range order) in the definite geometrical pattern is called *crystalline solid*. Ex. sodium chloride, Quartz
2. **Amorphous Solid** -If the arrangement of particles does not follow any regular pattern throughout the solid (short range order) it is called *amorphous* solid. Ex. quartz glass , rubber, polyvinyl chloride

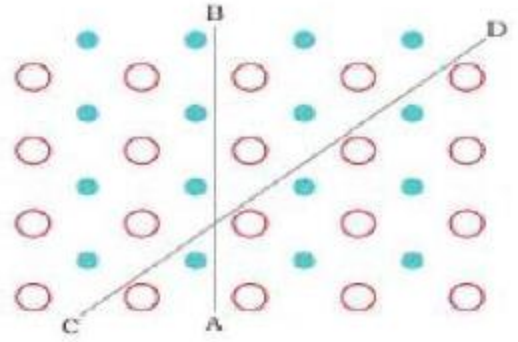
Arrangement of particles in solid

Crystalline solids

Amorphous solids

Characteristics of crystalline solid:

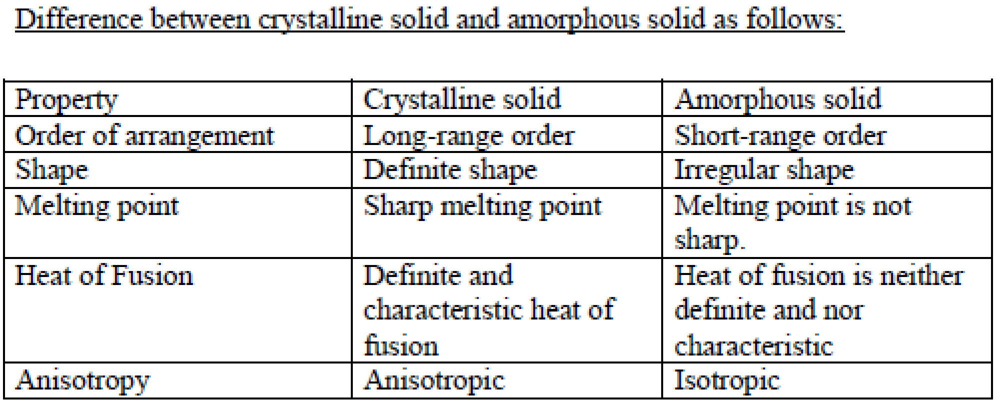
- It consists of large number of small crystals having a **definite geometrical** shape.
- The arrangement of constituent particles is regular throughout the solid (long range order). That is a fixed pattern of constituent particles repeat itself periodically over the entire range of solid.
- They have **sharp** melting points.
- They are **anisotropic** in nature ie may possess different magnitudes of physical properties in different direction.



Characteristics of amorphous solid:

- The arrangement of constituent particles is irregular throughout the solid. Regular pattern of constituent particle is visible in small areas only. That is it shows **short-range order.**
- Melting point is **not sharp**. Amorphous solid melts over a range of temperature.
- They have tendency to flow at slower rate. (called **supercooled liquid** .ex- glass)
- They are **isotropic** in nature.

  "**Isotropic** means no difference in properties taken from any direction."



Difference between crystalline solid and amorphous solid as follows:

Property	Crystalline solid	Amorphous solid
Order of arrangement	Long-range order	Short-range order
Shape	Definite shape	Irregular shape
Melting point	Sharp melting point	Melting point is not sharp.
Heat of Fusion	Definite and characteristic heat of fusion	Heat of fusion is neither definite and nor characteristic
Anisotropy	Anisotropic	Isotropic

Give answer of the following questions:

Q.1 Classify the following solids as crystalline and amorphous:

Sodium chloride, quartz glass, quartz, rubber, polyvinyl chloride, Teflon

Q.2 why glass is considered as super cooled liquid?

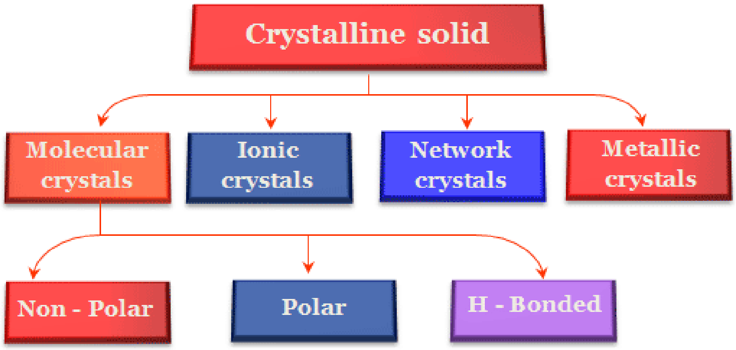
Q.3 why the window glass of old buildings show milky appearance with time?

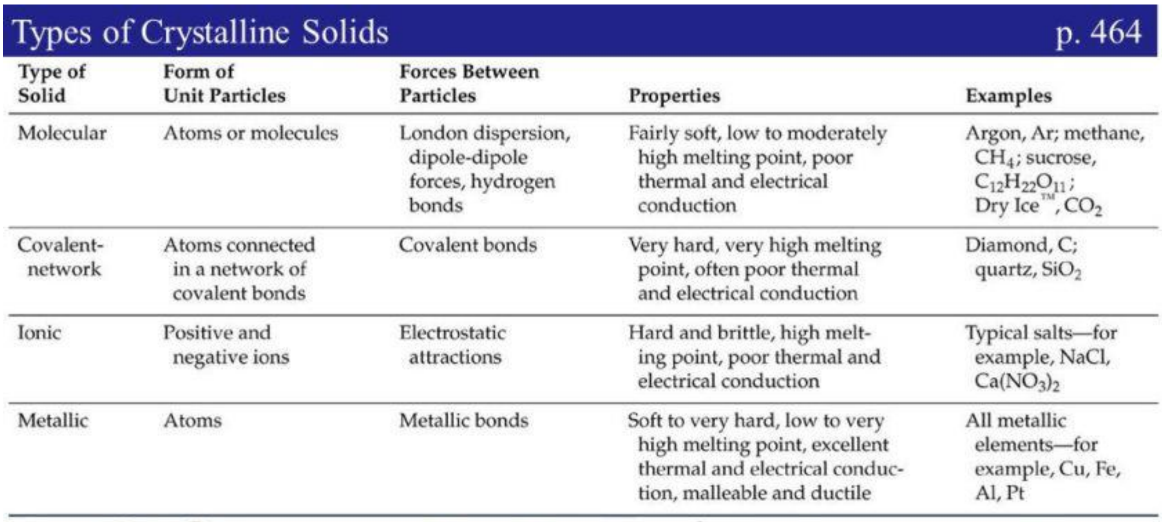
Q.4 why the glass panes fixed to window or doors of old building become slightly thicker at bottom?

