



MALLA REDDY COLLEGE OF ENGINEERING & TECHNOLOGY

(An Autonomous Institution – UGC, Govt.of India)

Recognizes under 2(f) and 12(B) of UGC ACT 1956

(Affiliated to JNTUH, Hyderabad, Approved by AICTE –Accredited by NBA & NAAC-“A” Grade-ISO 9001:2015 Certified)

ENGINEERING PHYSICS - II

B.Tech – I Year – II Semester

DEPARTMENT OF HUMANITIES AND SCIENCES



CONTENTS

UNIT	NAME OF THE UNIT
1	BONDING IN SOLIDS & CRYSTALLOGRAPHY
2	X RAY DIFFRACTION & DEFECTS IN CRYSTAL
3	DIELECTRICS
4	MAGNETIC PROPERTIES & SUPERCONDUCTIVITY
5	NANO TECHNOLOGY

MALLA REDDY COLLEGE OF ENGINEERING & TECHNOLOGY

B.TECH –I YEAR – II SEM

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(R17A0012) ENGINEERING PHYSICS-II

OBJECTIVES:

- To understand the basics of bonding in solids, crystal structures and characterization techniques.
- To make the students aware of X-ray diffraction and different techniques of it.
- To understand the behavior of dielectric materials, magnetic materials and nano materials.

UNIT-I

BONDING IN SOLIDS:

Types of bonds - Primary, Secondary, Forces between atoms, Expression for cohesive energy between two atoms.

CRYSTALLOGRAPHY:

Space lattice, Basis, Unit cell, lattice parameters, Crystal systems, Bravais lattices, Atomic number, coordination number, packing factor of SC,BCC,FCC crystals, Crystal planes and directions - Miller indices. Expression for inter planar distance in cubic crystal, Structure of NaCl and Diamond.

UNIT- II

X-RAY DIFFRACTION:

Bragg's law, Experimental techniques -Laue's method, powder method, Applications of x-ray diffraction.

DEFECTS IN CRYSTALS:

Classification of crystal defects, Point defects-Vacancies & Interstitials, Concentrations of Schottky and Frenkel defects, Line defects- edge dislocation and screw dislocation, Burger's vector.

UNIT-III

DIELECTRIC PROPERTIES:

Electric dipole, Dipole moment, Polarization vector (P), Displacement vector (D), Dielectric constant (K), Electric susceptibility (χ), Types of polarizations-Expression for Electronic and Ionic polarization, Internal fields in dielectrics, Clausius Mosotti relation, Piezo electricity and Ferro electricity, Applications of dielectric materials.

UNIT-IV

MAGNETIC PROPERTIES:

Magnetic permeability, Field intensity, Magnetic field induction, Magnetization, Magnetic susceptibility, Origin of Magnetic moment - Bohr magneton, Classification of magnetic materials-Dia, Para and Ferro, Ferri and Anti ferro magnetic materials, Explanation of Hysteresis loop on the basis of domain theory of ferromagnetism. Soft and hard magnetic materials.

SUPER CONDUCTIVITY:

Super conductivity, Properties of super conductors, Meissner effect, Types -I Type-II super conductors, Applications of super conductors.

UNIT-V

NANO SCIENCE & NANO TECHNOLOGY:

Nano scale, Types of Nano materials, Surface to volume ratio and Quantum confinement, Bottom up Fabrication- Sol gel ,Top down Fabrication- Physical Vapour Deposition, Characterisation of Nano particles –TEM and SEM, Applications of Nano materials.

TEXT BOOKS:

1. Engineering Physics - S Mani Naidu- Pearson Publishers.
2. A Text Book of Engineering Physics- P.G. Kshirsagar, Avadhanulu – S.Chand

REFERENCES:

1. Solid State Physics, Kittel- Wiley International.
2. Solid State Physics – AJ Dekker-Macmillan Publishers.
3. Engineering Physics, P.K. Palaniswamy, Scitech Publishers

OUTCOMES:

- The students would be able to learn the fundamental concepts on behavior of crystalline solids.
- The student will be able to think about the applications of dielectric, magnetic and nano materials.
- Finally Engineering physics course helps the student to develop problem solving skills and analytical skills.

Unit I Bonding in Solids & Crystallography

Introduction:

Bonding in any solids is the relation between the atoms in which it holds them together. The force which keeps these atoms together in a solid is called inter atomic force and is of two types- attractive force and repulsive force. Based on the strength of the bond, bonding in solids is classified in two categories- (i) primary bonding & (ii) secondary bonding.

Classification of chemical bonds:

Depending upon strength and directionality, bonds are divided into two type.

They are

- I. Primary bonds.
- II. Secondary bonds.

I. Primary bond or Interatomic bonds: The primary bonds are interatomic bonds. In this bonding interaction occurs only through the electrons in the outermost orbit, i.e., valence electrons. Primary bonds have bond energies in the range of 0.1-10 eV/bond. Primary bonds are stronger and more stable than secondary bonds. The primary bonds are further classified into three types namely

A. Ionic Or Electrostatic Or Electrovalent Bonds:

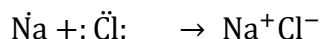
The bond formed between the two atoms by the transfer of electron is called Ionic Bond. These bonds are formed between a metal and non metal. Ex: NaCl, MgO, CaF₂,etc.

Formation of NaCl:

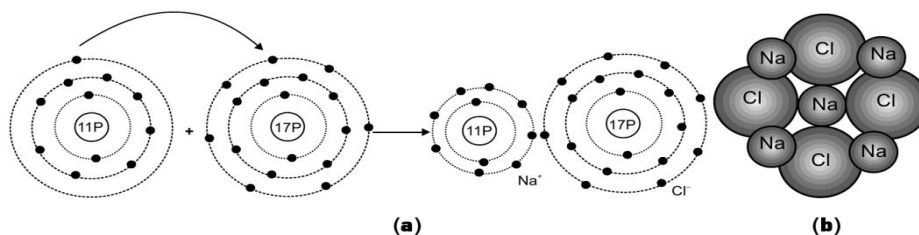
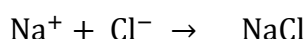
The electronic configuration of the sodium atom is (2,8,1). It has one electron more than neon. If it loses one electron from its outer most orbit it acquires a stable octet configuration (Neon).

The electronic configuration of the chlorine atom is (2,8,7). It has one electrons less compared to neon. If it gain one electrons acquires a stable octet configuration (Argon).

When atoms of sodium and chlorine approach each other an electron is transferred from Na to Cl atom. Both attain the octet electronic configuration of the nearest Inert gases neon and argon respectively. Sodium atom becomes Na⁺ and chlorine atom becomes Cl¹⁻.



These two oppositely charged ions attract each other due to opposition charges and form NaCl.



(a) Electron transfer from sodium to chlorine and (b) three-dimensional structure of sodium chloride

Properties of ionic substances:

- Ionic substances are rigid; possess geometrical shape, hard and soluble in water.
- It is easy to describe and visualize.
- Ionic compounds exhibit high melting points.
- Ionic compounds are soluble in polar solvents and insoluble in non polar solvents like benzene, CCl_4 , and other organic solvents.
- Ionic compound conducts electricity both in matter state and also in aqueous solutions.
- Ionic bond is non directional bond. i.e., the magnitude of the bond is equal in all directions around an ion.

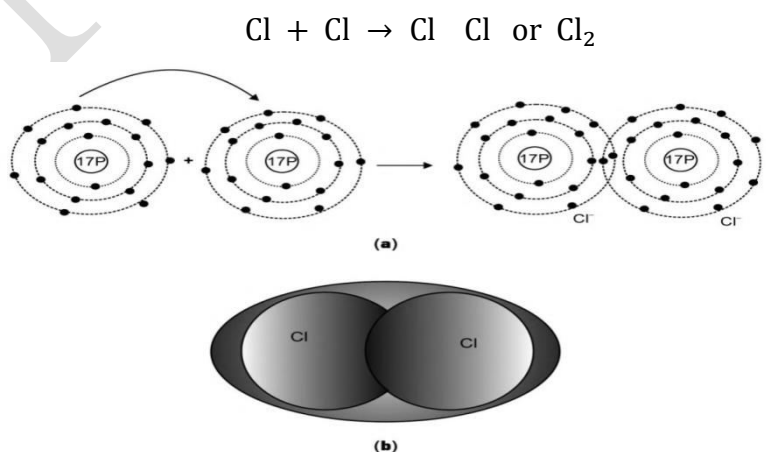
B. Covalent or Electron-pair Bond: The bond formed between two atoms by the mutual sharing of electron is called Covalent Bond. These bonds are formed between non-metals. Covalent bond is further classified into two types

1. Non - Polar covalent bond.
2. Polar Covalent bond.

Non- Polar covalent bond: When two identical atoms combine they equally share the bonding electron. Therefore each molecule has no charge separation and are called non polar molecules. The bond formed between these atoms is called Non –Polar covalent bond.

Ex: Cl_2 , O_2 , N_2 etc.

Formation of Cl_2 : Atomic number of chlorine is 17. It's electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$. Each chlorine atom need one more electron to attain stability (Ar electronic configuration). Each atom contributes one electron to form one pair of electron. Both atoms share electron pair equally and forms one covalent bond. After bond formation both the atoms gain the electronic configuration of Argon atom and the molecule becomes stable. Molecules whose atoms are joined by covalent bonds are called covalent molecules. The number of electron pairs shared in forming molecules is called covalence of the atom. This shared pair is called the bonding pair of electrons. One pair of bonding electrons makes one covalent bond. Thus a single bond forms between the two atoms in the chlorine molecule.



(a) Electron sharing in chlorine and (b) three-dimensional covalent bond in chlorine

Polar Covalent Bond: When two unlike atoms combine one of them may attract the bonding electrons more to itself than the other, resulting in unequal distribution of the electron pair between them. Such a bond is called Polar Covalent bond.
Ex; HCl, H₂O...

Formation of HCl: The electronic configuration of hydrogen and chlorine are $1s^1$ and $1s^2 2s^2 2p^6 3s^2 3p^5$ respectively. Each atom contributes one electron to form one pair of electron. Both atoms share electron pair unequally and forms one covalent bond. Chlorine atom attracts bonding electrons more than hydrogen atom and becomes partially negative charged (δ^-) so it is considered as more electro negative than hydrogen atom. Due to this hydrogen atoms acquires partial positive charge (δ^+). Such molecules possessing partial positive and partial negative charges are called polar molecules. The establishment of partial positive and partial negative centres in a bond is known as polarisation. Bond formed in this way is called polar bond



Properties of covalent compounds:

1. Covalent solids are hard, brittle and possess crystalline nature.
2. Covalent bond can be either very strong or very weak depending upon the atoms involved in the bond.
3. Melting and boiling points of covalent compounds are lower than ionic compounds.
4. Covalent compounds are soluble in non polar solvents and insoluble in polar solvents.
5. Covalent compounds are poor conductors of heat and electricity.
6. Covalent bond is not only rigid but is directional and has definite geometry about them.

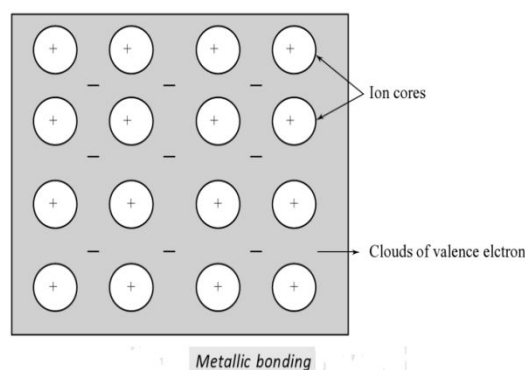
C. Metallic bond: The force that binds a metal atom to a number of electrons within its sphere of influence is called Metallic bond.

Ex: Na, Au, Cu, Ag.....

It is existing both in metals and their alloys. In metals, the metal atom lose their outer electron to form metal cations. The electrons from all the metal atoms form an electron sea or cloud which can flow throughout the space occupied by the atoms. Those electrons are often described as delocalised electrons. Metallic bonding is different from both ionic and covalent

bonding. The metal cations and electrons are oppositely charged, and hence, they are attracted by each other. The electrostatic forces are called Metallic Bonds.

The classical theory fails to explain the metallic character of solids based on the number of valence electrons. Elements (Na, K etc.) having only one electron in the outer most orbit are metallic in nature while elements (Mg, Al etc.) having 2 or 3 electrons in the outer most orbits are just metallic and the elements (tin and lead) having 4 electron in their outer most orbit are less metallic in nature. When the valence electrons



becomes 6 or 7 these elements lose their metallic character. According to the quantum mechanical concept, the metallic bond is regarded as an unsaturated covalent bond.

Properties of metallic solids:

1. Metallic bonds are relatively weak.
2. Metallic bond holds the atoms together in metals.
3. Metallic solids are malleable and ductile.
4. Metallic bond is non directional.
5. Metallic solids are not soluble in polar and nonpolar solvents.
6. Metals are opaque light.
7. They possess high electrical and thermal conductivity.
8. They have high number of electrons.
- 9.

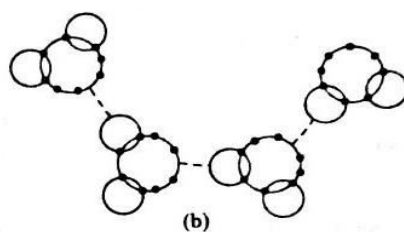
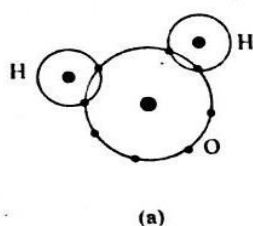
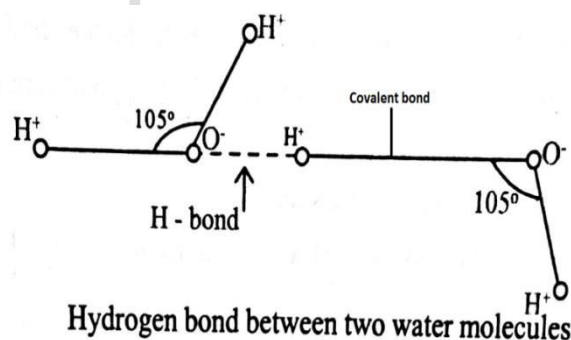
II.Secondary bond or Intermolecular bonds: Secondary bonds have energies in the range of 0.01 - 0.5 eV/bond. The secondary bonds are further classified into two types. They are

A. Hydrogen Bond: The electrostatic force of attraction between the hydrogen atom of molecule and more electronegative atom of the same or another molecule is called **Hydrogen Bond**. Molecules which are having non polar covalent bonds do not form hydrogen bonds. Polar molecules form Hydrogen bonds.

Ex : H_2O , CH_4 , NH_3

Explanation of Hydrogen bond in H_2O :

Hydrogen bond is primarily a covalent bond. The electron pair shared between the two atoms lies far away from the hydrogen atom. As a result, hydrogen atom becomes highly electropositive with respect to the oxygen atom. Since the electrons are displaced towards oxygen atom. It acquire partial negative charge while hydrogen atom gets partial positive charge. In other words , the bond $\text{O} - \text{H}$ becomes polar and may be represented as $\text{O}^{\delta-} - \text{H}^{\delta+}$. The positively charged hydrogen atom of one molecule attracts the negatively charged atom of the neighbouring molecule and thus bonding the molecules together. Due to this electrostatic force of attraction between the atoms the hydrogen bond formed. The attraction is weak because the charge transfer is small. This may be represented as



(a) Sharing of electrons between the hydrogen and oxygen atoms in a water molecule (b) scheme of bonding in different molecules.

The hydrogen atom act as a bridge between two atoms holding one atom by covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted (.....) line and the covalent bond is represented by solid line (—). Hence, hydrogen atom also known as Hydrogen bridge. A typical covalent bond is only 20 times stronger than an intermolecular hydrogen bond. These bonds can occur between molecules or within different parts of single molecule. The hydrogen bond lies in between a covalent bond and an electrostatic intermolecular attraction.

Properties of hydrogen solids:

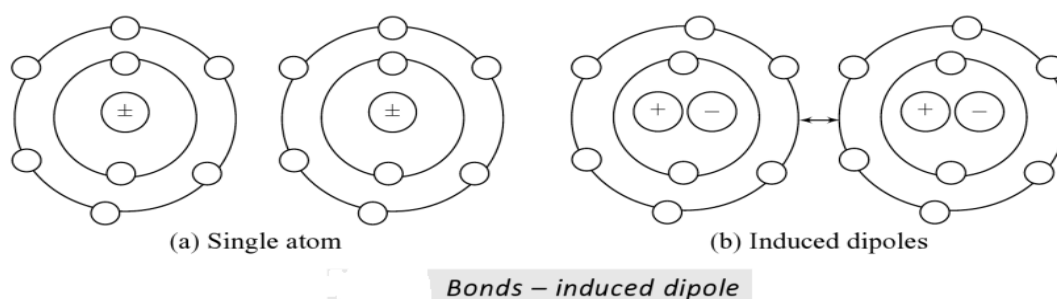
1. Hydrogen bonded solids do not have any valence electrons and hence, they are solid insulators.
2. Hydrogen bonds are weaker than primary bonds.
3. Hydrogen bonded solids are soluble both in polar and non polar solvents.
4. They are transparent to light.
5. They have low melting points.
6. Hydrogen bonds are directional.
- 7.

B. Van der Waals bond or Dispersion bond:

The bonds between the molecules that allow sliding and rupture to occur are called van der Waals forces or bonds.

Ex: Graphite, Inert gas solids like solid Argon, Organic symmetric molecule solids like solid Methane. etc ...

Explanation: Consider two atoms of an inert gas having completed electronic shells. When the atoms are at neutral, the positive and negative charge centres are exactly at the same location. When the two atoms are brought together, a displacement of positive and negative charge centres takes place relatively. Then, the positive and negative charges are separated. As a result it creates an electric dipole. This dipole induces another dipole in neighbouring atoms and force of attraction results. This force of attraction are usually called vander waals forces. This interaction is very much weaker than the covalent interaction. These forces are responsible for condensation of inert elements and gases like hydrogen, nitrogen, methane etc. at very low temperatures.



Properties of solids with vander wall bonding :

1. Van der waals bonds are non directional.
2. Van der waals bonding is weaker than the hydrogen bonding.
3. Van der waal bonded solids have low melting and boiling points.
4. They are usually transparent to light.
5. They are soluble in both polar and non polar liquids.

FORCES BETWEEN ATOMS:

When atoms are at infinite separation, then there is no interaction between them. As the atoms come close to each other to form solids, there exist two types of forces between the atoms 1. Attractive force 2. Repulsive force.