Q.5 Sodium chloride is a crystalline solid. It shows the same value of refractive index along all the direction. True/False. Give reason.

Q.6 Crystalline solids are anisotropic in nature. What does this statement means?

CLASSIFICATION OF CRYSTALLINE SOLIDS:



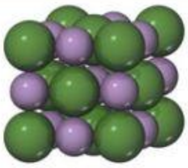


Types of Crystalline Solids p. 464

Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH_4; sucrose, $C_{12}H_{22}O_{11}$; Dry Ice™, CO_2
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, C; quartz, SiO_2
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, $Ca(NO_3)_2$
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt

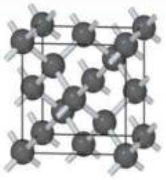
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



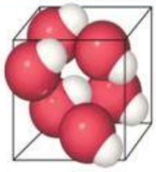
Ionic solids

Extended networks of ions held together by ion–ion interactions (NaCl, MgO)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H_2O)

Give answer of the following questions:

Q.1 Write a point of distinction between a metallic solid and an ionic solid other than metallic lustre?

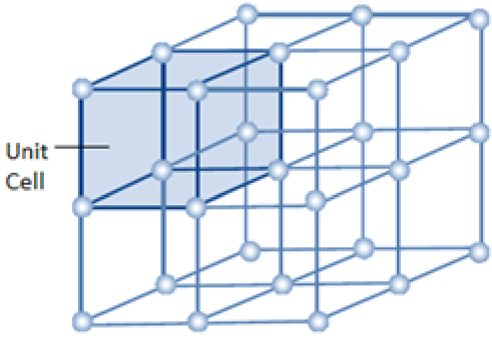
Q.2 Write a distinguish feature of metallic solid.

Q.3why graphite is good conductor of electricity although it is a network (covalent solid)?

CRYSTAL LATTICE AND UNIT CELL

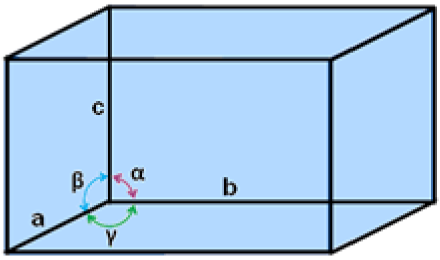
The regular three dimensional arrangement of constituent particle in a crystal is known as ***crystal lattice****.*

The smallest part of the crystal lattice is known as ***unit cell*.**



Crystal lattice

Characteristics of unit cell:



Parameters of a unit cell

A unit cell is characterised by **6 parameters**:

- 3- edges a, b and c (refer the diagram given above). The edges may or may not be perpendicular to each other.
- 3 angles α (between b and c) ,β (between a and c) and γ (between a and b).

Classification of unit cell:

*i) **Primitive unit cell or simple unit cell**(scc): The constituent particles are only present at corners of unit cell.

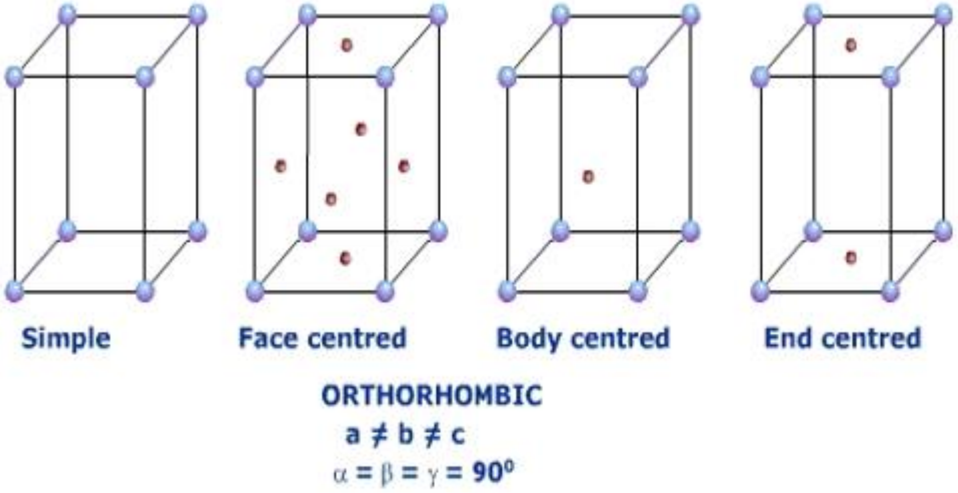
*ii) **non- primitive unit cell or centred unit cell**: The constituent particles occupy other positions also beside the corners.

Non-primitive unit cell can be further classified into 3-types:

*a) **Body- centred** unit cell (BCC): The unit cell in which the constituent particles are present at the corners as well as one particle is present at the centre.

*b) **Face-centred** unit cell (FCC): The unit cell in which the constituent particles are present at the corners as well as particle at the centre of each face of unit cell.

c) **End- centred** unit cell (ECC): The unit cell in which the constituent particles are present at the corners as well as particle at the centre of any two opposite faces of unit cell.

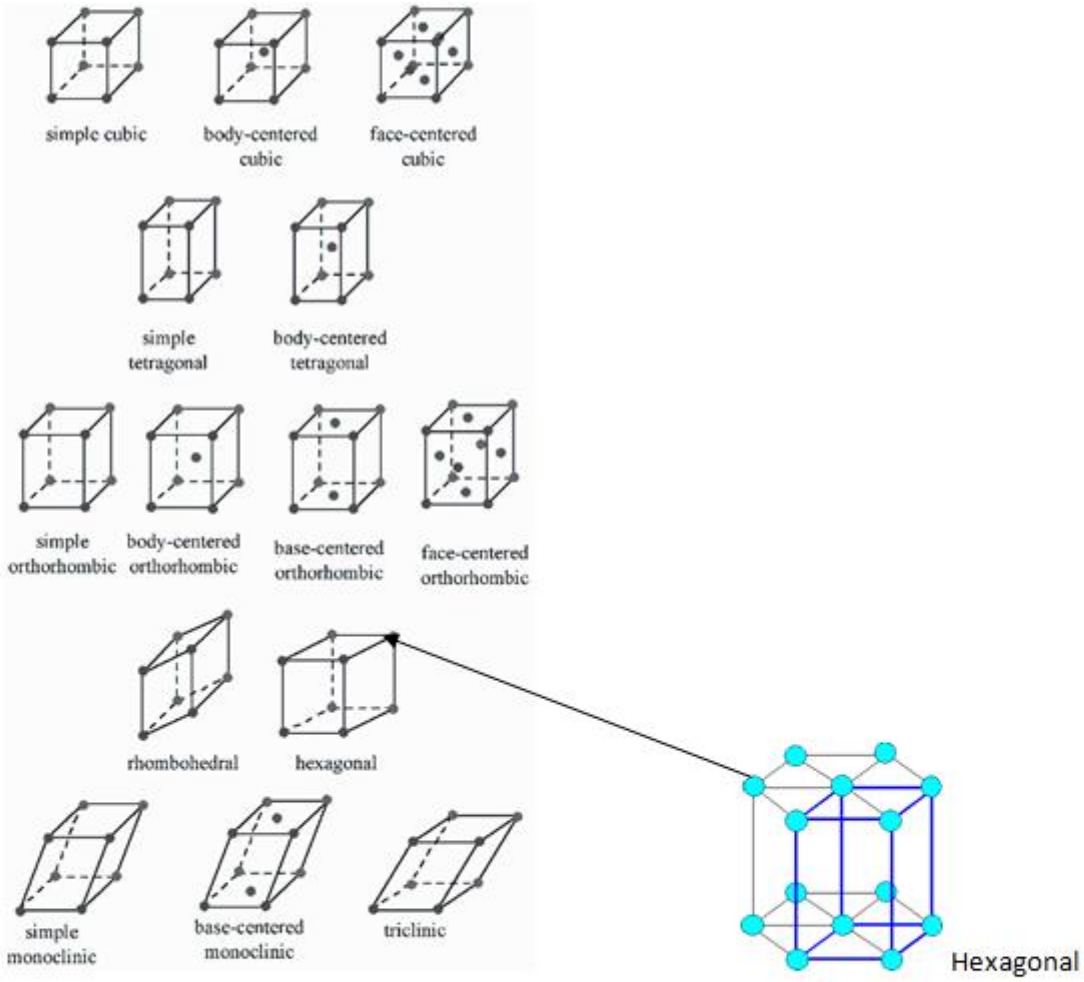


The total number of possible unit cells (primitive and centred) in 3-dimensional lattice is **14**. This is called ***Bravais Lattice**.* The detail of the lattice structure in tabular form is given below.

***Point to be noted is primitive unit cell structure is 7 but total (primitive + centred) is 14*.**

Crystal System	Possible variations	Edge length	Axial angles
CUBIC	Primitive	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$
	Body-centred		
	Face-centred		
TETRAGONAL	Primitive	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$
	Body-centred		
ORTHORHOMBIC	Primitive	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$
	Body-centred		
	Face-centred		
	End-centred		
HXAGONAL	Primitive	$a=b\neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$
RHOMBOHEDRAL or TRIGONAL	Primitive	$a=b=c$	$\alpha=\beta=\gamma\neq 90^\circ$
MONOCLINIC	Primitive	$a\neq b\neq c$	$\alpha=\gamma=90^\circ, \beta\neq 90^\circ$
	End-centred		
TRICLINIC	Primitive	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^\circ$

The structure of above mentioned 14 Bravias lattice is as follows:



Calculation of NUMBER OF ATOMS IN UNIT CELLS:

Primitive unit cell or simple cubic unit cell: In Primitive unit cell, atoms are present at corner only. Each corner atom is shared by 8 unit cells. Hence the contribution of each corner atom is 1/8 to the unit cell.

No. of corners in the unit cell – 8
Contribution of each corner atom in the unit cell – 1/8
Total no. of atoms in the SCC unit cell - 8×1/8 = 1

Body centred unit cell: In BCC atoms are present at the corners as well as at centre of body

- At corners

No. of corners in the unit cell – 8

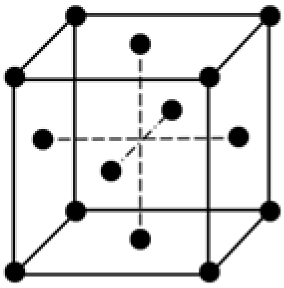
Contribution of each corner atom in the unit cell – 1/8

Total no. of atoms at the corners - 8×1/8 = 1

- At centre of body (atom completely present in the unit cell =1)

Total number of atoms present in BCC unit cell=1+1=2

Face-centred unit cell : In FCC atoms are present at the corners as well as at centre of each face.



FCC

Number of atoms present at different position is as follows:

- At corners

No. of corners in the unit cell – 8

Contribution of each corner atom in the unit cell – 1/8

Total no. of atoms at corners - 8×1/8 = 1

- At faces

No. of faces in the unit cell – 6

Contribution of each face atom in the unit cell – 1/2

Total no. of atoms at the faces - 6×1/2 = 3

Toal no. of atoms in FCC unit cell = 1+3 = 4

Example: A cubic solid is made of two elements X and Y. Atoms Y(anions) are at the corners of the cube and X(cations) at present at face-centre of the cubic lattice. What is the formula of the compound?

Ans: Number of X atom per unit cell = 1/2 x 6 = 3
Number of Y atom per unit cell = 1/8 x 8 = 1

Formula of compound = XY_3

Solve the following Questions:

Q.1 How many atoms can be assigned to its unit cell if an element forms (i) body centred cubic cell, and (ii) a face centred cubic cell?

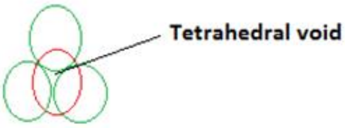
Q.2 A cubic solid is made up of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound?

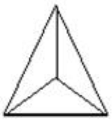
Voids: Voids in solid states mean the vacant space between the constituent particles in a closed packed structure.