ATTRACTIVE FORCE: The forces that bring atoms together are called forces of attraction. This force keep the atoms together and prevent the atoms moving away from each other. These attractive forces are inversely proportional to some power of distance between particles or ions. The potential energy due to this force is negative because the atoms do work of attraction.

Attractive force $F_a \propto -\frac{1}{r^m}$

$$F_a = -\frac{a}{r^m}$$

Where 'a' is proportionality constant, 'r' represents distance between particles or ions, and 'm' is usually 2 as per coulombs law.

REPULSIVE FORCE:

When the atoms approach closer than inter nuclear distance (r_0) the repulsive forces between the two nuclei developed. The repulsive forces are inversely proportional to some power of distance between particles or ions. The potential energy due to this force is positive because external work must be done to bring two such atoms close together so that they repel each other.

Repulsive force $F_r \propto \frac{1}{r^n}$

$$F_r = \frac{b}{r^n}$$

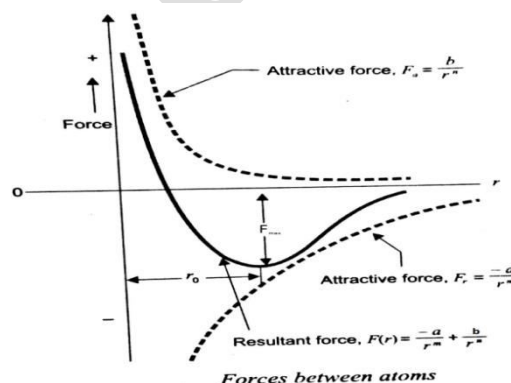
Where 'b' is proportionality constant, 'r' represents distance between particles or ions, and 'n' is usually in between 7 to 10.

Resultant Force: The resultant force can be expressed as sum of both repulsive and attractive forces.

$$F(r) = F_a + F_r$$

$$F(r) = -\frac{a}{r^m} + \frac{b}{r^n} \quad (n > m) \quad (1)$$

When the system is at equilibrium, the distance between particles or ions will be $r = r_0$ then the magnitudes of the F_a and F_r is equal and opposite. So the resultant force between atoms is zero.



$$-\frac{a}{r_0^m} + \frac{b}{r_0^n} = 0$$

$$\frac{a}{r_0^m} = \frac{b}{r_0^n}$$

$$r_0^{n-m} = \frac{b}{a}$$

$$r_0 = \left(\frac{b}{a}\right)^{\frac{1}{n-m}}$$

Cohesive energy or binding energy or dissociation energy:

Def: The energy required to break the atoms of the solid into isolated atomic species.

Calculation of Cohesive energy:

The potential energy between the atoms can be calculated by integrating the force of attraction.

$$\begin{aligned} U(r) &= -\int F(r) dr \\ &= -\int \left(-\frac{a}{r^m} + \frac{b}{r^n}\right) dr \\ &= \int \left(\frac{a}{r^m} - \frac{b}{r^n}\right) dr \\ &= a \left[\frac{r^{-m+1}}{-m+1}\right] - b \left[\frac{r^{-n+1}}{-n+1}\right] + c \\ &= -\left[\frac{a}{m-1}\right] \frac{1}{r^{m-1}} + \left[\frac{b}{n-1}\right] \frac{1}{r^{n-1}} + c \\ U(r) &= \frac{-A}{r^M} + \frac{B}{r^N} + c \end{aligned} \quad (2)$$

Let $A = \frac{a}{m-1}$, $B = \frac{b}{n-1}$, $M = m-1$, $N = n-1$ and 'c' is constant of propagation. Where A and B are force constants, M and N are positive integers. The value of 'c' can be obtained by applying boundary conditions.

When, $r \rightarrow \infty$, $U = 0$ Hence, $c = 0$

$$U(r) = \frac{-A}{r^M} + \frac{B}{r^N} \quad (3)$$

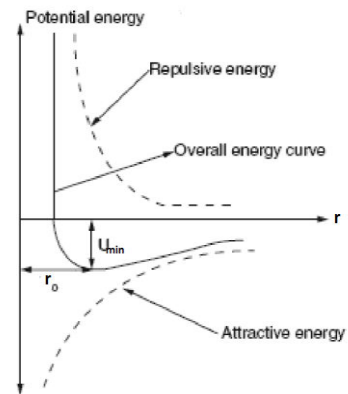
If the system is in equilibrium, then $r = r_0$ and $U(r)$ tends to minimum value, U_{min} . Therefore,

$$U_{r_0} = U_{min} = \frac{-A}{r_0^M} + \frac{B}{r_0^N} \quad (4)$$

Differentiating eq. (4) w.r.t 'r'

$$\frac{dU}{dr_0} = AMr_0^{-M-1} - BNr_0^{-N-1}$$

For minima, first derivative = 0



$$AMr_0^{-M-1} - BNr_0^{-N-1} = 0$$

$$AMr_0^{-M-1} = BNr_0^{-N-1}$$

$$\frac{r_0^N}{r_0^M} = \frac{BN}{AM}$$

$$r_0^N = r_0^M \left[\frac{B}{A} \right] \left[\frac{N}{M} \right] \quad (5)$$

Substituting eq. (5) in eq. (4)

$$U_{min} = \frac{-A}{r_0^M} + B \frac{1}{r_0^M} \left[\frac{A}{B} \right] \left[\frac{M}{N} \right]$$

$$U_{min} = -\frac{A}{r_0^M} \left(1 - \frac{M}{N} \right)$$

$$U_{min} = \frac{A}{r_0^M} \left(\frac{M}{N} - 1 \right)$$

This is the expression for cohesive energy of a molecule containing two atoms in a molecule. It is depending on distance between atoms, molecules and ions in a solid.

Crystal structures:

Crystallography:

Solid is characterized by structural rigidity and resistance to changes of shape or volume. It is of two types: one in which the atoms are tightly bound to each other in a regular geometric lattice (called crystalline solids) and another in which atoms are irregularly spaced (called a non-crystalline or an amorphous solids). "Crystallography is a branch of science that deals with the formation, properties and structure of crystals:

Crystalline Solids:

1. They have a regular periodic (three dimensional) arrangement of atoms, ions or molecules.
2. They have long range order.
3. They have sharp melting point i.e., they melt at a particular temperature.
4. They are anisotropic, i.e., they have different (optical and electrical) properties in different directions.
5. Examples: Metals, NaCl, diamond, etc.

Amorphous Solids:

1. They have an irregular three dimensional arrangement of atoms, ions or molecules.
2. They have short range order.
3. They do not have sharp melting point i.e., they melt over a range of temperature.

4. They are isotropic, i.e., they have same properties in all directions.
5. Examples: Glasses, rubber, plastic, etc.

Fundamental definitions:

(a) Lattice Point:

It is an imaginary point in space, which locates the position of atom (s) or ion (s) or radicals or molecules.

(b) Space Lattice:

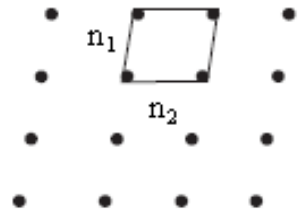
It is a three dimensional arrangement of lattice points in space in which every lattice point has an identical environment.



Image of space lattice

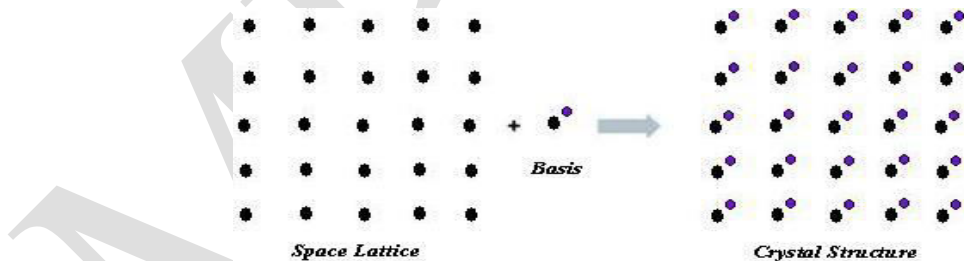
(c) Translational Vector:

The translation **vector** is the distance through which an atom must be moved (translated) in order to be in the next unit cell. In the crystal structure so formed, each lattice point has identical surroundings. It means that the lattice points are connected by a translation operator **T**, where **T** is defined as $\mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, where n_1 , n_2 , and n_3 are integers and **a**, **b**, **c** are primitive or fundamental translation vectors.



(d) Basis:

It represents a group of atoms or ions or radicals or molecules. Basis in combination with space lattice forms a crystal structure.



(e) Unit Cell:

It is defined as the smallest geometric figure (or pattern) the repetition of which, in three dimensions, gives the complete crystal structure.

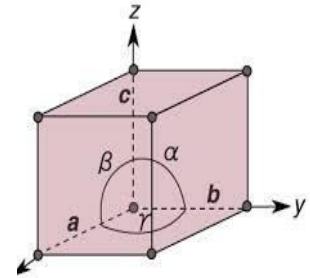


Primitive cell is a unit cell having only one lattice point. The atoms lie only at the corners.

Non-primitive cell is a unit cell having more than one lattice point. Atoms may lie on the faces or along the body diagonals apart from being present at the corners.

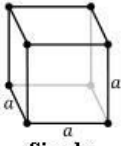
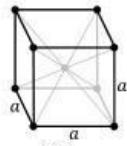
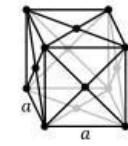
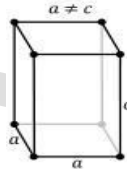
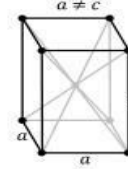
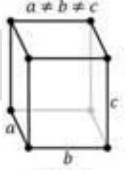
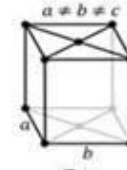
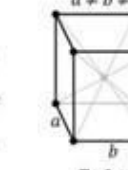
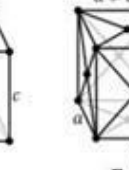
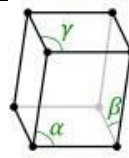
(f) Lattice parameter:

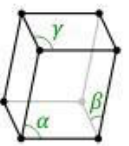
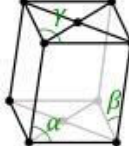
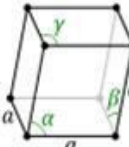
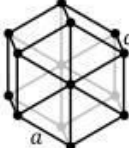
The lattice constant, or lattice parameter, refers to the physical dimension of unit cell in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as a , b , and c and three interfacial angles α , β and γ .

**(g) Bravais Lattice:**

There are 14 distinguishable ways of arranging the lattice points in space, which constitutes the seven crystal system.

In 3D there are 7 crystal systems as mentioned below:

Crystal System	Unit Cell Dimensions	Bravais Lattices	Examples
Cubic	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	 Simple Cubic (P)  Body Centered (I)  Face Centered (F)	NaCl, ZnS, Cu
Tetragonal	$a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$	 Simple Tetragonal (P)  Body Centered (I)	SnO ₂ , TiO ₂ , CaSO ₄
Orthorhombic	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$	 Simple Orthorhombic (P)  Base Centered (C)  Body Centered (I)  Face Centered (F)	KNO ₃ , BaSO ₄
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	 Simple Monoclinic (P)	Na ₂ SO ₄ ·10 H ₂ O

Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	  Simple Cubic (P) Base Centered (C)	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$
Trigonal/Rhombohedral	$a=b=c$ $\alpha=\beta=\gamma \neq 90^\circ$	 Simple Cubic (P)	Calcite ($CaCO_3$), Cinnabar (HgS)
Hexagonal	$a=b \neq c$ $\alpha=\beta=90^\circ$; $\gamma=120^\circ$	 Simple Cubic (P)	Graphite, ZnO , CdS

Definitions:

(a) Atomic Radius:

It is half of the distance between the centre of the two atoms.

(b) Coordination Number:

It is defined as the number of equidistant neighbouring atoms to a parent atom or reference atom.

(c) Packing Factor:

It is defined as the ratio of the volume of atoms to the volume of unit cell. Mathematically it is given by,

$$\text{Packing Factor} = \frac{\text{Volume of atoms } \left(\frac{4\pi r^3}{3}\right)}{\text{Volume of Unit Cell } (a^3)}$$

Packing Factor of Bravais Lattices

Simple Cubic Structure: It is a structure, in which eight atoms are present at the eight corners, such that:

Coordination number = 6

Number of atom(s) per unit cell (n) = $8 \times 1/8 = 1$

Atomic radius = r & lattice constant = a

Relation between a & r: From figure, $a=2r$

$$\text{Packing factor} = \frac{n \times \text{Volume of atom}}{\text{Volume of unit cell}}$$

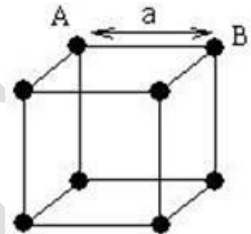
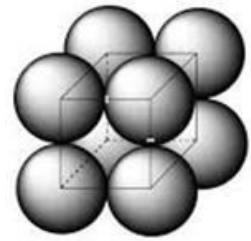
$$\text{Volume of atom of radius 'r'} = \frac{4\pi r^3}{3}$$

$$\text{Volume of unit cell of side 'a'} = a^3$$

$$\text{Therefore, P.F.} = \frac{1 \times \frac{4\pi r^3}{3}}{a^3} \quad (\text{where } a=2r)$$

$$\text{P.F.} = \frac{1 \times \frac{4\pi r^3}{3}}{(2r)^3}$$

By solving the above equation, P.F. = 0.52.



Body Centered Cubic (BCC): It is a structure in which eight atoms are present at the eight corners and one at the centre of the body (along the body diagonal), such that:

Coordination number = 8

Number of atom(s) per unit cell (n) = $(8 \times 1/8) + 1 = 2$

Atomic radius = r & lattice constant = a

Relation between a & r:

From figure: $AC^2 = AB^2 + BC^2$

$$AC^2 = a^2 + a^2 \Rightarrow AC^2 = 2a^2$$

$$\Rightarrow AC = \sqrt{2} a$$

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

$$AD^2 = 2a^2 + a^2 \Rightarrow AD^2 = 3a^2$$

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

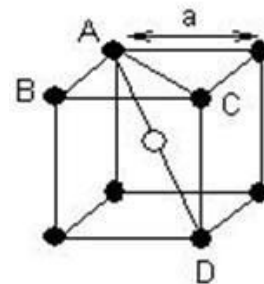
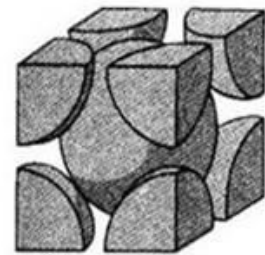
From figure, $AD = 4r = \sqrt{3} a$ or, $a = 4r/\sqrt{3}$

$$\text{Packing factor} = \frac{n \times \text{Volume of atom}}{\text{Volume of unit cell}}$$

$$\text{Therefore, P.F.} = \frac{2 \times \frac{4\pi r^3}{3}}{a^3} \quad (\text{where } a=4r/\sqrt{3})$$

$$\text{P.F.} = \frac{1 \times \frac{4\pi r^3}{3}}{\left(\frac{4r}{\sqrt{3}}\right)^3}$$

By solving the above equation, P.F. = 0.68.



Face Centered Cubic (FCC): It is a structure in which eight atoms are present at the eight corners and six on the six faces of the cube (along the face diagonal), such that:

Coordination number = 12

Number of atom(s) per unit cell (n) = $(8 \times 1/8) + (6 \times 1/2) = 4$

Atomic radius = r & lattice constant = a

Relation between a & r :

From figure: $AD^2 = AC^2 + CD^2$

$$AD^2 = a^2 + a^2 \Rightarrow AD^2 = 2a^2$$

$$\Rightarrow AD = \sqrt{2} a$$

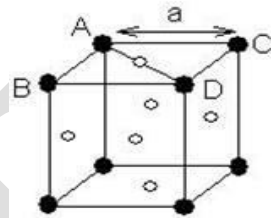
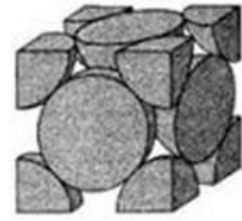
From figure, $AD = 4r = \sqrt{2} a$ or, $a = 4r/\sqrt{2}$

$$\text{Packing factor} = \frac{n \times \text{Volume of atom}}{\text{Volume of unit cell}}$$

$$\text{Therefore, P.F.} = \frac{4 \times \frac{4\pi r^3}{3}}{a^3} \quad (\text{where } a = 4r/\sqrt{2})$$

$$\text{P.F.} = \frac{1 \times \frac{4\pi r^3}{3}}{\left(\frac{4r}{\sqrt{2}}\right)^3}$$

By solving the above equation, P.F. = 0.74.



Crystal directions and planes- Miller Index:

It is often necessary to specify certain directions and planes in crystals, as many material properties and processes vary with direction in the crystal. Directions and planes are described using three integers called Miller Index.

Crystal directions-Method:

1. Draw vector, and find the coordinates of the head (x_2, y_2, z_2) and the tail (x_1, y_1, z_1)
2. Subtract coordinates of tail from coordinates of head
3. Remove fractions by multiplying by smallest possible factor
4. Enclose the above whole number obtained in square brackets i.e., **[h k l]** called Miller index.

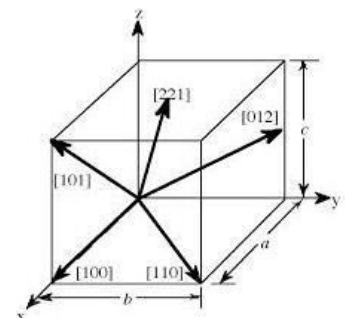
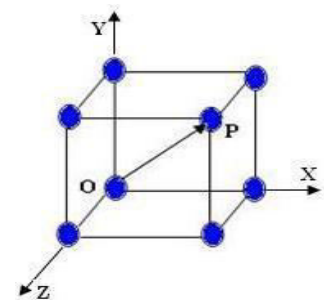
Example: To obtain the direction of **OP**.

Consider the coordinates of O & P as (0, 0, 0) & (1, 1, 1) respectively.

- Subtract the coordinates of P from the coordinates of O i.e., (1-0, 1-0, 1-0)
- Convert the fractions, if any so, into whole number by multiplying the fractions by smallest possible factor
- Enclose the above whole number in square brackets i.e., [1 1 1] which represents the Miller index corresponding to the direction OP.

The figure shows some of the crystal directions:

[1 0 0]; [1 1 0]; [1 0 1]; [0 1 2] & [2 2 1]



Crystal Planes-Miller Index:

Miller index of a plane is the smallest value (or integer) obtained from the reciprocal of the intercepts of the plane in the crystal. It is denoted by (h k l).

Method:

1. Obtain the intercept of the plane, let it be $pa + qb + rc$ where p, q, r are value of the intercepts
2. Take the reciprocal of p, q, r i.e., $1/p, 1/q, 1/r$
3. Convert the above fractional values into whole numbers (by taking the LCM of the denominator and multiplying each fractional value)
4. We obtain the Miller index (h k l)

Example: If intercept made by a plane is (2a, 3b, c) then find its Miller index.

Soln: Intercept value: 2, 3, 1

Reciprocal: $1/2, 1/3, 1/1$

LCM of denominator: 6

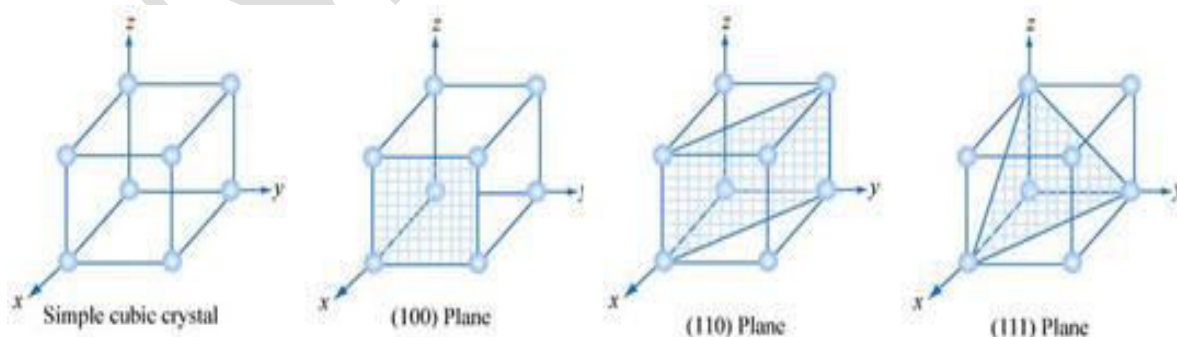
Therefore, $6 \times 1/2, 6 \times 1/3, 6 \times 1/1$ i.e., 3, 2, 6

Miller Index, (h k l) = (3 2 6)

Features of Miller Indices:

1. The intercept of a plane parallel to any axis is infinity and thereby its corresponding Miller index is zero.
2. When the intercept of a plane is negative, the corresponding Miller index is represented by putting a bar on it.
3. All equally spaced parallel planes have same index number (h k l).
4. If a normal is drawn to a plane (h k l), the direction of the normal is [h k l].

Examples of crystal planes with Miller Index: (100); (110) and (111)



Interplanar Spacing (or interatomic spacing) between successive (h k l) crystal planes:
For Cubic Crystal System:

Consider a cubic crystal system of sides 'a' unit, consisting of n successive parallel planes represented by Miller index (h k l).

Assume a plane ABC, shown in figure-(a), at a distance of $ON=d_1$ from the origin. The angle made by the plane ABC with the respective X, Y and Z axes is given by α , β , and γ .

From figure, $OA=a/h$; $OB=a/k$ and $OC=a/l$

$\cos \alpha = d_1/OA$; $\cos \beta = d_1/OB$ and $\cos \gamma = d_1/OC$

From cosine law:

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

$$\therefore (d_1/OA)^2 + (d_1/OB)^2 + (d_1/OC)^2 = 1$$

$$\Rightarrow \left(\frac{d_1}{a/h}\right)^2 + \left(\frac{d_1}{a/k}\right)^2 + \left(\frac{d_1}{a/l}\right)^2 = 1$$

$$\Rightarrow \text{solving further, } d_1^2 = \frac{a^2}{(h^2 + k^2 + l^2)}$$

$$d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \dots \dots (1)$$

To determine the interplanar spacing, consider another plane $A'B'C'$ at a distance of $OM=d_2$ from the origin and making same angles α , β , and γ with the respective X, Y and Z axes.

Therefore,

$$OA' = 2a/h; OB' = 2a/k \text{ and } OC' = 2a/l$$

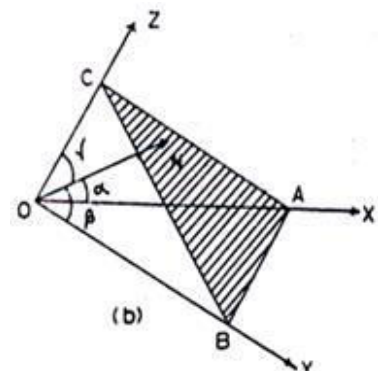
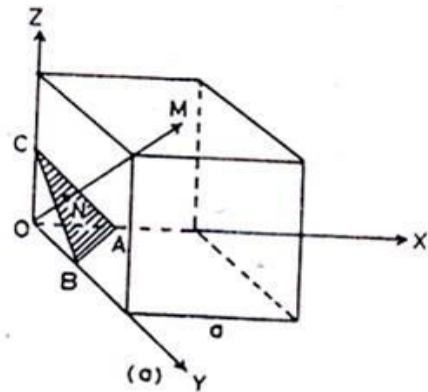
$$\cos \alpha = d_2/OA'; \cos \beta = d_2/OB' \text{ and } \cos \gamma = d_2/OC'$$

From cosine law:

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

Therefore,

$$(d_2/OA')^2 + (d_2/OB')^2 + (d_2/OC')^2 = 1$$



$$\Rightarrow \left(\frac{d_2}{2a}\right)^2 + \left(\frac{d_2}{2a}\right)^2 + \left(\frac{d_2}{2a}\right)^2 = 1$$

Solving further,

$$d_2^2 = \frac{4a^2}{(h^2 + k^2 + l^2)}$$

$$d_2 = \frac{2a}{\sqrt{(h^2 + k^2 + l^2)}} \dots \dots \dots (2)$$

From equations (1) and (2):

$$d = d_2 - d_1 \Rightarrow d = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \dots \dots \dots (3)$$

Equation (3) shows the interplanar spacing between successive (h k l) planes which is equal to the distance of first plane ABC from the origin.

For a **tetragonal crystal system**: $a=b \neq c$ and $\alpha=\beta=\gamma=90^\circ$ therefore,

$$d^2 = \frac{1}{\frac{1}{\left(\frac{h}{a}\right)^2} + \frac{1}{\left(\frac{k}{a}\right)^2} + \frac{1}{\left(\frac{l}{c}\right)^2}}$$

$$d = \left[\frac{1}{\frac{1}{\left(\frac{h}{a}\right)^2} + \frac{1}{\left(\frac{k}{a}\right)^2} + \frac{1}{\left(\frac{l}{c}\right)^2}} \right]^{\frac{1}{2}}$$

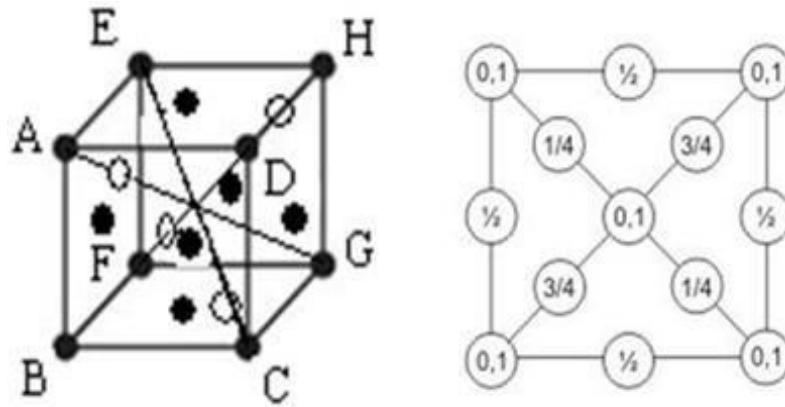
Similarly for **Orthorhombic crystal system**: $a \neq b \neq c$ and $\alpha=\beta=\gamma=90^\circ$

$$d = \left[\frac{1}{\frac{1}{\left(\frac{h}{a}\right)^2} + \frac{1}{\left(\frac{k}{b}\right)^2} + \frac{1}{\left(\frac{l}{c}\right)^2}} \right]^{\frac{1}{2}}$$

Other Crystal Structure:

Diamond:

Diamond structure is formed by the interpenetration of one FCC sub-lattice into another FCC lattice. The resultant structure formed consists of eight atoms at eight corners and six atoms on the six faces, belonging to one FCC sub-lattice, and four atoms along the four body diagonals, belonging to second FCC sub-lattice.



The four atoms present along the body diagonals are arranged in the lattice in such a manner that- two atoms is at a distance of $a/4$ and other two atoms at $3a/4$.

From figure the four body diagonal atoms are:

Along AG and CE at $a/4$ from face ABCD and along BH and DF at $3a/4$ from face ABCD. The arrangement of four atoms along the body diagonals looks symmetric from all the faces.

Number of atoms per unit cell = $(8 \times 1/8) + (6 \times 1/2) + 4 = 8$

Coordination Number = 4; Packing Factor = 0.34

Sodium Chloride (NaCl) Structure:

NaCl structure is formed by the interpenetration of one FCC sub lattice into another FCC lattice. It consists of Na and Chloride ions occupying the alternate positions in the structure as shown in figure. The various positions of:

Na ion: $(1/2, 0, 0)$; $(0, 1/2, 0)$; $(0, 0, 1/2)$; $(1/2, 1/2, 1/2)$; etc.

Cl ion: $(0, 0, 0)$; $(1, 0, 0)$; $(0, 1, 0)$; $(0, 0, 1)$; $(1, 1, 1)$; etc.

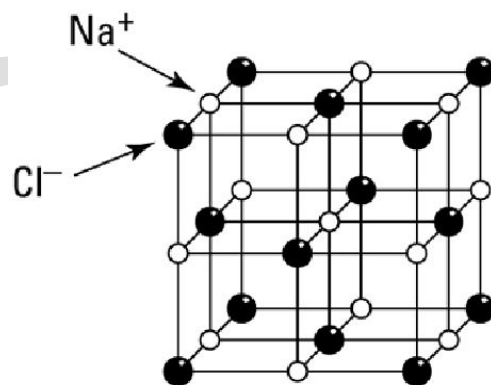
Number of atoms per unit cell: 8

Top face = $(4 \times 1/8) + (1 \times 1/2) + 4 \times 1/4 = 2$

Middle layer = $(4 \times 1/4) + 1 + (4 \times 1/2) = 4$

Bottom layer = $(4 \times 1/8) + (1 \times 1/2) + 4 \times 1/4 = 2$

Coordination Number = 6



UNIT II

X-RAY DIFFRACTION

X-RAY DIFFRACTION BY CRYSTAL PLANES:

X-ray diffraction is defined as bending of x-rays around the obstacle. x-rays are EM waves like ordinary light, therefore they should exhibit interference and diffraction. The X-rays produce diffraction when the size of opaque obstacle must be comparable to the wavelength. If x-rays wavelength is less than the opaque obstacle, it can't produce x-ray diffraction. To obtain diffraction effects with x-rays the rulings in a diffraction grating must be spaced only a few nano meters. But this is very complicated or practically this is not possible. To avoid this problem Laue suggested a crystal because of the distance between atoms are very low and it works as 3D grating. Hence it is known as crystal grating, whereas optical grating is a 2D plane grating.

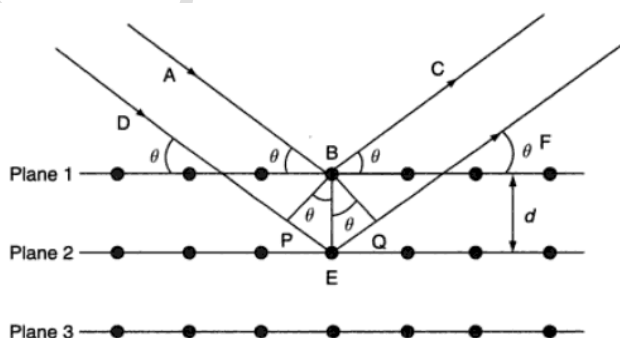
W.L. Bragg observed x-ray diffraction when X-rays are incident on the crystal surface nearly at Bragg's angles. Bragg's angle or glancing angle means the angle between incident ray and crystal plane at which diffraction occurs.

BRAGG'S LAW:

Statement: The X-rays reflected from different parallel planes of a crystal interfere constructively when the path difference is integral multiple of the wavelength of X-rays.

Explanation:

Let us consider a crystal made up of a equidistant parallel planes of atoms with the inter planar spacing 'd'. Let a narrow beam of X-rays of ' λ ' be incident on the planes with a glancing angle θ then a part of the X-ray beam AB incident at B in plane-1 is scattered along the direction BC. Similarly a part of the X-ray beam DE incident at E in plane-2 is scattered along the direction EF and it is parallel to BC. Let the beams AB and DE make angle θ with the planes. This angle θ is called as angle of diffraction or glancing angle. The path lengths of ABC and DEF are not same. To find the path difference between ABC and DEF, extend the rays AB to cut EF at Q and CB to cut DE at P. Path length of the ray DEF greater than the path length of ABC by an amount (PE+EQ).



$$\therefore \text{The path difference between two rays reflected from adjacent planes } (\delta) = PE + EQ \quad (1)$$

The rays BC and EF will be in phase only when,

$$\delta = n\lambda \quad (n = 0, 1, 2, 3, \dots)$$

From the fig. ΔPBE and ΔQBE are each equal to θ only. The length BE is equal to 'd'.

$$\text{From } \Delta PBE, \sin\theta = \frac{PE}{BE} = \frac{PE}{d}$$

$$PE = d \sin\theta \quad (2)$$

$$\text{Similarly, } \Delta QBE, EQ = d \sin\theta \quad (3)$$

Sub (2) and (3) in eq. (1)

$$\therefore \text{ path difference } (\delta) = PE + EQ.$$

$$\therefore \text{ path difference } (\delta) = d \sin\theta + d \sin\theta$$

$$\therefore \text{ path difference } (\delta) = 2d \sin\theta$$

Therefore, for the rays in phase, $2d \sin\theta = n\lambda$

Since the maximum possible value for θ is 1. $\frac{n\lambda}{2d} \leq 1$

The wavelength λ should not be exceed twice the inter planar spacing for diffraction to occur.

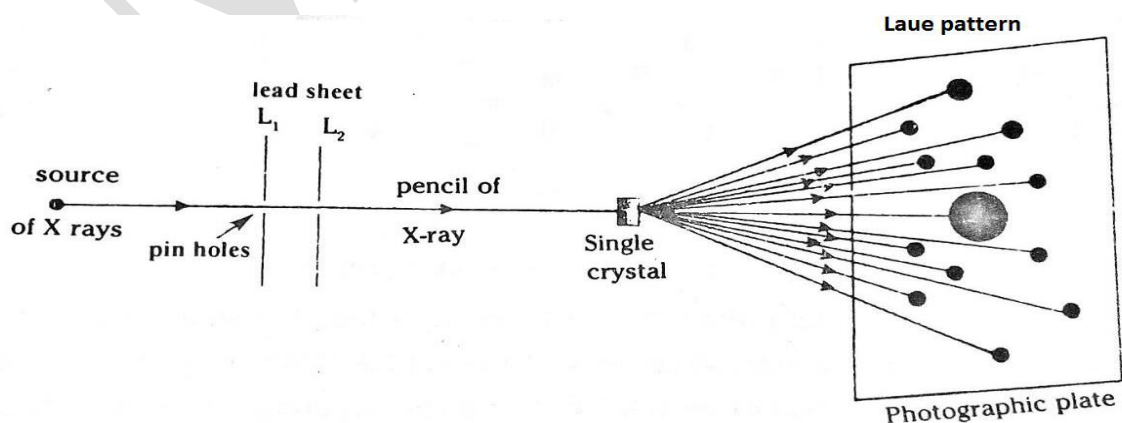
Methods to determine crystal structure:

According to Bragg's equation, for a given wavelength, diffraction can take place only when ' θ ' and ' d ' are matched. For this purpose either θ or d has to be allowed to vary continuously so that Bragg's condition is satisfied and diffraction takes place.

As an alternative, we make θ and d constant and use a continuous range of wavelengths. This can be accomplished by three main X – ray diffraction methods by which the crystal structures can be analyzed.

- I. Laue method : – For single crystal.
- II. Powder method : – Polycrystalline powder.
- III. Rotating crystal method : – For single crystals.

Laue method:



Laue diffraction arrangement and Laue spots

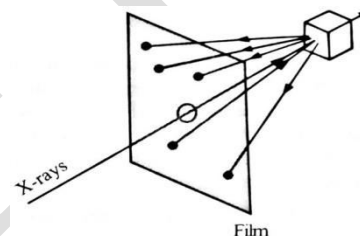
In this method, white X – rays (X – radiation with continuous wavelength) over a wide range of wavelengths preferably from 0.2 to $2 \text{ \AA}$ sent through pin holes made up of a lead sheets to obtain fine sharp beams.

The sharp beam of x – rays are made to incident on the crystal which is kept stationary on a crystal holder. Thickness of crystal are usually 0.5 mm and its length and breadth are about $3 \text{ mm} \times 3 \text{ mm}$. The crystal act as a 3D diffraction grating. The rays after passing through the crystal are diffracted and are recorded on the photographic film placed at certain distance from the crystal. Developed photographic film consists of large number of dots. Each dot is known as Laue spot and the entire spots are called as Laue diffraction pattern. Each Laue spot represents a set of Miller indices of plane in the crystal. The diffracted X – rays from a set of plane produce constructive interference, if they are in phase and form an intense beam and this produce dark spot on photographic film. If the diffracted rays are out of phase, destructive interference takes place so that photographic film is unaffected.

There are two practical variants of Laue method

Transmission Laue method - In this the film is placed behind the crystal to record beams which are transmitted through the crystal. In this Laue pattern look like either ellipse.

Back reflection Laue method – In this the film is placed between the x – ray source and the crystal. The beams which are diffracted in a backward direction are recorded. In this Laue pattern look like hyperbola.



Advantages:

1. The shape of the unit cell can be established from the symmetry of the Laue pattern.
2. Practically this method is used to evaluate $(h k l)$ values of various planes from different Laue spots.
3. Laue technique is extensively used to study defects in solids under mechanical and thermal treatments.

Disadvantages:

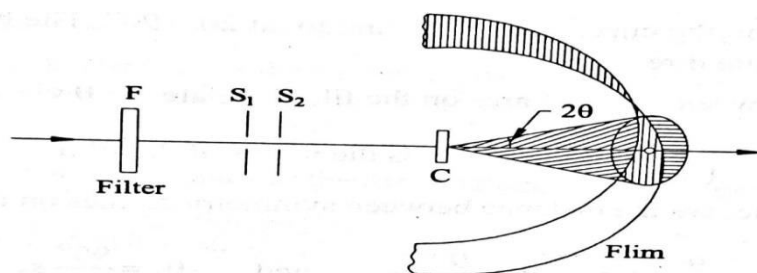
Cell parameters of a crystal cannot be determined using Laue method. For transmission Laue method the crystal should be thin. This method is not very useful in the overall study of the crystal structure.