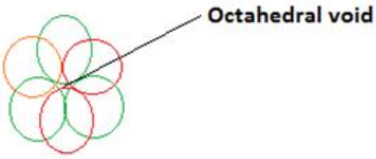
Types of voids:

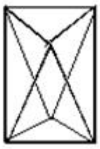
i) Tetrahedral voids: the void is surrounded tetrahedrally by four spheres called tetrahedral voids.

ii) Octahedral voids: The vacant space formed by combining the triangular voids of the first layer and that of the second layer are called Octahedral Voids**.**




Tetrahedron




Octahedron

CLOSED PACKED STRUCTURE

As the constituent particles in solid are in form of sphere. The spheres in solid are arranged in different way to leave minimum vacant space. These arrangements of spheres in different layers form the closed packed structure of solid. The crystals are formed in closed packed structures. Similarly spheres in solid are also arranged in 3-dimension to form close-packed structure.

a) Close-packing in one-dimension :

- Spheres are arranged in a row with touching each other as shown below :

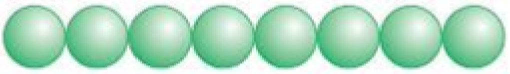


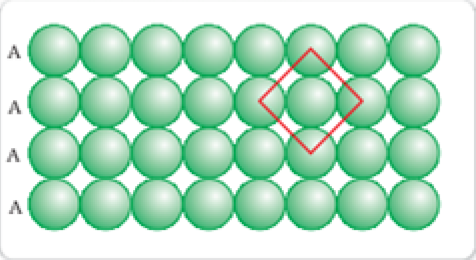
Fig. : Close packing of spheres in one dimension

b) Close-packing in two- dimension :

There are two possible ways to arrange spheres in two dimensions.

(i) Square-closed packing in two dimension :

- Sphere in the first row are exactly aligned with sphere of second row.



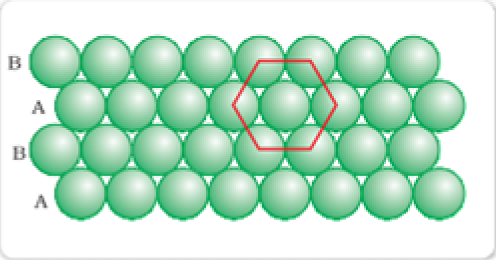
(a)

In this type of arrangement, each sphere is in contact with 4 other sphere that forms a square. The 4 other sphere that are in direct contact of the central sphere is known as *nearest neighbour*. Since each layer is exactly same, this type of arrangement is known as AAA type of closed packing.

Coordination number or nearest neighbour :- The number of atoms surrounding a central atom in crystal is called coordination number.

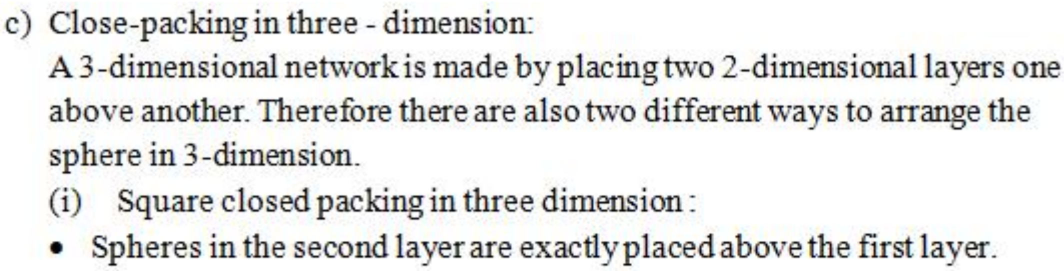
(ii) Hexagonal-closed packing in two dimension:

- Spheres in the second row are fit in the depression of first row.



(b)

In this type of arrangement, each sphere is in contact with 6 other sphere that forms a hexagon. Here the number of nearest *neighbour* is 6. The second layer is not exactly aligned with the first layer hence it is termed as B. The third layer is aligned exactly with first layer. This type of arrangement is known as ABAB type of closed packing.



c) Close-packing in three - dimension:

A 3-dimensional network is made by placing two 2-dimensional layers one above another. Therefore there are also two different ways to arrange the sphere in 3-dimension.

(i) Square closed packing in three dimension :

- Spheres in the second layer are exactly placed above the first layer.

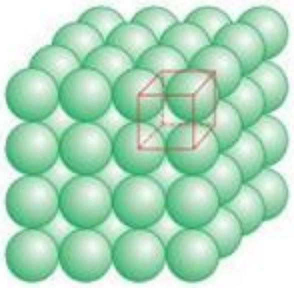
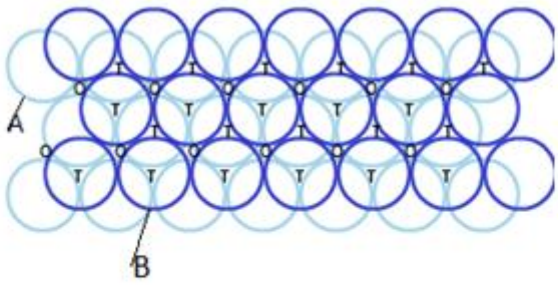
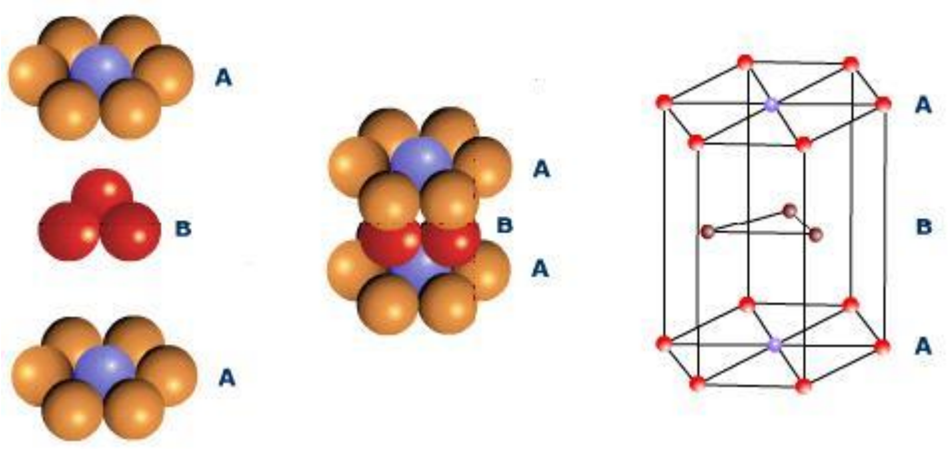


Fig. : Simple cubic lattice formed by A A A .... arrangement

In this type of arrangement spheres of both the layers are perfectly aligned horizontally and vertically. This type of arrangement is known as AAA type closed packing of sphere in 3-dimension. The possible smallest geometrical 3-dimensional shape would be cube. Thus this type of arrangement generate simple cubic lattice with primitive type of unit cell.