Limitations:

Interpretation of Laue pattern is quite complex. Special methods such as stereographic projections have to be adopted.

Powder method (Debye and Scherrer Method):

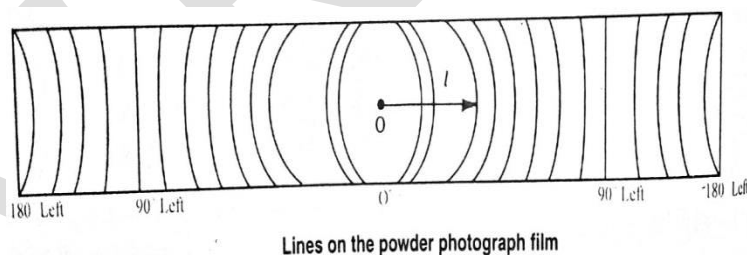
This method is a power full experimental technique which can be used for substances which are not obtained easily in the form of single crystal of appreciable sizes. This method was developed by Debye and Scherrer.



EXPERIMENTAL ARRANGEMENT - POWDER METHOD

In this method a sample of the crystal is crushed into powder and placed in a thin walled glass tube and fixed at the centre of cylindrical Debye Scherrer camera. A strip of X- ray photographic film is arranged along the inner side of the curved surface of the camera. The powder contains millions of tiny crystals oriented at random in all possible directions. A beam of monochromatic X – rays are passed through collimator to obtain narrow fine beam of X- rays. This beam falls on the powder and gets diffracted. For get better results the specimen may be made rotate about its own axis.

The diffraction takes place for the values of θ and d which satisfy the Bragg's condition. i.e., $2d \sin\theta = n\lambda$. When fine sharp beam of X-rays incident on the plane of the tiny crystal get diffracted. The diffracted rays corresponding to fixed values of θ and d lie on the surface of cone. Different cones are observed for different sets of θ and d for a particular value of ' n '. These reflected cones are recorded by the photographic film. On the film these appears arcs of the circles. From the film it's observed that when the rays are diffracted through small angles they make arcs around central spot. The arc produced by reflected rays appear dark on the developed film. When they diffract through an angle 90° they appear as straight line after wards the curvature is reversed and the angle approaches to 180° the traces are nearly circular. The transmitted X-rays moves out of the camera through an exit hole located diametrically opposite to the entrance of the camera.

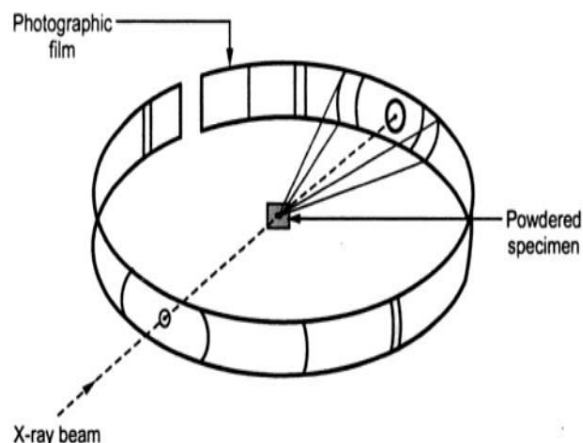


Lines on the powder photograph film

Let ' l ' be the distance of a particular arc from centre ' O ' and R be the radius of the camera

$$\therefore \theta = \frac{l}{2R}$$

Using these values of θ in Bragg's equation, interplanar spacing ' d ' can be calculated. Use of geometrical relation between crystallographic axes, the miller indices ($h k l$) can be obtained and from the relation we can calculate the lattice parameter d .



$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Uses: The powder method is a standard technique used to study the structure of micro crystals. This technique gives useful information regarding the size of the crystals, presence of impurities, distortions, preferred orientation etc.

Applications:

X- ray diffraction are used

1. In analysis of solid and liquid samples.
2. In the study of nanometer composition.
3. In structural quality of pharmaceutical and organic compounds.
4. It is much useful to study crystal symmetry.
5. In determining the percentage of material in crystalline form versus amorphous.
6. In measuring residual stress in bulk metals and ceramics.

CRYSTAL DEFECTS

Introduction:

The metals are made up of infinite number of atoms in space whose arrangement conforms to a particular symmetry. The deviations from periodicity in the solid are called the defect in a solid. Crystal imperfections refer to some irregularities in crystal structure in one or more atomic distances. Sometimes, crystal defects are introduced intentionally into the lattice in a controlled manner to achieve the required properties.

The solid materials are crystalline in structure. The crystals are divided into two groups, real crystals (or grown crystals) and ideal crystals (or sound crystals). If the arrangement of atoms in a crystal is perfect, regular and continuous throughout the crystal, it is known as an 'ideal crystal'. In practice, the ideal crystals rarely exist. The crystals in any material have many defects, which may be due to various reasons. There will be irregularity or defects in the arrangement of atoms within the crystal. These types of crystals are known as 'real crystals'. The defects influence few properties of solid like colour of crystals, plasticity, increased conductivity of pure semiconductors, melting, strength of crystals, luminescence, diffusion of atoms through solids etc.

Reasons for crystal imperfections :

1. Improper growth of crystals during crystallization.
2. Presence of impurities.
3. Application of local pressure on crystalline solid.
4. Effect of temperature.

Effect of defects on properties of solids :

1. It lowers the tensile strength.
2. It increases brittleness.
3. It lowers mechanical strength (hardness, toughness, etc.)
4. Impurities of the crystal, lowers melting point of the crystal.
5. It changes refractive index.
6. Formation of holes/ vacancies increases thermal/ electrical conductivity.

Defects are produced by various methods :

1. By heating & rapid cooling
2. By applying external strength
3. By bombarding with high energy particles like neutrons or particles from cyclotron

Classification of defects:

The defects are generally classified according to their dimensions are as follows :

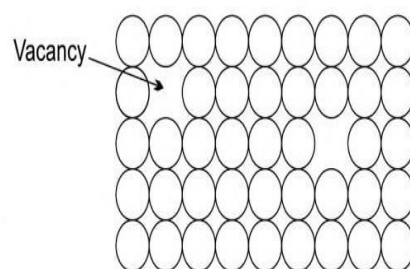
Crystalline defects

- I. 0 – Dimensional defects (or) Point defect.
 1. Vacancies
 2. Interstitial
 3. Compositional defects
 - i. Substitutional impurity
 - ii. Interstitial impurity.
 4. Electronic defects
- II. 1 – Dimensional defects (or) Line defects (or) dislocations.
 1. Edge dislocation
 2. Screw dislocation
- III. 2 – Dimensional defects (or) Surface defects.
 1. Grain boundaries
 2. Twin boundaries
 3. Tilt boundaries
 4. Stacking fault
- IV. 3 – Dimensional defects (or) Volume defects.
 1. Air bubbles
 2. Internal cracks
 3. Empty spaces

Zero – dimensional defects (OR) point defect:

Zero dimensional defects arise due to missing of an atom from the regular position, presence of impurity atom or atom in the wrong place during crystallization. The presence of point defect in a crystal increases its internal energy compared to that of perfect crystal. The effect of such defect is local and produces distortion inside the crystal. These are small defects which extends its influence in all directions but limited to one or two atomic diameters in the crystal lattice. Hence, the mechanical strength at that point gets reduced. There are different kinds of point imperfections.

Vacancy: A vacancy is lattice site from which the atom is missing from their regular position. The vacancies are formed due to the imperfect packing during crystallization or due to thermal vibrations of the atom at high temperature. Vacancies may be single, two or more depending on crystal type. For most of the

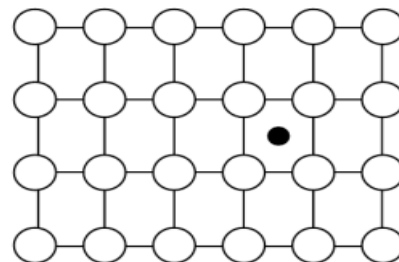


crystals, in order to create one vacancy thermal energy of 1.1 eV is required.

Interstitial defect:

This defect arises when an atom of same kind or different kind occupies the void space (empty space between the atoms) between the regular atomic sites.

The interstitial atom may be present in the crystals which have low packing fraction. This atom causes some mechanical strain on the surrounding atoms. The amount of the strain depends on the size of the interstitial atom. This atom is considerably smaller than the parent atoms otherwise it will produce atomic distortion. Interstitials may be single interstitial, di-interstitials and tri-interstitials.



Compositional defects:

Compositional defects arise due to presence of either unwanted impurities or purposely doped impurities during the process of crystallization. These defects play an important role in semiconductors which are specially prepared for diodes, transistors, etc. Impurity atoms are present at the sites of regular parent atoms or in the interstitial spaces. These defects are two types.

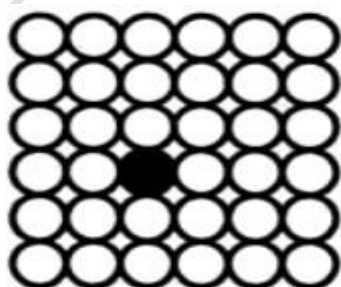
Substitutional impurities:

This defect arises when an impurity atom replaces or substitutes parent atom in the crystal lattice. If the size of substitutional impurity is same as parent atom then the amount of strain around will be less, otherwise it will be more.

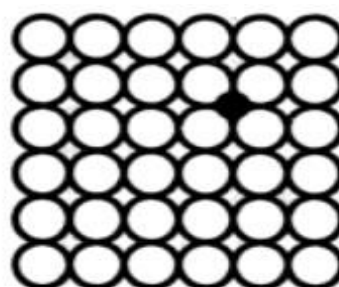
Ex: In extrinsic semiconductors either third or fifth group atoms occupy the sites of silicon or Germanium atoms.

Interstitial impurity: This defect arises when small sized foreign atom occupying an interstice or void space in the parent crystal without disturbing any of the parent atoms from their regular sites.

Ex: In steel, carbon atom ($0.77 \text{ \AA}$), being smaller in size, occupies interstitial position in Iron ($2.250 \text{ \AA}$).



Substitutional impurity



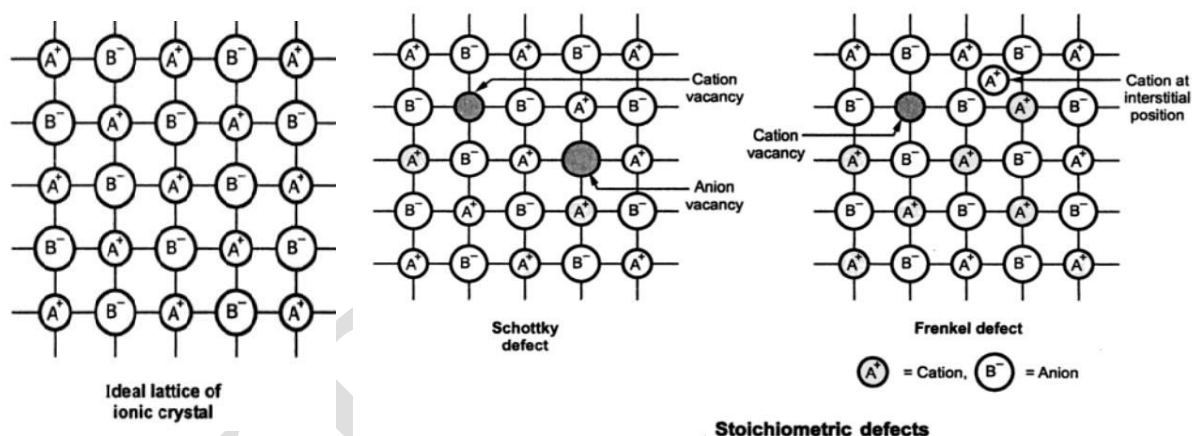
Interstitial impurity

Point defects in ionic crystal:

In ionic crystal, point defects are of two types.

- A. Stoichiometric defect.
- B. Non – Stoichiometric defect.

Stoichiometric defect: The compounds in which the number of cation and anions are exactly in the same ratio as represented by their chemical formula are called stoichiometric compounds. The defects that do not disturb the ratio of cations and anions are called stoichiometric defect.



Schottky defect:

The defect arises when equal number of cations and anions are missing from the lattice is called schottky defect. This ion pair moves to the surface of the crystal, so that charge neutrality is maintained in the vacancy region. Schottky defect decreases density of crystalline substance. In this defect both anion and cation have similar sizes. This type of defect occurs in ionic solids with high co-ordination number

Ex: Alkali halides (NaCl, CsCl, etc.)

Frenkel defect:

The defect arises when some of the ions (cations) of the lattice occupy an interstitial sites leaving lattice sites vacant is known as Frenkel defect. Anions do not get displaced like cation, as the void space is just too smaller for their size. Here, charge neutrality is maintained. Due to this defect there is no change in the density of the crystal. In this defect anions are larger in size as compared to cations. This type of defect occurs in ionic solids with comparatively low – co ordination number.

Ex : CaF_2 , AgBr , AgI , etc.

Non – Stoichiometric defect (Electronic defect):

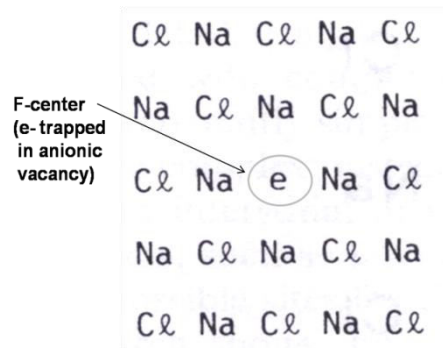
If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula; the defects are called **non – stoichiometric defects**. These defects arise either due to excess of metal atoms or non metal atom or presence of impurities / foreign particle. By the influence of external electrical field, these defects move freely within the crystal. In semiconductors, temperature variation change charge concentration, so variation of temperature [i.e., thermal energy] leads to electronic defect. Non-stoichiometric Defects is mainly of two types –

Metal Excess Defect:

Metal excess defects are of two types:

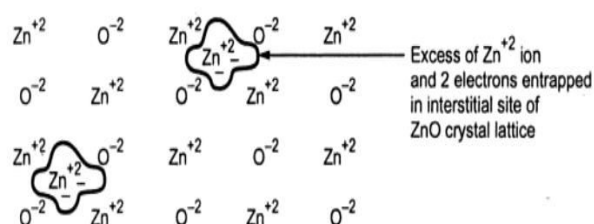
(a) **Metal excess defects due to anionic vacancies:** A negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron there by maintaining an electrical balance. The trapped electrons are called F-centers or colour centers because they are responsible for imparting colour to the crystal. Alkali halides like NaCl and KCl shows this type of defect.

Ex: When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl . This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called F-centres (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl . The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.



(b) **Metal excess defects due to the presence of extra cations at interstitial sites:** Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality can cause metal excess. This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

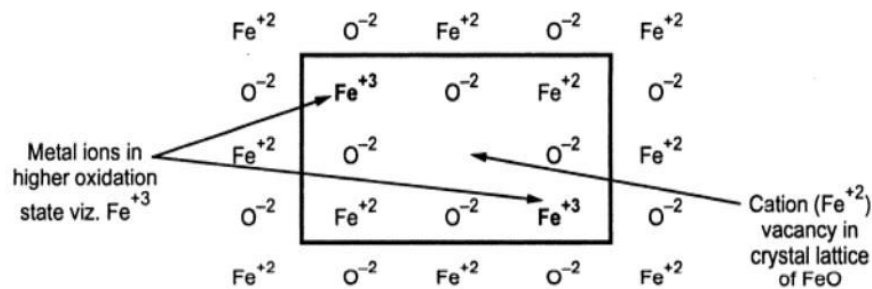
For example : In Zn_yO , where $y > 1$, the excess of cations occupy interstitial voids, while heating the compound in a zinc vapour, 2



electrons are released in a from zinc atom and stays around an interstitial cation.

Metal Deficiency Defect: This defect occurs when metal shows the variable valency.

Ex: In Fe_xO where $x < 1$, vacant cation sites are present. By heating a stoichiometric FeO in oxygen atmosphere, such compound can be produced. The two electrons required by each excess oxygen atom is donated by two Fe^{2+} (ferrous) ions, which become Fe^{3+} (ferric) ions.



Calculation of number of vacancies at any temperature. Or an expression for the energy for formation of vacancy:

Energy supply to a crystal moves some of the atoms present at regular atomic sites in the interior of the crystal to the surface, so that vacancies are formed inside the crystal. If energy is supplied to a ionic crystal then either cation – anion pairs are moved to the surface (schotky defect) or cations are moved to interstitial spaces (Frenkel defect), so that vacancies are formed inside the crystal.

In Metallic Crystals:

Let a crystal contains N number of atoms. The energy required to move an atom at a regular atomic site in the interior of the crystal to the surface is E_V . i.e., the energy required to create a vacancy.

To create 'n' number of isolated vacancies the energy required is $U = nE_V$ (1)
the total number of ways to move 'n' number of atoms out of N number of atoms in crystal on to its surface will be

$$P = {}^N C_n = \frac{N!}{(N-n)!n!} \quad (2)$$

The vacancies created inside the crystal produces disorder in the crystal. The disorders can be measured interms of entropy (S).

The increase in entropy due to increase of vacancies is

$$S = K_B \log P \quad (3)$$

where K_B is Boltzmann constant which will be equal to 1.38×10^{-23} J/molecule $^\circ\text{K}$.

Substituting eq. (2) in eq. (3) , we have

$$S = K_B \log \left[\frac{N!}{(N-n)! n!} \right] \quad (4)$$

The creation of vacancies produces not only change in entropy but also change in free energy (F) of the crystal.

$$\therefore F = U - TS \quad (5)$$

where, U is internal energy of a crystal at temperature at T K.

Substituting eq. (1) & (4) in eq. (5)

$$F = nE_V - K_B T \log \left[\frac{N!}{(N-n)! n!} \right]$$

$$F = nE_V - K_B T [\log N! - \log(N-n)! - \log n!] \quad (6)$$

The logarithmic term in the above equation can be simplified using stirling's approximation,

$$\log x! = x \log x - x$$

$\therefore$ Equation (6) becomes

$$F = nE_V - K_B T [N \log N - N - (N-n) \log(N-n) + (N-n) - n \log n + n]$$

$$F = nE_V - K_B T [N \log N - (N-n) \log(N-n) + (N-n) - n \log n] \quad (7)$$

At thermal equilibrium at constant volume, free energy is constant and minimum with respect to 'n', hence,

$$\left[\frac{\partial F}{\partial n} \right]_T = 0$$

$$E_V - K_B T \log \left[\frac{(N-n)}{n} \right] = 0$$

$$\frac{E_V}{K_B T} = \log \left[\frac{(N-n)}{n} \right] \quad (8)$$

Taking exponential on both sides of eq. (8), we have

$$\exp \left[\frac{E_V}{K_B T} \right] = \frac{N-n}{n}$$

$$n = (N-n) \exp \left[\frac{-E_V}{K_B T} \right]$$

If $n \ll N$ then

$$n \approx N \exp \left[\frac{-E_V}{K_B T} \right]$$

The above eq. shows that the number of vacancies decreases as temperature increases.

Ionic crystals:

A. Calculation of Number of Schottky defects at a given temperature

In ionic crystals equal number of cations (positive ions) and anion (negative ions) vacancies are formed i.e., usually cation – anion paired vacancies are formed, so that charge neutrality is maintained in the crystal. The energy required to move a cation and an anion from interior of the crystal to the surface is E_p . Therefore the amount of energy required to produce 'n' number of isolated ion pair vacancies will be $U = nE_p$ (1)

The total number of ways these 'n' pairs of vacancies are created is given by

$$P = \left[\frac{N!}{(N-n)! n!} \right]^2 \quad (2)$$

The vacancies created inside the crystal produces disorder in the crystal. The disorder can be measured in terms of entropy (S).

The increase in entropy, due to creation of 'n' of vacancies is

$$S = K_B \log P \quad (3)$$

where K_B is Boltzmann constant which will be equal to 1.38×10^{-23} J/molecule °K.

Substituting eq. (2) in eq. (3), we have

$$S = K_B \log \left[\frac{N!}{(N-n)! n!} \right]^2 \quad (4)$$

The vacancies produce not only change in entropy but also change in free energy (F) of the crystal.

$$\therefore F = U - TS \quad (5)$$

where, U is internal energy of a crystal at temperature at T K.

Substituting eq. (1) & (4) in eq. (5)

$$F = nE_p - K_B T \log \left[\frac{N!}{(N-n)! n!} \right]^2$$

$$F = nE_p - 2K_B T [\log N! - \log(N-n)! - \log n!] \quad (6)$$

The logarithmic term in the above equation can be simplified using stirling's approximation,

$$\log x! = x \log x - x$$

∴ Equation (6) becomes

$$F = nE_p - 2K_B T [N \log N - N - (N - n) \log(N - n) + (N - n) - n \log n + n]$$

$$F = nE_p - 2K_B T [N \log N - (N - n) \log(N - n) + (N - n) - n \log n] \quad (7)$$

At thermal equilibrium at constant volume, free energy is constant and minimum with respect to 'n', hence,

$$\left[\frac{\partial F}{\partial n} \right]_T = 0$$

$$E_p - 2K_B T \log \left[\frac{(N - n)}{n} \right] = 0$$

$$\frac{E_p}{2K_B T} = \log \left[\frac{(N - n)}{n} \right] \quad (8)$$

Taking exponential on both sides of eq. (8), we have

$$\exp \left[\frac{E_p}{2K_B T} \right] = \frac{N - n}{n}$$

$$n = (N - n) \exp \left[\frac{-E_p}{2K_B T} \right]$$

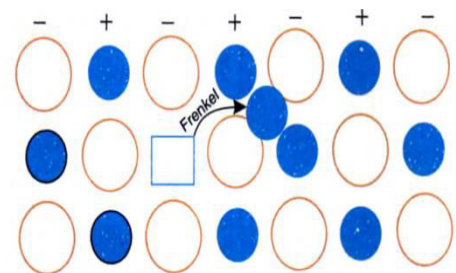
If $n \ll N$ then

$$n \approx N \exp \left[\frac{-E_p}{2K_B T} \right]$$

B. Calculation of Number of Frenkel defects at a given temperature

Let the ionic crystal contains N number of atoms and N_i number of interstitial spaces in a perfect crystal ($N_i < N$). The amount of energy required to displace an atom (cation) from regular atomic site to an interstitial position is E_i .

At some thermal equilibrium temperature, let there be 'n' number of cation site vacancies and same number of interstitial atoms.



The amount of energy required to produce 'n' Frenkel defects is $U = nE_i$ (1)

The total number of ways in which 'n' Frenkel defects can be formed is

$$P = \frac{N!}{(N-n)!n!} \times \frac{N_i!}{(N_i-n)!n!} \quad (2)$$

The vacancies created inside the crystal produces disorder in the crystal. The disorder can be measured in terms of entropy (S).

The increase in entropy due to increase of vacancies is

$$S = K_B \log P \quad (3)$$

where K_B is Boltzmann constant which will be equal to 1.38×10^{-23} J/molecule °K.

Substituting eq. (2) in eq. (3), we have

$$S = K_B \log \left[\frac{N!}{(N-n)!n!} \times \frac{N_i!}{(N_i-n)!n!} \right] \quad (4)$$

The creation of vacancies produces not only change in entropy but also change in free energy (F) of the crystal.

$$\therefore F = U - TS \quad (5)$$

where, U is internal energy of a crystal at temperature at T K.

Substituting eq. (1) & (4) in eq. (5)

$$F = nE_i - K_B T \log \left[\frac{N!}{(N-n)!n!} \times \frac{N_i!}{(N_i-n)!n!} \right]$$

$$F = nE_i - K_B T \left[\log \frac{N!}{(N-n)!n!} + \log \frac{N_i!}{(N_i-n)!n!} \right]$$

$$F = nE_i - K_B T [\log N! - \log(N-n)! - \log n! + \log N_i! - \log(N_i-n)! - \log n!] \quad (6)$$

The logarithmic term in the above equation can be simplified using Stirling's approximation,

$$\log x! = x \log x - x$$

$\therefore$ Equation (6) becomes

$$F = nE_i - K_B T [N \log N - N - (N-n) \log(N-n) + (N-n) - n \log n + n + N_i \log N_i - N_i - (N_i-n) \log(N_i-n) + (N_i-n) - n \log n + n]$$

$$F = nE_i - K_B T [N \log N + N_i \log N_i - (N-n) \log(N-n) - (N_i-n) \log(N_i-n) - 2n \log n]$$

$$F = nE_i - K_B T \log \left[\frac{(N-n)(N_i-n)}{n^2} \right] \quad (7)$$

At thermal equilibrium at constant volume, free energy is constant and minimum with

respect to 'n', hence,

$$\left[\frac{\partial F}{\partial n} \right]_T = 0$$

$$E_i - K_B T \log \left[\frac{(N - n)(N_i - n)}{n^2} \right] = 0$$

$$\frac{E_i}{K_B T} = \log \left[\frac{(N - n)(N_i - n)}{n^2} \right] \quad (8)$$

Taking exponential on both sides of eq. (8), we have

$$\exp \left[\frac{E_i}{K_B T} \right] = \frac{(N - n)(N_i - n)}{n^2}$$

$$n^2 = (N - n)(N_i - n) \exp \left[\frac{-E_i}{K_B T} \right]$$

If $n \ll N_i$ then

$$n^2 \approx NN_i \exp \left[\frac{-E_i}{K_B T} \right]$$

or

$$n \approx (NN_i)^{1/2} \exp \left[\frac{-E_i}{2K_B T} \right]$$

In silver halides, the most prevalent defects below 700K are Frenkel defects.

COMPARISON BETWEEN SCHOTTKY DEFECT AND FRENKEL DEFECT		
S.No	SCHOTTKY DEFECT	FRENKEL DEFECT
1	It arises when a pair of cation and anion is missing from site in ionic solid causing a pair of vacancy	It arises when a cation leaves its lattice site and enters into an interstitial site.
2	Cation vacancy as well as anion vacancy is observed	Only cation vacancy is observed
3	Density of crystalline substance is observed	No change in overall density of crystalline substance is observed
4	Overall electrical neutrality of crystal is maintained	Overall electrical neutrality of crystal is maintained
5	This type of defect occurs in ionic solids with 1. High co - ordination number 2. Cations and anions of similar sizes	This type of defect occurs in ionic solids with 1. Comparatively low co-ordination number 2. Anions are larger in size as

Ex : NaCl, CsCl etc.	compared to cations 3. Open crystal structure with large interstices. Ex: CaF_2 , ZnS etc.
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One- dimensional defects (OR) line defects (OR) dislocations:

If a Crystal plane ends somewhere in the crystal, then along the edge of that incomplete plane produces defect in the crystal called line defect. The effect of these defects appears along a line in the crystal geometry.

Line defects are also known as dislocations.

Causes of dislocations:

1. Thermal stress of External stress
2. Crystal growth
3. Phase transformation
4. Segregation of solute atoms causing mismatch

Types of dislocations:

The line defects is of two types they are

1. Edge dislocation
2. Screw dislocation

Edge dislocations:

A perfect crystal is composed of several parallel vertical planes which are extended from top to bottom completely and parallel to side faces. The atoms are in equilibrium positions and the bond lengths are in equilibrium value.

If one of these vertical planes does not extend from top to bottom face of the crystal, but ends in midway within the crystal, it is called as edge dislocation.

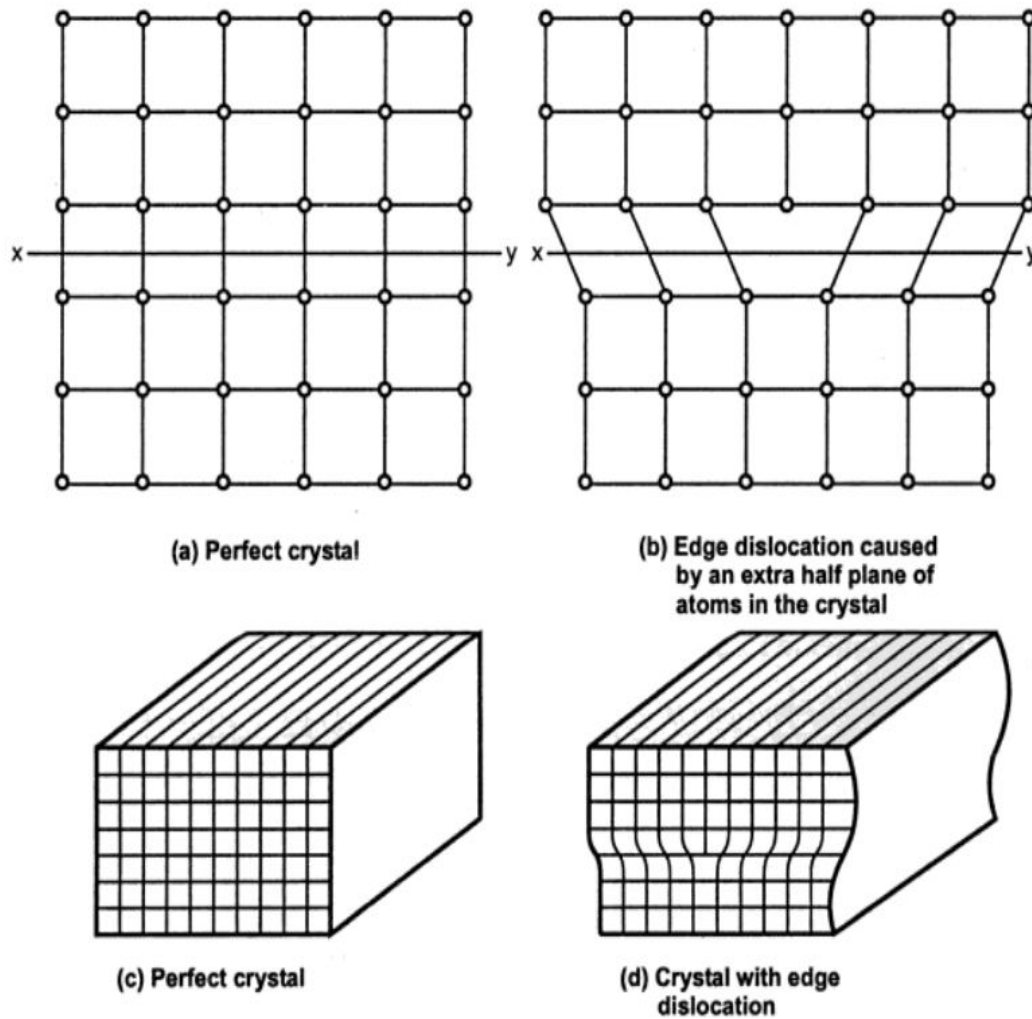
In imperfect crystal all the atoms above the dislocation plane are squeezed together and compressed there by the bond length decreases. And all the atoms below the dislocation plane are elongated by subjecting to the tension and thereby the bond length increases.

There are two types of edge dislocation. They are

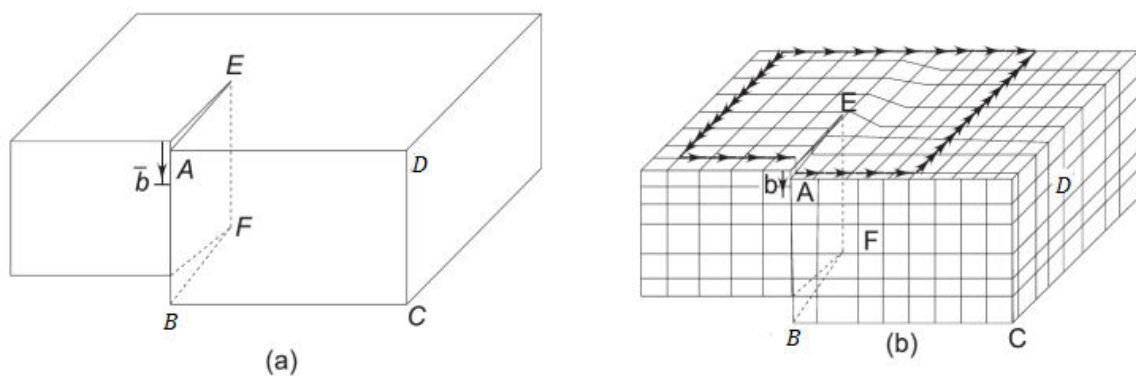
1. Positive edge dislocation
2. Negative edge dislocation.

Positive edge dislocation: If the vertical plane starts from top of the crystal and never reaches to the bottom. It is represented by inverted tee ($\perp$).

Negative edge dislocation: If the vertical plane starts from bottom of the crystal and never reaches top. It is represented by tee (**T**).

**Edge dislocation****Screw dislocation:**

The defect produced by displacement of atoms in two separate perpendicular planes is known as Screw dislocation.

**Screw dislocation**

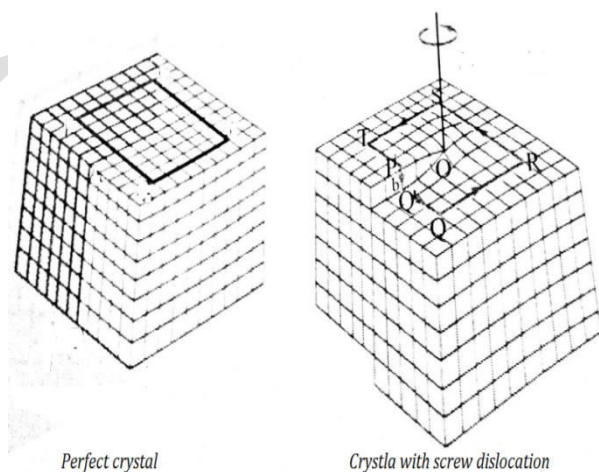
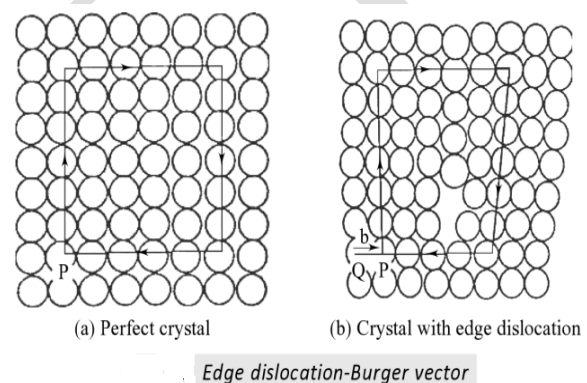
It can be explained by cutting a part of perfect crystal at AB with the help of a cutting plane. It means crystal is not breaking up into two parts. Now, apply a shear stress parallel to the cutting plane such that the right (front) portion of the crystal moves down with respect to the left portion of the crystal. It is observed that the effect on the crystal appears as a screw or a helical surface or it resembles a spiral staircase. The portion or region of distorted crystal is at least a few atoms in diameter.

Burger vector:

The magnitude and direction of the displacement of crystal planes due to dislocation can be represented by a vector called Burger's vector. To understand the concept of Burger's vector, let us consider two crystals one perfect and another with dislocation.

Perfect crystal: let us consider a starting point P in a crystal and move X –times (6 atoms) the atomic distance in the upward direction from the starting point P. This is followed by Y-times the atomic distance (5 atoms) to the right in the horizontal direction. Then it is processed with X -times the atomic distance (6 atoms) towards the downward direction and finally Y-times the atomic distance (5 atoms) to the left in the horizontal direction. Finally the starting point P is reached. The closed circuit drawn is known as Burger circuit.

Crystal with dislocation: In the case of dislocation crystal, if the starting point is P, then the ending point will be Q. It means both initial and end points are separated by one atomic distance PQ denoted by a vector $\vec{b}$ drawn from the end point Q to the starting point P of Burger circuit. The connecting vector between the starting point and ending point is known as Burger's vector of the dislocation.



DIFFERENCES BETWEEN EDGE DISLOCATION AND SCREW DISLOCATION		
S.No	EDGE DISLOCATION	SCREW DISLOCATION
1.	Edge of an atomic plane is formed internal to the crystal	Distortion of the lattice in the vicinity of the screw dislocation takes place.
2.	Tensile, compressive and shear stress fields may be present.	Only shear stress field.
3.	It is perpendicular to the Burger's vector.	It is parallel to its Burger's vector.
4.	Edge dislocation moves in the direction of the Burger vector.	It moves perpendicular to the Burger vector.
5.	Involves an extra row of atoms above or below the slip plane.	Distortion follows a helical path either right hand or left hand.
6.	Force required to form and move an edge dislocation is small.	Larger forces are required to form and move screw dislocations.