(i) Hexagonal closed packing in three dimension: when the tetrahedral voids of the second layer is covered by the spheres of the third layer. so that the spheres of the third layer are exactly aligned with those of the first layer, we get a pattern of spheres which is repeated in alternate layers. This pattern can be written in the form of ABAB .... pattern. This structure is called hexagonal close packed (hcp) structure. Magnesium and zinc metals have this pattern.



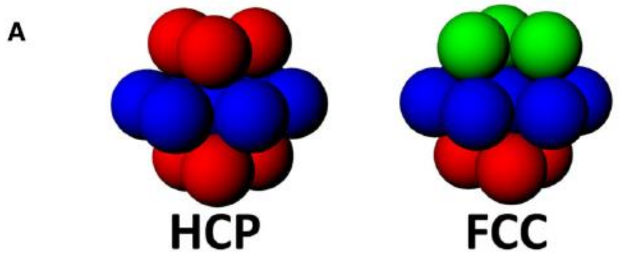


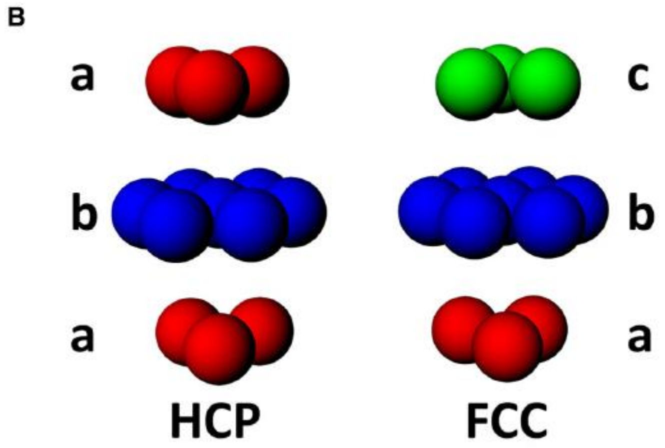
Hexagonal close packing (HCP)

(ii) Cubic close packing (ccp) or (fcc)

When the third layer is placed above the second layer in a manner such that its spheres cover the octahedral voids. and the spheres of the third layer are not aligned with first or the second layer, arrangement is called “C’ type .This pattern of layers is often written as ABCABC .... This structure is called cubic close packed (ccp)

This forms the ABCABC... type of arrangement of sphere and is known as *Cubic closed packing* (ccp) or *face centred cubic* (fcc) structure.





Coordination number: The number of nearest neighbour touching a particle in closed packed structure is known as the coordination number of constituent particles.

In both type of crystal lattice (hcp, ccp or fcc) the coordination number for the constituent particle is 12.

Example:

Q.1 What is the coordination number of each type of ion in rock-salt type crystal structure.

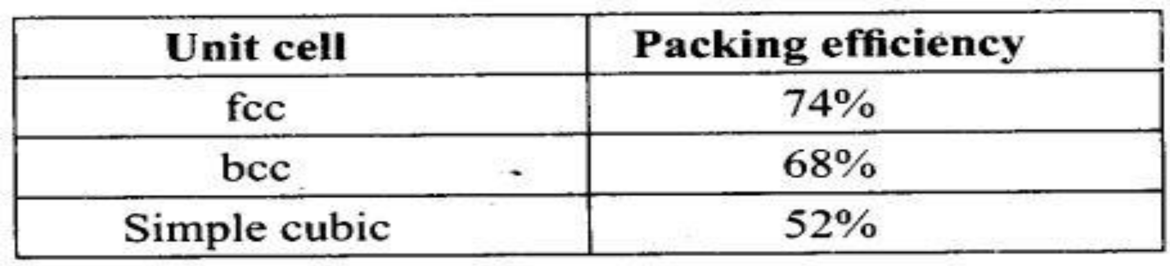
Ans : Rock salt (NaCl) has fcc type of crystal structure.

In fcc the cations in voids touches 6 nearest neighbour as well as anion at lattice point also touches 6 nearest neighbour.

Coordination number of Na$^+$ = 6
Coordination number of Cl$^-$ = 6

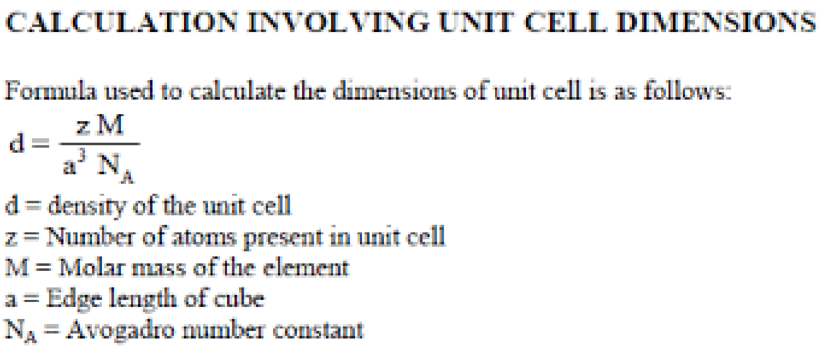
PACKING EFFICIENCY:

Packing efficiency is defined as percentage of total space occupied by the constituent particles in crystal.