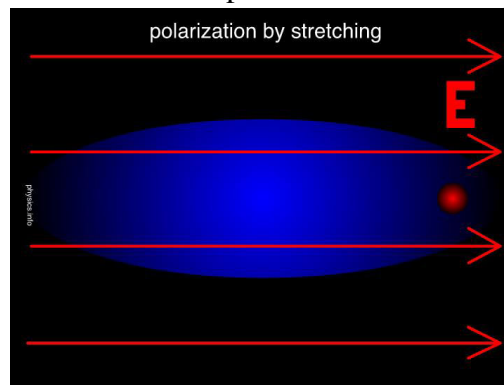
The Burger's vector is perpendicular to the edge dislocation and is parallel to the screw dislocation.

UNIT III

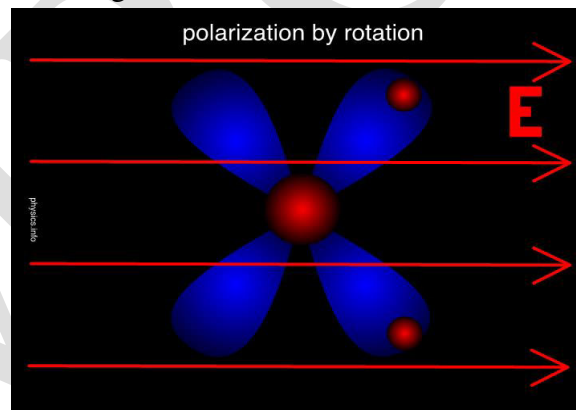
DIELECTRIC PROPERTIES

Introduction:

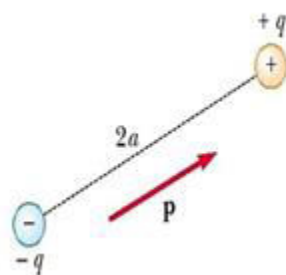
All dielectric materials are insulators but all insulators are not perfect dielectric materials. There are no free charges available for conduction in a dielectric. All the electrons are tightly bound to their nucleus of the atoms. When the dielectric is placed in an electric field, then separation of positive and negative charges takes place in a dielectric, causing polarization of dielectric. Dielectrics are characterized by polarization & dielectric constant. Dielectric materials store large amounts of electro-static fields. There are two principal methods by which a dielectric can be polarized: stretching and rotation. Stretching an atom or molecule results in an induced dipole moment added to every atom or molecule.



Rotation occurs only in polar molecules — those with a permanent dipole moment like the water molecule shown in the diagram below.

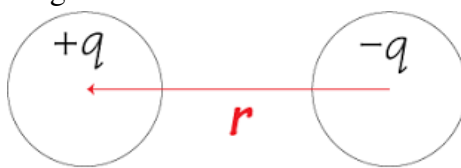
**Basic Definitions:**

(1) Electric Dipole: Two opposite charges of equal magnitude separated by a finite distance constitutes an electric dipole.



An electric dipole consists of two charges of equal magnitude but opposite sign separated by a distance of $2a$. The electric dipole moment $\mathbf{p}$ is directed from $-q$ to $+q$.

(ii) **Dipole moment(μ):** Electric dipole moment is defined equal to product of one of the charges and the charge separating distance.



$$\mu = qr$$

Units: c-m or Debye, 1 Debye = 3.3×10^{-30} c-m

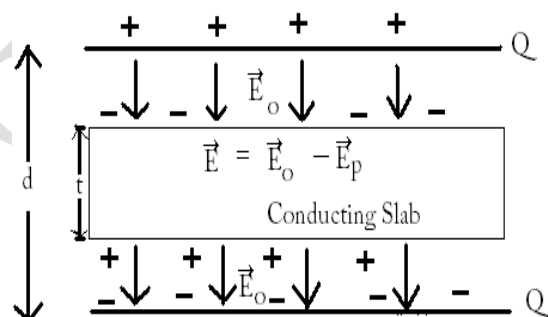
(iii) **Permittivity (ϵ):** Permittivity represents the easily polarizable nature of the dielectric or medium.

$$\epsilon_0 = \text{permittivity of free space} = 8.854 \times 10^{-12} \text{ F/m}$$

(iv) **Dielectric constant(ϵ_r):** Dielectric constant is the ratio between the permittivity of the medium and the permittivity of free space.

Let us take a parallel plate capacitor. Suppose the separation distance between the plates is d . Use air or vacuum as a medium for this experiment.

Suppose $+Q$ is the charge on one plate and $-Q$ is charge on the second plate. Bring a rectangular slab made up of conducting material



between the plates of the capacitor. The thickness of the slab must be less than the distance between the plates of the capacitor. When the electric field will be applied then polarization of molecules will be started. The polarization will take place in the direction same as that of electric field. Consider a vector that must be polarized, name it as P . The polarization vector must be in the direction of electric field E_o . Then this vector will start its functioning and will produce an electric field E_p in the opposite direction to that of E_o . The net electric field in the circuit is shown by the figure.

$$\epsilon_r = \epsilon / \epsilon_0$$

$$E = E_o - E_p$$

Dielectric constant, property of an electrical insulating material (a dielectric) equal to the ratio of the capacitance of a capacitor filled with the given material(c) to the capacitance of an identical capacitor (c_0) (in a vacuum without the dielectric material).

$$\epsilon_r = c / c_0$$

(v) **Dielectric polarization (p):** Dielectric polarization or Electric polarization is the induced dipole moment (μ) per unit volume (v) of the dielectric in the presence of an electric field.

Electric polarization, slight relative shift of positive and negative electric charge in opposite directions within an insulator, or dielectric, induced by an external electrical field.

$$P = \mu / v$$

Units: c-m⁻²

If " μ " is the average dipole moment per molecule and " N " is the number of

molecules per unit volume then

$$P = N \mu$$

(vi) Dielectric polarisability (α): Di-electric polarisability is the net dipole moment induced per unit applied electric field.

$$P = N \mu = N \alpha E$$

Units: F-m^2

(vii) Electric susceptibility (χ): It measures the the amount of polarization in a given electric field produced in a dielectric. Polarization proportional to the product of ' ϵ_0 ' and applied electric field

$$X = p / \epsilon_0 E$$

(viii) Electric flux density or Electric displacement (D): It is defined as the total number of electric lines of force passing through the dielectric material is known as electric flux density (D).

Mathematically it is represented by the following equation

$$\begin{aligned} D &= \epsilon_0 E + p \\ \epsilon E &= \epsilon_0 E + p \\ \epsilon &= \epsilon_0 \epsilon_r \\ \epsilon_0 \epsilon_r E &= \epsilon_0 E + p \\ p &= \epsilon_0 E (\epsilon_r - 1) \end{aligned}$$

Types of polarization mechanisms in dielectrics:

There are four types of polarization processes in dielectric.

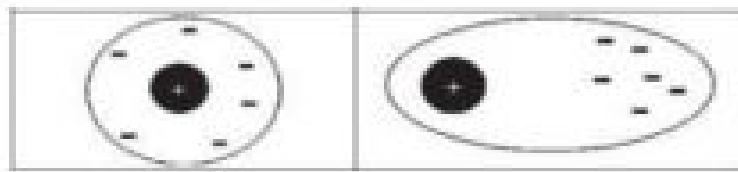
1. Electronic –polarization(p_e)
2. Ionic – polarization(p_i)
3. Orientation-polarization or di-polar polarization(p_o)
4. Space-charge polarization(p_s)

1. Electronic –polarization(p_e) or Atomic Polarization:

It is defined as polarization of rare-gas atoms in presence of an static electric field or polarization due to displacement of an electron-cloud from positive charge of nucleus in an atom in the presence of an electric field in a dielectric material is known as electronic-polarization(p_e). This involves the separation of the centre of the electron cloud around an atom with respect to the centre of its nucleus under the application of electric field

2. Ionic – polarization(p_i):

The polarization that occurs due to relative displacement of ions of the molecules in the presence of an external electrical field. This happens in solids with ionic bonding which automatically have dipoles but which get cancelled due to symmetry of the crystals. Here, external field leads to small displacement of ions from their equilibrium positions and hence inducing a net dipole moment. **Ex:** Nacl molecule

Expression for Electronic polarization of a dielectric material:

Dielectric Polarization in Nonpolar Molecules. The electric field causes the shifting of charges

The displacement of the positively charged nucleus and the (negative) electron of an atom in opposite directions, on application of an electric field, result in electronic polarization.

On application of external electric field E , the electron cloud around the nucleus readily shifts towards the positive end of the field. Because of this, dipole moment is created, within each atom due to the separation of positive and negative charges. This separation or shift is proportional to field strength (E).

∴ Dipole moment is the product of charge and the separation between the charges.

∴ Induced dipole moment $\mu \propto E$

$$\mu = \alpha_e E$$

α_e is constant of proportionality or electronic polarizability and it is independent of temperature.

Calculation of Electronic polarizability:

By taking classical model of an atom, the nucleus of charge Ze is surrounded by an electron cloud of charge $-Ze$ distributed in a sphere of radius R .

Then the charge density (Z – atomic number) is given by

$$\rho = \frac{-Ze}{\frac{4}{3}\pi R^3} = -\frac{3}{4}\left(\frac{Ze}{\pi R^3}\right) \rightarrow (1)$$

When an external electric field E is applied, the nucleus and electrons experience Lorentz forces of magnitude ZeE in opposite direction. Because of this, the nucleus and electron cloud are pulled apart. If separation is there in between nucleus and electron cloud, a coulomb force develops which is attractive.

When Lorentz and Coulomb force are equal and opposite, equilibrium is reached.

Let 'x' be the displacement under this condition. Here, nucleus is much heavier than the electron cloud; it is assumed that only the electron cloud is displaced when the external field is applied.

$$\text{Lorentz force} = -ZeE$$

$$\text{Coulomb force} = Ze \times \frac{\text{charge enclosed in the sphere of radius } x}{4\pi\epsilon_0 x^2}$$

$$\text{The charge enclosed} = \frac{4}{3}\pi x^3 \rho$$

$$= \frac{4}{3} \pi x^3 \left(\frac{-Ze}{\frac{4}{3} \pi R^3} \right) = \frac{4}{3} \pi x^3 \left(\frac{-3}{4} \right) \frac{Ze}{\pi R^3} = \frac{-Zex^3}{R^3}$$

$$\text{Coulomb force} = Ze \times \left(\frac{-Zex^3}{R^3} \right) \times \frac{1}{4\pi\epsilon_0 x^2} = \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3}$$

$$\text{In the equilibrium position, } -ZeE = \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3}$$

$$\text{or } x = \frac{4\pi\epsilon_0 R^3 E}{Ze}$$

Thus, displacement of electron cloud is proportional to applied field

$$x \propto E$$

∴ The electric charges $+Ze$ and $-Ze$ are separated by a distance x under the influence of E constituting induced dipoles (moment).

Induced electric dipole moment,

$$\begin{aligned} \mu_e &= Zex \\ &= Ze \cdot \frac{4\pi\epsilon_0 R^3 E}{Ze} \\ &= 4\pi\epsilon_0 R^3 E \end{aligned}$$

$$\text{i.e. } \mu_e = \alpha_e E$$

where $\alpha_e = 4\pi\epsilon_0 R^3$ is called electronic polarizability

It is the dipole moment per unit volume & is independent of temperature.

$$\begin{aligned} P_e &= N\mu_e \\ &= N\alpha_e E \quad (\text{where, } N \text{ is the no. of atom/m}^3) \end{aligned}$$

$$P_e = \epsilon_0 E (\epsilon_r - 1) = N\alpha_e$$

$$\epsilon_r - 1 = \frac{N\alpha_e}{\epsilon_0}$$

$$\text{Hence, } \alpha_e = \frac{\epsilon_0 (\epsilon_r - 1)}{N}$$

Expression for Ionic polarization of a molecule:

The ionic polarization is due to the displacement of cation and anions in opposite direction and occurs in an ionic solid.

Consider an electric field is applied in the positive x direction then the positive ions move to the right by x_1 and the negative ions move to left by x_2 . If we assume, each unit cell has one cation and one anion.

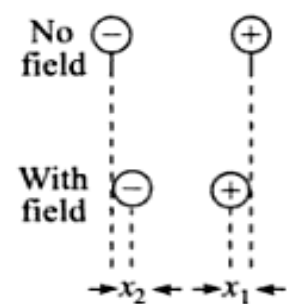
The resultant dipole moment per unit cell due to ionic displacement is

$$\mu = e(x_1 + x_2)$$

If β_1 and β_2 are restoring force constants of cation and anion, Newton is the force due to applied field. Then

$$F = \beta_1 x_1 = \beta_2 x_2$$

$$\text{Hence, } x_1 = \frac{F}{\beta_1}$$



Restoring force constants depends upon the mass of the ion and angular frequency of the molecule in which the ions are present.

$$x_1 = \frac{eE}{m\omega_0^2} \text{ \& } x_2 = \frac{eE}{M\omega_0^2}$$

where m - mass of the positive ion & M-mass of the negative ion

$$x_1 + x_2 = \frac{eE}{\omega_0^2} \left(\frac{1}{M} + \frac{1}{m} \right)$$

$$\mu = e(x_1 + x_2) = \frac{e^2}{\omega_0^2} \left(\frac{1}{M} + \frac{1}{m} \right)$$

$$\boxed{\alpha_i = \frac{\mu}{E} = \frac{e^2}{\omega_0^2} \left(\frac{1}{M} + \frac{1}{m} \right)}$$

The polarizability α_i is inversely proportional to the square of natural frequency of the ionic molecule and to its reduced mass which is equal to

$$\left(\frac{1}{m} + \frac{1}{M} \right)^{-1}$$

Internal fields in solids [Lorentz Method]:

Now a dielectric material is placed between the two parallel plate capacitor and there be an imaginary spherical cavity around the atom 'A' inside the dielectric. By taking that the radius of the cavity is large compared to the radius of the atom. Now, the internal field at the atom site 'A' can be considered to be made up of four components namely E_1 , E_2 , E_3 and E_4

Field E_1 : - E_1 is the field intensity at A due to the charge density on the plates

From the field theory.

$$E_1 = \frac{D}{\epsilon_0}$$

$$D = P + \epsilon_0 E$$

$$\therefore E_1 = \frac{P + \epsilon_0 E}{\epsilon_0}$$

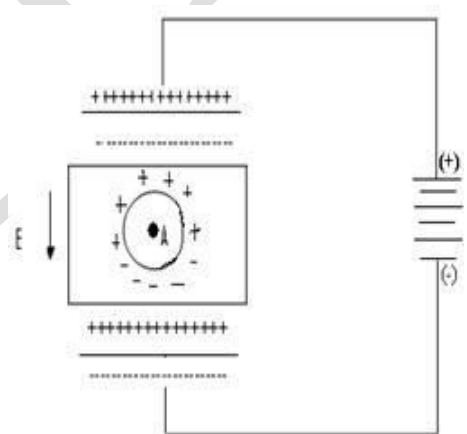
$$\boxed{\therefore E_1 = E + \frac{P}{\epsilon_0}} \rightarrow (1)$$

Field E_2 : -

E_2 is the field intensity at A due to charge density induced on the two sides of the dielectric

Therefore

$$E_2 = \frac{-P}{\epsilon_0} \rightarrow (2)$$



Field E_3 :-

E_3 is the field intensity at A due to other atoms contained in the cavity. If we assume a cubic structure then $E_3=0$ because of symmetry.

Field E_4 :

E_4 is the field density due to polarization charges on the surface of the cavity and it is calculated by Lorentz. The enlarged view of the cavity is shown.

If dA is the surface area of the sphere of radius r lying between θ and $\theta+d\theta$ (where θ is the direction with reference to the direction of the applied force)

Then $dA = 2\pi(PQ)(QR)$

$$\sin\theta = \frac{PQ}{r} \Rightarrow PQ = r\sin\theta$$

$$\text{and } d\theta = \frac{QR}{r} \Rightarrow QR = rd\theta$$

Hence,

$$dA = 2\pi(r\sin\theta)(rd\theta)$$

$$dA = 2\pi r^2 \sin\theta d\theta$$

The charge dq on the surface dA is equal to the normal component of the polarization multiplied by the surface area. $\therefore dq = p\cos\theta dA =$

$$P(2\pi r^2 \sin\theta \cos\theta d\theta)$$

Field due to this charge at the centre 'A' is denoted by dE_4 and is obtained by imagining a unit charge at point 'A'

$$dE_4 = \frac{dq \times l \times \cos\theta}{4\pi\epsilon_0 r^2}$$

$$= \frac{P(2\pi r^2 \sin\theta \cos\theta d\theta) \cos\theta}{4\pi\epsilon_0 r^2}$$

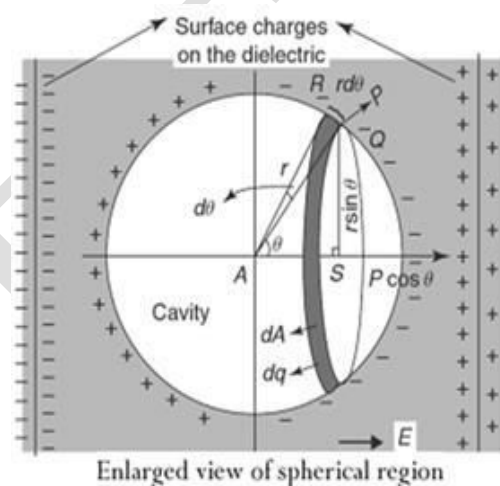
$$dE_4 = \frac{P}{2\epsilon_0} \cos^2\theta \sin\theta d\theta \rightarrow (3)$$

Thus, the total field E_4 due to the charges on the surface of the entire cavity is obtained by integrating

$$\therefore \int dE_4 = \frac{P}{2\epsilon_0} \int_0^\pi \cos^2\theta \sin\theta d\theta$$

$$= \frac{P}{2\epsilon_0} \int_0^\pi \cos^2\theta d(-\cos\theta)$$

$$= -\frac{P}{2\epsilon_0} \left(\frac{\cos^3\theta}{3} \right)_0^\pi = -\frac{P}{6\epsilon_0} (-1 - 1) = \frac{P}{3\epsilon_0}$$



i.e.

$$E_i = E + \frac{P}{3\epsilon_0} \rightarrow (4)$$

where E_i is the internal field (or) Lorentz field.

Clausius – Mosotti relation: -

The relation between the dielectric constant and the polarizability of a polarized dielectric is known as Clausius – Mosotti equation. Consider the dielectric having cubic structure, here there are no ions and permanent dipoles in these materials, the ionic polarizability α_i and orientational polarizability α_0 are zero.

i.e. $\alpha_i = \alpha_0 = 0$

$$\begin{aligned} \text{Polarization } P &= N\alpha_e E_i \\ &= N\alpha_e \left(E + \frac{P}{3\epsilon_0} \right) \\ P \left(1 - \frac{N\alpha_e}{3\epsilon_0} \right) &= N\alpha_e E \quad (\text{or}) \quad P = \frac{N\alpha_e E}{\left(1 - \frac{N\alpha_e}{3\epsilon_0} \right)} \rightarrow (1) \end{aligned}$$

$$\begin{aligned} \text{We have, } D &= P + \epsilon_0 E \\ P &= D - \epsilon_0 E \\ \frac{P}{E} &= \frac{D}{E} - \epsilon_0 \\ &= \epsilon - \epsilon_0 \\ &= \epsilon_0 \epsilon_r - \epsilon_0 \\ \therefore \boxed{P} &= E\epsilon_0(\epsilon_r - 1) \rightarrow (2) \end{aligned}$$

Using (1) and (2):

$$P = E\epsilon_0(\epsilon_r - 1) = \frac{N\alpha_e E}{\left(1 - \frac{N\alpha_e}{3\epsilon_0} \right)}$$

$$1 - \frac{N\alpha_e}{3\epsilon_0} = \frac{N\alpha_e}{\epsilon_0(\epsilon_r - 1)}$$

$$1 = \frac{N\alpha_e}{3\epsilon_0} \left(1 + \frac{3}{\epsilon_r - 1} \right)$$

$$\Rightarrow \frac{N\alpha_e}{3\epsilon_0} = \frac{1}{\left(1 + \frac{3}{\epsilon_r - 1} \right)}$$

$$= \frac{\epsilon_r - 1}{\epsilon_r + 2}$$

N is the no. of atoms by knowing ϵ_r , we can determine α_e

Piezoelectricity:

The material which is polarized when subjected to mechanical deformation is called piezoelectric material. Piezoelectric materials are very important since they permit the conversion of the mechanical energy into electrical energy and the process is reversible.

Example: Quartz, Barium Titanate [BaTiO_3] etc.

In Greek, Piezo (the term) means 'pressure' and it refers to the creation of opposite kinds of charges at one pair of opposite faces of the piezo electric crystal when it is subjected to mechanical compression. It is to develop the electrical energy through dielectric by the application of mechanical force.

Inverse piezoelectricity:

When a d.c. power supply is connected across the electrical axis of the quartz crystal then mechanical strain in the form of either expansion or contraction will be produced. This phenomenon is known as Inverse – piezo electricity.

Instead, when A.c. electric field is applied across the electrical axis, then mechanical vibration will be produced in the form of positive half cycle of a.c. field contraction takes place and for the negative half cycle expansion takes place.

Piezoelectric materials and their applications:

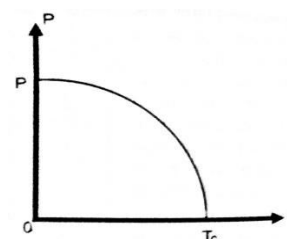
- Quartz crystal is very widely used for filter, resonator. And this crystal responds to pressure variations ,so, it is used as pressure transducers
- Rochelle salt is used as transducer in gramophone pick-ups, ear phones, hearing aids, microphones etc.
- Piezo electric semiconductors such as GaS, ZnO and CdS are finding applications as amplifiers of ultrasonic waves.
- The natural frequency of quartz crystal does not vary with temperature, using this property, this crystal is used to produce highly stable RF oscillations for broadcasting purposes and in quartz watches to maintain accurate time.

Ferro electricity:

The dielectric materials which are having spontaneous polarization in the absence of electric field are called ferroelectric materials. And the phenomenon of possessing spontaneous polarization in the absence of electric field is called ferroelectricity.

Properties:

1. All ferroelectric material possess spontaneous polarization below a certain temperature.
2. As temperature increases the spontaneous polarization decreases and at a particular temperature, the spontaneous polarization vanishes. This temperature is known as Curie temperature.



- Curie temperature can also be defined as the temperature at which ferroelectric material converts into para electric material.
- Below curie temperature the dielectric constant depends on field strength. i.e., it is no longer constant.
- Above curie temperature dielectric constant varies with temperature according to curie – wises law,
i.e.,

$$\epsilon_r = \frac{C}{T - T_c}$$

(Provided $T > T_c$)

- All ferroelectric materials exhibit the property of piezo electricity and pyro electricity.
- The most important property of ferroelectrics is hysteresis under the action of an alternating voltage.

Ex: - BaTiO_3 , Lithium Niobate, Lithium Tantalate, etc.

HYSTERESIS:

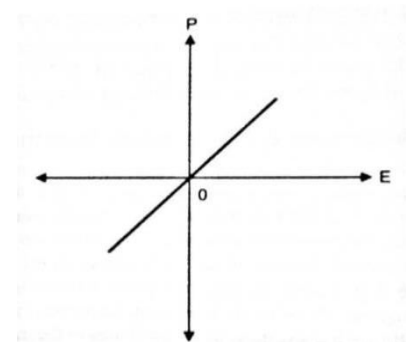
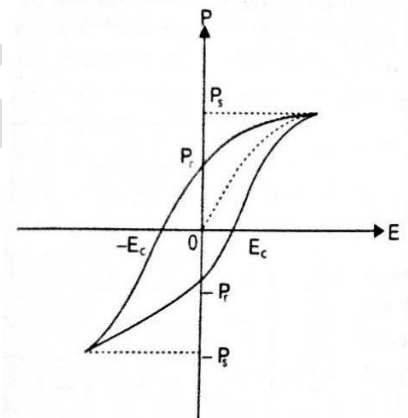
When an electric field is applied on the ferroelectric specimen, the polarization increases non - linearly and reaches saturation at a certain value of P_s . The polarization will not change even if E is increased further. When the field is reduced to zero, then the value of polarization does not return to zero a certain amount of polarization called remanent polarization P_r , is still present in the material.

To remove this polarization, a electric field E_c known as coercive field must be applied in the opposite direction.

- The shape of the hysteresis loop changes with temperature.
- The height and width of the hysteresis decreases with increase of temperature.
- At certain temperature, the loop merges into a straight line. This temperature is known as ferroelectric curie temperature and the ferroelectric behavior of the material disappears.
- The hysteresis loop area represents the dielectric loss that occurs in dielectric materials.

The spontaneous polarization of the ferroelectric material depends upon

- Shape of the hysteresis loop.
- Dimensions of the specimen and temperature.
- The thermal and electrical properties of the crystal.



Applications of Dielectric materials:

1. Almost any type of electrical equipment employs dielectric materials in some form or another.
2. Wires and cables that carry electrical current, for example, are always coated or wrapped with some type of insulating (dielectric) material.
3. Quartz crystal is used for the preparation of ultrasonic transducers, crystal oscillators, delay lines, filters, etc...
4. Barium Titanate is used for preparation of accelerometer.
5. Lead Zirconate titanate is used to preparation of earphones, microphones, spark generators.
6. The Insulating dielectric liquids are used in transformers, switch gears and generators. It's also used in radiation detectors, Thermo ionic valves, strain gauges, capacitors, resistors and many other Electric devices.
7. The electro optic devices are prepared using dielectric materials.

UNIT IV

MAGNETIC PROPERTIES

Introduction:

Magnetism has its own application in the field of physics. Magnetic properties have been the subject of special interest because of the information they yield about the constitution of matter. Magnetics have wide range of application in electrical machinery and in magnetic tapes in computers. Magnetic materials are classified into three, namely diamagnetic, paramagnetic and ferromagnetic materials.

Magnetic field: The 3D region around a magnet in which it's magnetic force is felt is called magnetic field of that magnet. It is a scalar quantity.

Magnetic dipole: It's a system consisting of two equal and opposite magnetic poles separated by a small distance of $2lm$

Or

Two poles of equal strength separated by a very small distance is called a magnetic dipole.

Pole strength (m): The ability of a pole of magnet to attract or repel another magnetic pole is called it's pole strength.

Magnetic dipole moment (μ): It can define in three ways depending on situation.

1. In case of bar magnet it is defined as the product of pole strength and distance between them.

$$\mu = 2lm$$

2. In case of current carrying conductor, it is the product of current (i) and cross section area (A) of the conductor.

$$\mu = iA$$

3. In case of atom, it is the product of current (i) developed by orbital motion of electron and the area covered by the orbital.

$$\mu = iA$$

It is a vector quantity. Its direction is from south pole to the north pole.
Its SI unit is ampere/m².

Magnetic flux(Φ): The total number of magnetic lines of force passing normal to a surface in a magnetic field is called magnetic flux.

Or

The number of magnetic lines of force passing through a point is called magnetic flux.
Its SI unit is weber or tesla – m²

Magnetic field induction or magnetic flux density (B): The magnetic flux passing through a unit normal area of substance is defined as magnetic flux density and is denoted by B. It is

commonly known as magnetic induction. Let Φ be the flux passing through a substance of area A, then flux density is

$$B = \frac{\Phi}{A} = \frac{F}{m} \text{ or } \Phi = \mathbf{B} \cdot \mathbf{A} = BA \cos \theta.$$

It is a vector quantity.

Its SI unit is weber/m² or tesla and CGS unit is Gauss(= maxwell/cm²).

1Tesla= 10⁴Gauss.

Magnetising field(force) or Magnetic intensity(H): The force acting on a unit north pole placed at the point. It is independent of the medium.

$$B = \mu H$$

It is vector quantity. Its SI unit is ampere/m.

Permeability: It's ability to allow the magnetic lines of force to pass through it *or* to allow itself to be influenced by magnetic field (μ).

Relative magnetic permeability(μ_r): The ratio of its absolute magnetic permeability(μ) of the material to the magnetic permeability of free space (μ_0).

$$\mu_r = \frac{\mu}{\mu_0}$$

It is purely a number, it has no units.

The permeability of free space or vacuum is $\mu_0 = 4\pi \times 10^{-7}$ H/m.

Magnetization: The ability of a material to get magnetized when placed in an external magnetic field is called magnetization.

It is measured by a quantity called intensity of magnetization(I).

The net magnetic dipole moment acquired by a substance per unit volume is defined as intensity of magnetization (I).

$$I = \frac{\text{net magnetic dipole moment of material}}{\text{Volume of the material}} \text{ A/m}$$

It is vector quantity. Its SI unit is A/m .

Relation between B,H and I: _

The flux density B in a material due a to magnetizing force H, as the sum of the flux density B_0 in vacuum produced by magnetizing force and flux density B_m due to magnetization of material.

Therefore

$$B = B_0 + B_m$$

Also we know that $B_0 = \mu_0 H$ and $B_m = \mu_0 I$

Therefore, $B = \mu_0 H + \mu_0 I$

$$B = \mu_0(H + I)$$

It is the relation in SI unit

Magnetic Susceptibility(χ): The ratio of magnetization to the magnetic intensity.

$$\chi = \frac{I}{H}$$

It has no units when a material has high susceptibility then it can be easily magnetized.

Relation between Permeability and Susceptibility:

We know that $B \propto (H+I)$

$$B = \mu_0 (H+I)$$

In vacuum $B = \mu_0 H + \mu_0 I$

$$\frac{B}{H} = \mu_0 + \mu_0 \frac{I}{H}$$

Also,

$$\frac{B}{H} = \mu$$

(permeability of the material) and

$$\chi = \frac{I}{H} \quad (\text{Susceptibility})$$

$$\therefore \mu = \mu_0 + \mu_0 \chi \quad \text{or} \quad \mu = \mu_0 (1 + \chi)$$

$$\frac{\mu}{\mu_0} = (1 + \chi)$$

$$\mu_r = (1 + \chi)$$

$$\mu_r - 1 = \chi$$

$$\boxed{\mu_r = \chi + 1}$$

Origin of magnetic moment:

Materials are made up of atoms. These atoms consist of positively charged nucleus, surrounded by cloud of electrons. In all atoms electrons are revolving around the nucleus in different orbits and also spin about their own axis. These revolving electrons constitute an electrical current in the orbits. These revolving electrons produces its own orbital magnetic dipole moment, measured in Bohr magneton (μ_B) and there is also a spin magnetic moment associated with it (spin of orbital electrons and spin of nucleus). In most materials there is no resultant magnetic moments, due to the electrons being grouped in pairs causing the magnetic moment to be cancelled by its neighbour. Under external applied

magnetic field these dipoles experience torque in the direction of applied field and the atom acquires certain magnetism. So, the magnetic moment of an atom is due to

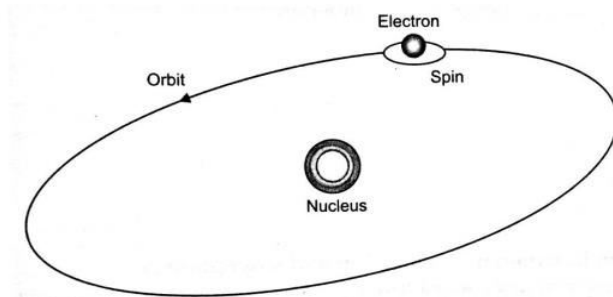
1. Orbital magnetic moment of the electrons.
2. Spin magnetic moment of the electrons.
3. Spin magnetic moment of the nucleus.

The orbital magnetic moment of the electrons(Bohr Magneton):

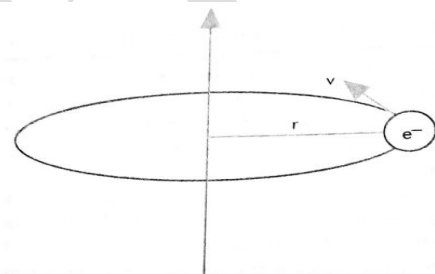
The magnetic moment contributed by a single electron is known as Bohr Magneton. Mathematically it can express as

$$\mu_B = \frac{e\hbar}{2m}$$

Proof:



The orbit of a spinning electron about the nucleus of an atom



Motion of electron in a orbital

Let us consider an electron revolving in a circular orbit of radius r with a speed v . Consider a point p on the circle. The electron crosses this point once in every revolution. In one revolution the electron travels $2\pi r$ distance.

The current i due to the electron motion in the circular loop (orbit) is

$$i = \frac{\text{charge of electron}(q)}{\text{time}(T)} = \frac{-e}{T}$$

Where, T is time for one revolution of electron about the nucleus.

$$T = \frac{\text{distance travelled by an electron}}{\text{speed of an electron}} = \frac{2\pi r}{v}$$

$$i = \frac{-e}{\left[\frac{2\pi r}{v}\right]} = \frac{-ev}{2\pi r}$$

The magnetic moment μ_l associated with the orbit due to orbital motion of electron is

$$\mu_l = iA$$

Where, ' i ' is current produced by the orbital motion of the electron and A is area covered by the orbital(πr^2).

$$\mu_l = \frac{-ev}{2\pi r} \times \pi r^2$$

Dividing and multiplying above eq. by the mass of the electron

$$\mu_l = \frac{-evr}{2} \times \frac{m}{m} = \left(\frac{-e}{2m}\right) [mvr]$$

$$= \left(\frac{-e}{2m} \right) [L]$$

w.k.t the angular momentum of an electron revolving in circular orbit is equal to integral multiple of

$$\frac{h}{2\pi}$$

$$L = mvr = \frac{lh}{2\pi}$$

$$\mu_l = \left(\frac{-eh}{4\pi m} \right) l$$

$$\mu_l = \mu_B l$$

where $l = 0, 1, 2, \dots$

Where, l = orbital quantum number.

$$\mu_B = \frac{-eh}{4\pi m}$$

Bhor magneton

$$= \frac{1.6 \times 10^{-19} \times 6.626 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31}} = 9.27 \times 10^{-24} \text{ A - m}$$

Here – sign indicates that magnetic moment is anti parallel to the angular momentum L .

Spin magnetic moment of the electrons:

In addition to orbital motion, the electron spins around its own axes. The magnetic moment due to spin of electron is represented as μ_s

$$\mu_s = 2 \frac{e}{2m} \left(\frac{sh}{2\pi} \right)$$

The factor 2 is due to the variation in the moment of inertia.

$$\text{W k t } S = \pm \frac{1}{2}$$

$$\mu_s = 2 \frac{eh}{2m} \left(\frac{1}{2} \right)$$

$$\mu_s = \mu_B$$

Spin magnetic moment of the nucleus:

The nucleus of the atom posses nuclear spin hence magnetic moment is associated with this. The nuclear magnetic moment is expressed in the units of nuclear magneton (μ_n)

$$\mu_n = \frac{eh}{2m_p}$$

$$= 5.05 \times 10^{-29} \text{ A - m}^2$$

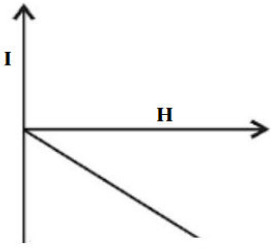
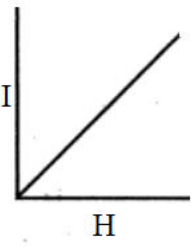
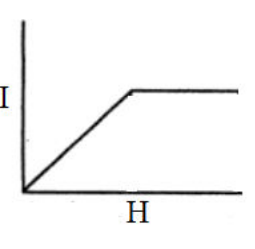
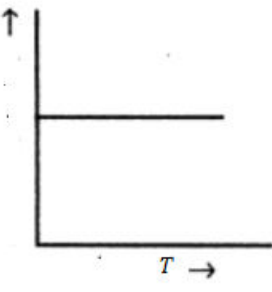
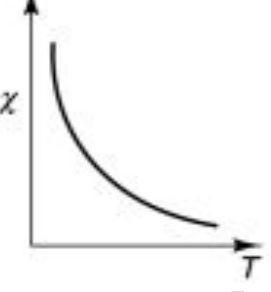
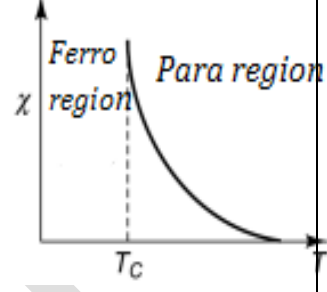
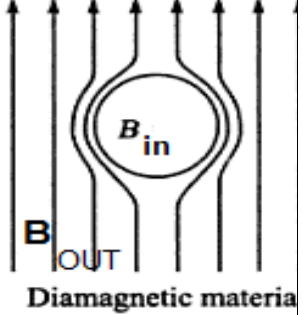
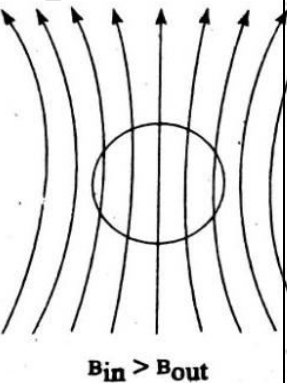
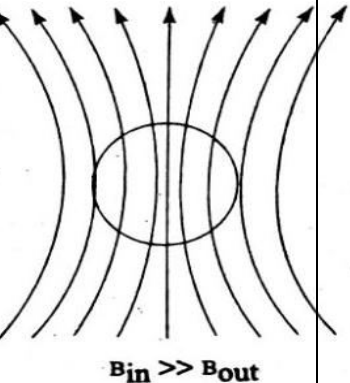
Where, m_p - mass of the proton.