Unit cell	Packing efficiency
fcc	74%
bcc	68%
Simple cubic	52%

Calculation of density of unit cell :



CALCULATION INVOLVING UNIT CELL DIMENSIONS

Formula used to calculate the dimensions of unit cell is as follows:

$$d = \frac{z\,M}{a^3\,N_A}$$

d = density of the unit cell
z = Number of atoms present in unit cell
M = Molar mass of the element
a = Edge length of cube
N_A = Avogadro number constant

Solve the following questions

1. Copper crystal has face centred cubic lattice structure. Its density is 8.93 g/cm3 .What is the length of the unit cell? (NA = 6.023 × 1023 mol−1 ; Atomic mass of Cu = 63.5)?
2. The density of chromium metal is 7.2 cm3 . If unit cell is cubic with edge length of 289 pm, determine the type of unit cell (Simple/BCC/FCC) At mass of Cr = 52 amu.
3. An element crystallizes in a structure having FCC unit cell of an edge of 200 pm. Calculate its density if 200 g of this element contains 24×10^{23} atoms .

4. A metal has FCC crystal structure. The length of its unit cell is 404 pm. What is the molar mass of metal atoms if the density of the metal is 2.72 g/cm3 (NA = 6.023 × 10^{23})?
5. The unit cell of an element of atomic mass 96 and density 10.3 g cm−3 is cube with edge length 314 pm. Find the structure of the crystal lattice. (Simple cubic, FCC , BCC) (Avogadro constant = 6.023 × 10^{23} mol^{-1}
6. An element (Atomic mass = 60) having FCC unit cell, has density of 6.23 g cm−3 . What is the edge length of the unit cell?
7. The compound CuCl has ZnS structure and the edge length of the unit cell is 500 pm. Calculate the density. (Atomic mass of Cu = 63, Cl = 35.5 Avogadro constant = 6.023 × 10^{23} mol−1)
8. What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and C atom at the body centre
   (A) AB_2C (B) A_2BC (C) AB_3C (D) ABC_3
9. The space occupied by b.c.c. arrangement is approximately
   (A) 50% (B) 68% (C) 74% (D) 56%

IMPERFECTION IN SOLIDS

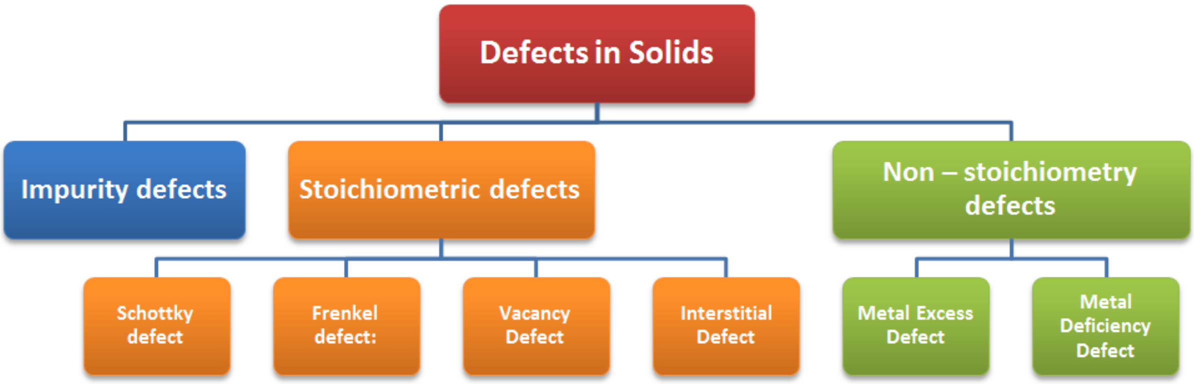
Although in crystalline solid there is regular arrangement of constituent particles but yet the crystals are not perfect. There is always some kind of irregularity in arrangement of constituent particles in small crystals. These

Irregularities are known as *defects* in crystal. There are 2 types of defects known in crystal lattice.

- **Point defect-** Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
- **Line defect**

In our syllabus only point defects are included so we will focus our study on point defects only.

Types of point defect:



- Stoichiometric defects: The defects that do not disturb the ratio of cations and anions are called stoichiometric defect.
- Non- stoichiometric defects: If as a result of imperfection, the ratio of number of cation to anion are different , the defects are called non – stoichiometric defects.
- Impurity defects

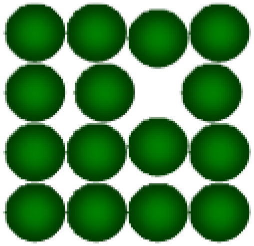
Types of stoichiometric defects and Non- stoichiometric defects are mentioned in tabular form.

Stoichiometric defects	**Non- stoichiometric defects**
Vacancy defect	Metal excess defect
Interstitial defect	Metal deficiency defect
Frenkel defect	
Schottky defect	

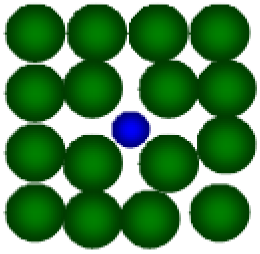
Vacancy defect:

It arises when some of the lattice point remains unoccupied during the crystal formation.

- It occurs in non-ionic compounds
- It decreases the density of solid
- It can be created by heating



Vacancy



Interstitial impurity

Interstitial defect:

It arises when some of the constituent particles occupy the interstitial sites other than the lattice points.

- It occurs in non-ionic compounds
- It increases the density of solid

Frenkel defect: If an ion is missing from its lattice site (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained.

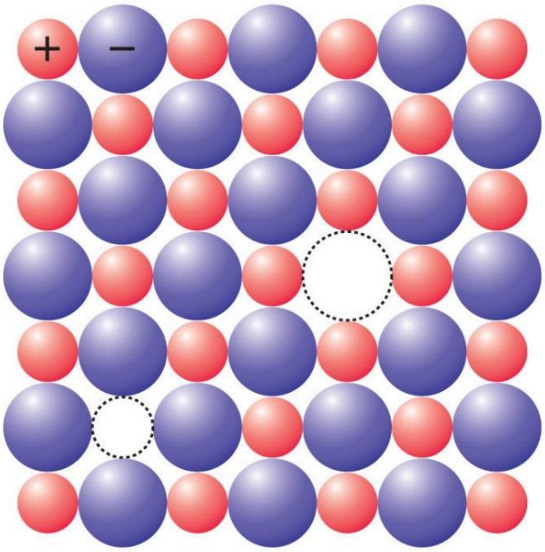
This type of defect is called Frenkel defect. Since cations are usually smaller it is more common to find the cations occupying interstitial sites.

This type of defect is present in ionic compounds which have

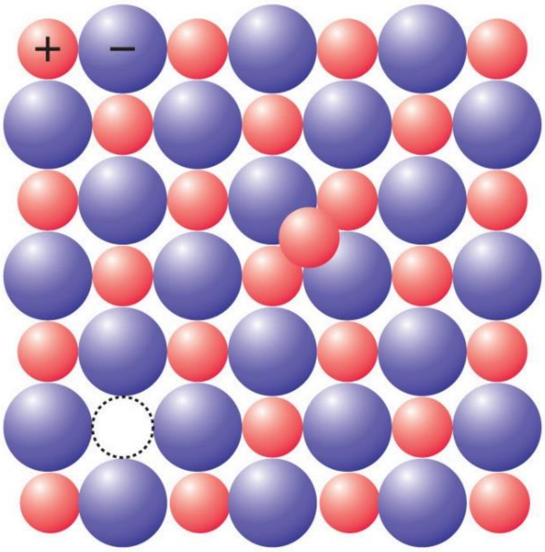
- Low co- ordinations number
- Larger difference in size of cation and anions

Compounds having highly polarising cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc .

- It occurs in ionic compounds
- It does not change the density of solid



(a) Schottky defect



(b) Frenkel defect

Schottky defect: If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect.
This type of defect is shown by highly ionic compounds which have

- High Co – ordination number and
- Small difference in the sizes of cations and anions

- It occurs in ionic compounds
- It decreases the density of solid
- Shown by ionic compound having similar size of cation and anion

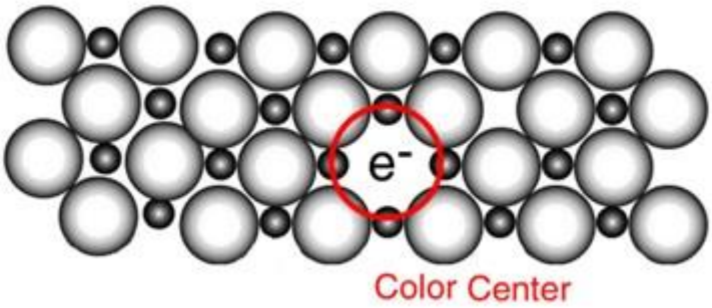
For example: NaCl, KCl, AgBr.

Important point: AgBr shows both Frenkel and schottky defect.

Metal excess defect:

Due to anionic vacancies:

anionic vacancies are created due to reaction of anion of the crystal with excess of metal present in the atmosphere. For example when crystal of NaCl is heated in presence of sodium vapour, the sodium atoms are deposited on the surface of crystal and later on forms the bond with Cl- ion by losing an electron.
In this way it creates a vacancy for Cl- ion. But the electron removed by sodium metal diffuse in the crystal and occupies the anionic site. This creates a F-centre.The presence of unpaired electron at vacant anionic site in metallic crystal is known as F-centre. This F-centre is responsible for imparting colour to the crystal. Like as:



NaCl – yellow colour

LiCl – pink

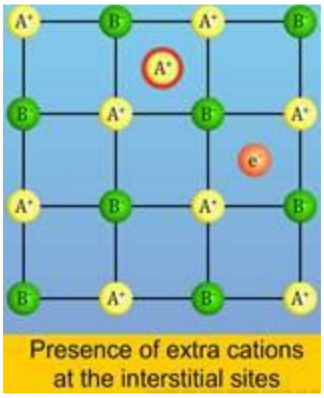
KCl-violet.

- It occurs in ionic compounds
- It is responsible for imparting colour to the crystal through F-centres.

For example: NaCl, KCl, LiCl.

Due to presence of extra cations:

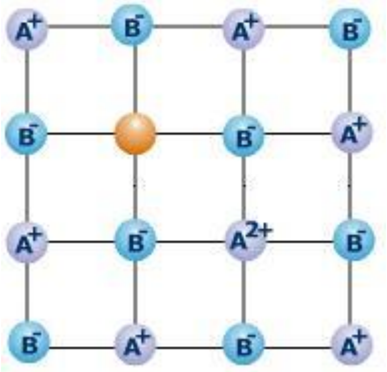
This type of defect arises when an extra cation is present in an interstitial site.the electrical neutrality is maintained by the presence of an electron in some other interstitial site. The excess of Zn^{2+} ions occupy the interstitial site and electron lost by oxide ion occpy the neighbouring site, in this way maintain the electrical neutrality of crystal.



- It occurs in ionic compounds
- It is responsible for imparting colour to the crystal through free electrons.

For example: ZnO (white at room temperature, yellow on heating)

Metal deficiency defect:



This defect arises when a metal ion is missing from its normal lattice site and the charge is balanced by a nearby metal ion having higher positive charge.EX:Crystals of FeO, FeS and NiO show this type of defects.

ELECRTICAL PROPERTIES:

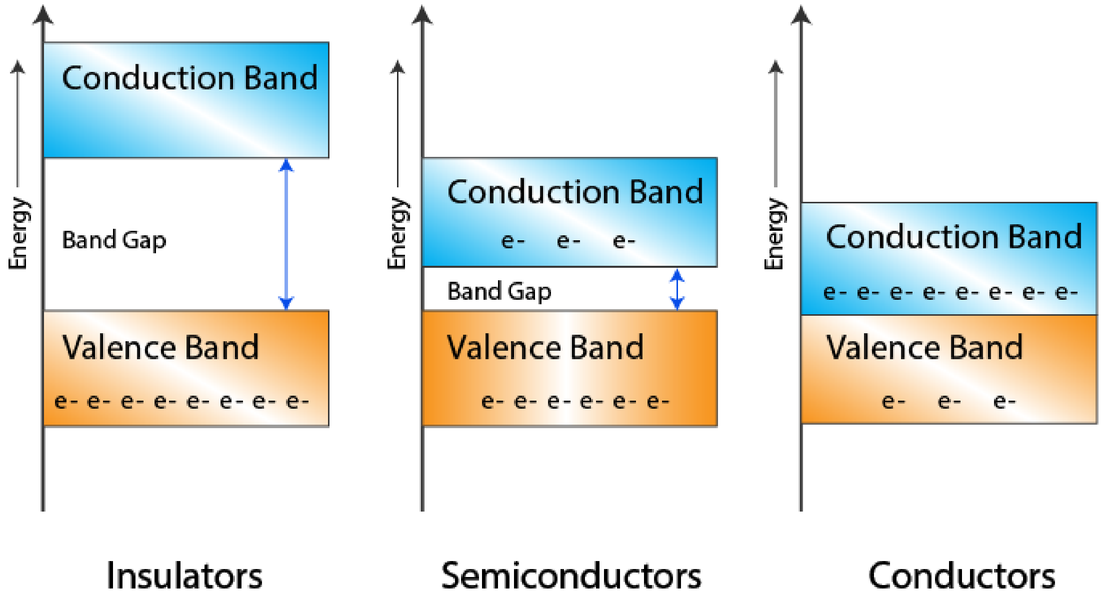
Solid are classified as conductor, semi-conductor and insulator on the basis of the magnitude of electrical conductivity.

- Conductor: electrical conductivity range 10^4 to 10^7 $ohm^{-1}m^{-1}$
- Semi-Conductor: electrical conductivity range 10^{-6} to 10^7 $ohm^{-1}m^{-1}$.
- Insulator: electrical conductivity range 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$

CONDUCTION OF ELECTRICITY

As we know that free electrons are responsible for the conduction of electricity in metals. Electrons are occupied in atomic orbital. The atomic orbital forms molecular orbital in metallic crystal. Molecular orbital are very closer in energy and known as bands. To be a conductor there must be some electrons in conduction band. But electrons are mainly occupied in valance band. On the basis of conductivity solids are classified in 3 types: Conductor, semi-conductor, insulator.

- In case of conductor there is an overlapping of valance band and conduction band.
- In semi-conductor there is small gap of energy between valance band and conduction band. Some of the electron may jump and show some activity. The metal showing this type of activity is known as intrinsic semi-conductors. For example : Silicon and Germanium.



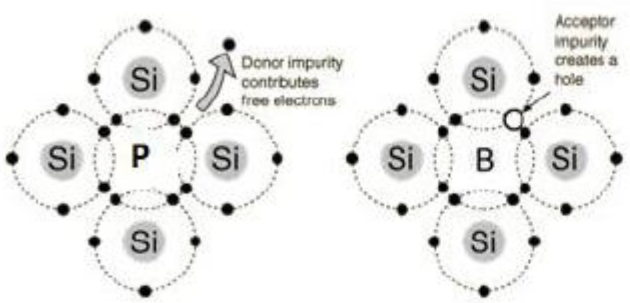
- In case of insulator there is a large energy difference between valance band and conduction band

Classification of semi-conductors:

The electrical conductivity of semi-conductors can be increased by adding some electron rich impurity or electron deficient impurity. This is called doping.

n-type semiconductor : When the conductivity of semi-conductor is increased by adding electron rich impurity. It generates n-type semi-conductor. For Example: when Silicon is doped with phosphorus, phosphorus also occupies some lattice site. The covalency of Si is 4 but that of P is 5. So, one electron per atom left unused and it delocalise from its location. This delocalise electron help in increasing conductivity of semi-conductor.

p-type semiconductor : When the conductivity of semi-conductor is increased by adding electron deficient impurity. It generates p-type semi-conductor. For Example: when Silicon is doped with boron, boron also occupies some lattice site. The covalency of Si is 4 but that of B is 3. So, one of the position of electron is left unused. This is called electron hole. The electron from neighbouring atom moves to fill this hole but creates a new hole. This looks like movement of electron hole throughout the system. Electrons move through these hole under the influence of electric fields. In this way electrical conductivity increases.



Application of n-type and p-type semiconductors:

By the combination of n-type and p-type semi-conductors many electronic devices are prepared.

- Diode (is a device that allows the current in one direction only) is used as amplifier
- pnp and npn sandwiching is done in making transistors
- As photo diode in solar cells
- In lasers

MAGNETIC PROPERTIES:

Electrons are charged particles and it generates a magnetic field around itself. The magnetic field arises due to the spinning of electron at its own axis and movement of atomic orbital around nucleus.

Classification of magnetic properties:

I. Paramagnetism :

- Weakly attracted by magnetic fields
- Alignment of magnetic dipole in the same direction of magnetic field
- Loose magnetism in absence of magnetic field
- They have unpaired electrons

Ex. Cu 2+, Fe 3+

II. Diamagnetism :

- Weakly repelled by magnetic fields
- Alignment of magnetic dipole in the opposite direction of magnetic field
- They have all the electrons paired

Ex. H2O, NaCl

III. Ferromagnetism :

- strongly attracted by magnetic fields

- Permanently magnetised.

  Ex. Fe, Co, Ni etc.

IV. Anti-Ferromagnetism :

- strongly repelled by magnetic fields
- Alignment of magnetic domains (group of metal ions)in the opposite direction of magnetic field..

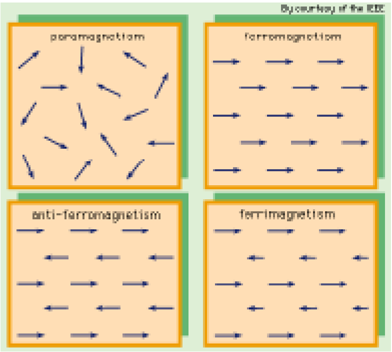
  Ex. MnO

V. Ferrimagnetisms :

- Weakly attracted by magnetic fields
- Alignment of magnetic domains (group of metal ions)in the parallel and anti parallel direction with direction of magnetic field and unequal in number.
- Loss magnetic moment on heating.

  Ex. Fe3O4(magnetite)

Ex. Fe_3O_4(magnetite)



Questions:

Q.1 what is a semi-conductor? Describe the two main types of semi-conductor.

Q.2 What type of substances exhibit anti ferromagnetism ?

Q.3 Which crystal defect lowers the density of solid?

Q.4 Name an element with which silicon may be doped to give p-type semi-conductor.

Q.5 which point defect in the crystal does not alter the density of solid?

Q.6 Which point defect in its crystal unit increases the density of a solid?

Q.7 How do metallic and ionic substances differ in conducting electricity?

Q.8 what are F-centres?

Q.9 What is meant by doping in a semi-conductor?

Q.10 what type of substance would make better permanent magnet, ferromagnetic or ferromagnetic?

Q.11 What type of stoichiometric defect is shown by AgCl?

Q.12 what type of semi-conductor is obtained when silicon is doped with arsenic?

Q.13 What is mean by intrinsic semiconductor?

Q.15 what are n-type semiconductor?