CLASSIFICATION OF MAGNETIC MATERIAL:

Depending on the direction and magnitude of magnetization and also the effect of temperature on magnetic properties, all magnetic materials are classified into dia, para and ferro materials. Depending upon the spin orientation of the electrons, ferro magnetic materials are classified into two types. They are

- a. Antiferro magnetic material.
- b. Ferrimagnetic materials.

PROPERTY	DIA MAGNETIC SUBSTANCES	PARA MAGNETIC SUBSTANCES	FERRO MAGNETIC SUBSTANCES
Defination	The substance in which the resultant magnetic moment of individual atoms is zero.	The substance in which the resultant magnetic moment of individual atoms is not zero.	The substance in which the resultant magnetic moments of individual atoms align themselves in parallel by giving rise to spontaneous magnetization
Cause	Orbital motion of electrons.	Spin motion of electrons.	Formation of domains.
Susceptibility (χ)	Low and negative	Low and positive.	High and positive.
χ depend on T	Does not depend on T . except Bi at low T .	$\chi = \frac{c}{T}$ (curie law) c is curie constant.	$\chi = \frac{c}{T-T_c} : T > T_c$ (curie wise law) T_c is curie temperature.
χ depend on H	Does not depend	Does not depend	Does not depend
Relative permeability (μ_r)	< 1	> 1	$\gg 1$
I	It's direction is opposite to that of H and value is very low.	It's in direction of H and value is high.	It's in direction of H and value is very high.
spin alignment	No spin alignment is present.	All spins or magnetic moments are randomly oriented. 	All spins or magnetic moments are orderly oriented. 

I-H curve.			
$\chi - T$ curve			
Transition of material at T_c	Do not change.	On cooling these are converted into ferromagnetic material.	Converted into para magnetic material above T_c .
Nature of effect.	Distortion effect.	Orientation effect.	Hysteresis effect.
In the presence of magnetic field.	The magnetic lines of force are pulled out from the material. Hence, magnetic flux density is greater, outside the material than inside. 	The magnetic lines of force are attracted towards the centre of the material and hence the B_{in} material is greater than the B_{out}. 	The magnetic lines of force are highly attracted towards the centre of the material and hence the B_{in} material is very greater than the B_{out}. 
Example:	Bi, Zn, H_2O , Gold.....	Al, Pt, Mn, $cucl_2$	Fe, Ni, Co, Mno, Fe_2O_3

Antiferro magnetic materials:

These are the ferromagnetic materials in which the magnetic interaction between any two dipoles aligns themselves anti parallel to each other. All the dipoles are equal in magnitude. Therefore the resultant magnetization is zero.

Properties:

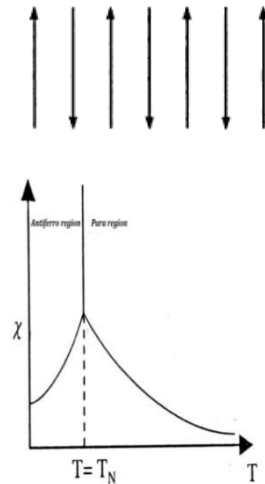
1. Susceptibility is small and positive for these materials.
2. Spin alignment is systematic, but in anti parallel manner.
3. Initially, the susceptibility increases slightly as the temperature increases, and beyond a particular temperature known as Neel temperature the susceptibility decreases with temperature.
4. The temperature at which anti ferromagnetic material converts into paramagnetic material is known as Neel's temperature.
5. Susceptibility is inversely proportional to the temperature. The variation of susceptibility with temperature is expressed as

$$\chi = \frac{C}{T + T_N} \quad \text{When } T > T_N$$

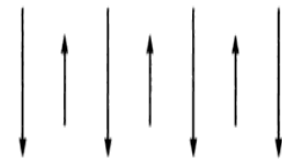
$$\chi \propto T \quad \text{When } T < T_N$$

Where 'c' is the curie constant and the T_N is Neel temperature.

Ex: FeO, MnO, Cr₂O₃

**Ferrimagnetic materials:**

These are the ferromagnetic materials in which the magnetic interaction between any two dipoles align themselves anti parallel to each other. But the magnitudes of any two adjacent dipoles are not equal. Therefore, if we apply a small value of magnetic field, it will produce a large value of magnetization.

**Properties:**

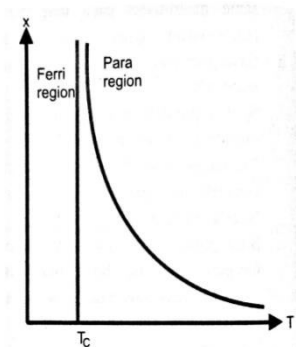
1. Susceptibility is positive and very large for these materials.
2. Spin alignment is systematic, but in anti parallel of different magnitudes.
3. Ferrimagnetic materials possess net magnetic moment.
4. Above curie temperature becomes paramagnetic while below it behaves as ferrimagnetic material.
5. Ferrimagnetic domains become magnetic bubbles to act as memory elements.
6. Susceptibility is inversely proportional to the temperature. The variation of susceptibility with temperature is

$$\chi = \frac{C}{T \pm T_N}$$

for $T > T_N$

Where, C is curie constant and T_N is Neel temperature.

7. Ferrites are the best examples of ferromagnetic materials.
 8. General formula of ferrites are $\text{Me}^{2+}\text{OFe}_2\text{O}_3$ or $\text{Me}^{2+}\text{Fe}_2\text{O}_4$
- Examples: $\text{Zn}^{2+}\text{Fe}_2\text{O}_4$, CuFe_2O_4

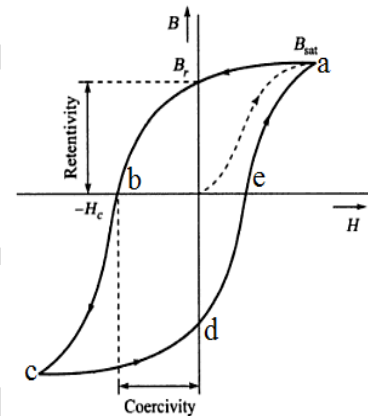


HYSTERESIS CURVE:

It means retardation. [or] Lagging of an effect behind the cause of the effect [or] The phenomenon of B lagging H . [or] It is also defined as a phenomenon of flux density (B) with the change in magnetic field strength (H) in a ferromagnetic material.

Explanation: When the magnetic field H is applied on an unmagnetized ferromagnetic material the magnetic induction increases first rapidly and then slowly from 0 to a . The increase is non linear, after that the rate of induction slows down and attaining a saturation value B_{sat} , with further increase in H , there is no increase in B . If applied magnetic field H on the material is decreased at this stage, naturally B decreases and B will not travel in that initial path, creates a new path.

When H is reduced to zero, B does not vanish, the value of B that remains in the material is called as retentivity B_r or residual magnetisation. To remove retentivity in the material sufficient negative magnetic field $-H_c$ or H_c is applied in opposite direction then the retentivity B_r becomes zero. This is (field) known as coercive field. On increasing H further B reaches saturation in the opposite direction denoted by 'c'. Then reducing H to zero B reaches 'd' and then increasing H in the positive direction B reaches again to B_{sat} and a curve is obtained. This completes a closed loop called hysteresis loop. It includes some area. This area indicates the amount of energy wasted in one cycle of operation.



Domain Theory of Ferromagnetism:

The concept of domains was proposed by Weiss in order to explain the properties of ferromagnetic materials and their hysteresis effects.

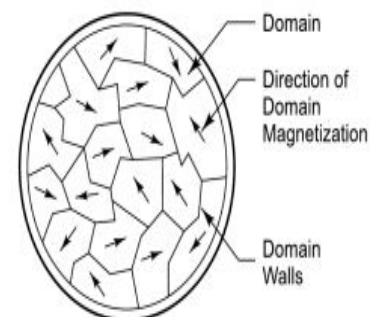
Magnetic Domains: Every ferromagnetic material is made of a very large number of miniature (very small) regions which are known as domains. The boundaries separating the domains are called domain walls, also known as Bloch walls.

In each domain the magnetic dipoles align parallel to each other and produce spontaneous magnetization. The direction of spontaneous magnetization varies from domain to domain.

Process of Domain magnetization:

When the external field is applied there are two possible ways of alignment of random domains.

1. By the motion of domain walls.
2. By rotation of domains.

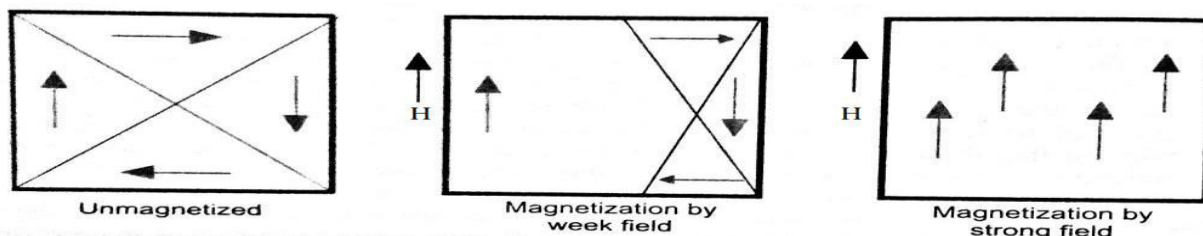


Motion of Domain walls: When a small amount of magnetic field is applied on a ferromagnetic material then the domains of the material whose magnetic moments are parallel or nearly parallel to the direction of applied field can grow in size whereas the domains are not

parallel to field can diminish in size. This change produces large magnetization for the bulk materi

Rotation of Domains:

When the magnetic field is increased further to a large value (i.e., near saturation), further domains growth becomes impossible and hence fully grown domains can rotate into the field direction and specimen is said to be saturated.

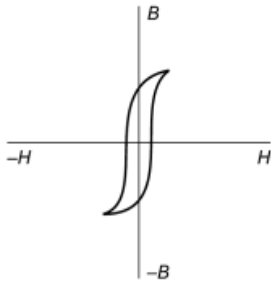
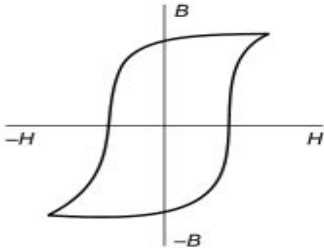


Magnetization of a ferro magnetic material

SOFT AND HARD MAGNETIC MATERIALS:

Ferromagnetic materials are classified into two types based on the characteristic parameters such as hysteresis and magnetisation. They are

1. Hard magnetic materials
2. Soft magnetic materials

S.NO	SOFT MAGNETIC MATERIAL	HARD MAGNETIC MATERIAL
1	Materials which can be easily magnetized and demagnetized are called Soft magnetic materials.	Materials which can't be easily magnetized and demagnetized are called hard magnetic materials.
2	The nature of hysteresis loop is very steep 	The nature of hysteresis loop is very large. 
3	They are prepared by annealing process.	They are prepared by quenching process.
4	Due to small hysteresis loop area, they have small hysteresis loss.	Due to large hysteresis loop area, they have large hysteresis loss.
5	They have large value of permeability and susceptibility.	They have low value of permeability and susceptibility.
6	The coercivity and retentivity are small.	The coercivity and retentivity are large.
7	They are free from irregularities.	They have large amount of impurities and lattice defects.
8	They are used To produce temporary magnets.	They are used To produce permanent magnets.

	• In the preparation of magnetic core materials used in transformers, electric motors, magnetic amplifiers, magnetic switching circuits, etc.,	• In loud speakers, toys, in measuring meters, microphones, magnetic detectors, magnetic separators, etc.,
9	Ex: Iron and silicon alloys, Nickel – Iron alloy, Iron – Cobalt alloy.	Ex: High carbon steel, Cobalt steel, Barium ferrite.

SUPER CONDUCTIVITY

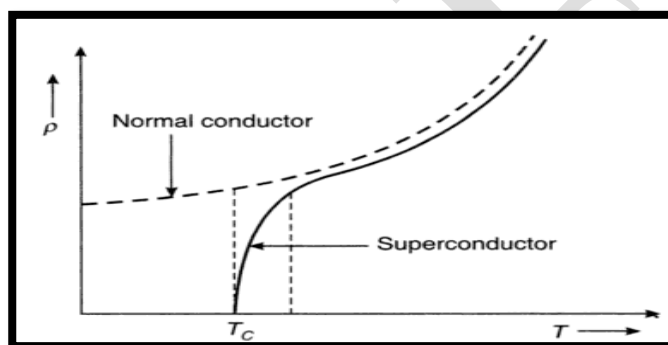
Introduction: Certain metals & alloys exhibit almost zero resistivity (infinite conductivity), when they are cooled sufficiently to low temperature is known as Super conductivity.

Super conductivity has got important applications like energy fields, energy technology, tele communications, computing, super fast transportation, medicine e.t.c

General properties:

The temperature at which the transition from normal stage to the Super conducting stage takes place on cooling in the absence of magnetic field is called critical temperature (T_C) is also known as Transition temperature.

H.K onnes by studying the electrical conductivity of metals he came across this phenomenon. He found that when pure mercury was cooled down below 4^0 K the resistivity suddenly dropped to zero. A similar behavior is observed in case of metal 'tin' the sudden drop in resistivity is graphically shown below.



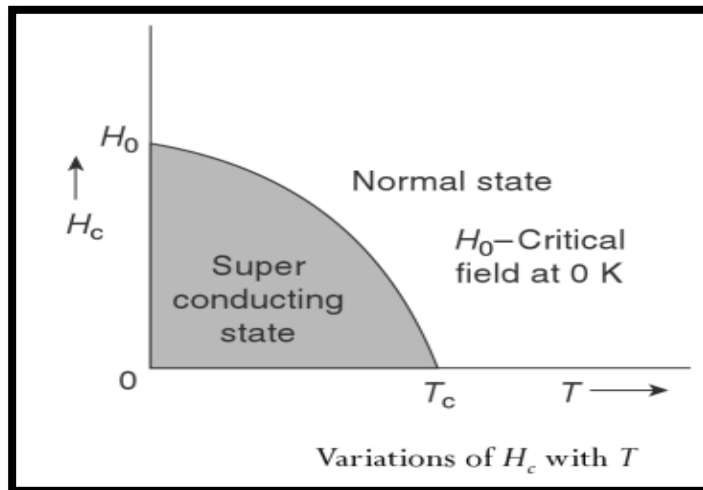
Properties observed:

1. T_C is different for different substances.
2. For chemically pure & structurally perfect Super conducting transition is very sharp.
3. Super conductivity substance in general lies in the inner column of periodic table.
4. Super conductivity is found in metallic substance in which the valence electron no lies in between 2&8.
5. From the periodic table it is observed that (T_C) of the elements & square of atomic no (Z^2) are having direct proportionality relation .
6. Transition metals having odd no of electrons exhibit Super conductivity.
7. Materials having high normal resistance exhibit Super conductivity.
8. Super conductivity is also observed in a substances having in all atomic volume with small atomic mass.
9. Ferro & anti Ferro magnetic substances do not exhibit Super conductivity.
10. In addition to dropping of electrical resistivity to zero the following changes are also observed.
 - a) The magnetic flux lines are rejected from the super conductor is known "MEISSNER EFFECT" .

- b) There is discontinuous change in specific heat.
- c) There are changes in thermal conductivity & volume of the substance.

Effect of magnetic field on super conductors:

Super conductivity disappears if the temperature of the specimen is raised above ' T_C '. In other words super conductivity is destroyed above ' T_C ', same effect is observed if the super conductor is subjected to magnetic field. In other words magnetic field destroys super conductivity. It can be indicated in graph below.



At temp $T = T_C$, $H_C = 0$. As T decreases, H starts increasing up to critical value (H_C), thus, applied magnetic field as the function of ' T ' can be written as

$$H_C(T) = H_C(0) \left[1 - \left(\frac{T}{T_C} \right)^2 \right] \text{-----} \rightarrow (1)$$

$H_C(0)$ ----- $\rightarrow$ Critical magnetic field at 0^0K

$H_C(0)$ & T_C ----- $\rightarrow$ are constants & also the characteristics of substance.

Numerical: A superconducting material has $T_C = 3.7\text{K}$ at zero magnetic field.

$H_C = 0.0306$ at 0K , find H_C at $T = 2\text{K}$ (0.02166T)

$$\text{Soln: } H_C(T) = H_C(0) \left[1 - \left(\frac{T}{T_C} \right)^2 \right]$$

$$H_C(T) = 0.0306 \left(1 - \left(\frac{2}{3.7} \right)^2 \right) = 0.0216591$$

Meissner effect:

When a weak magnetic field is applied to a super conducting specimen at a temperature below T_C , the magnetic flux lines are expelled from the specimen as shown in fig below:

The specimen acts as an ideal dia-magnet this is known as "meissner effect"

It is reversible, that when a temperature of specimen is raised below T_C at $T = T_C$, the flux lines suddenly start penetrating the specimen.

The specimen comes back to normal stage, under these conditions magnetic induction of a specimen $B = \mu_0 (H+I) \rightarrow (2)$

where, $H \rightarrow$ applied magnetic field.

$\mu \rightarrow$ magnetization.

As, $B=0$; $\mu_0 (H+I) = 0 \rightarrow (3)$

$$H = -I;$$

$$\chi = \frac{I}{H} = -1.$$

Hence susceptibility is -1, the substances are diamagnetic.

In case of super conductor resistivity ($\rho = 0$),

But electric field, $\varepsilon = J \rho \rightarrow (4) \Rightarrow \varepsilon = 0$.

Also from $\nabla \times E = \frac{dB}{dt} \rightarrow \frac{dB}{dt} = 0$; so, B should be constant.

This contradicts meissner effect itself.

Hence we can say that, super conducting substance or specimen behave differently from that of normal specimen. Ultimately, in super conducting stage $E=0$, & $B=0$

Effect of current:

To destroy the super conducting property critical magnetic field (H_C) is required. As the current is flowing through the super conductor the specimen can produce its own magnetic field if superconductivity is to be destroyed. In other words if the current in the specimen is increased to critical value I_C . So that H_C is produced, super conductivity disappears.

Hence, I_C can be related as $I_C = 2\pi r H_C \rightarrow (5)$

Mathematically I_C is related to H_C & is clear from following example.

Numerical:

Calculate critical current passing through the wires having diameter 1mm, at temp=4.2K, T_C for lead is 7.18k, value of $H_0 = 6.5 \times 10^4$ A/m.

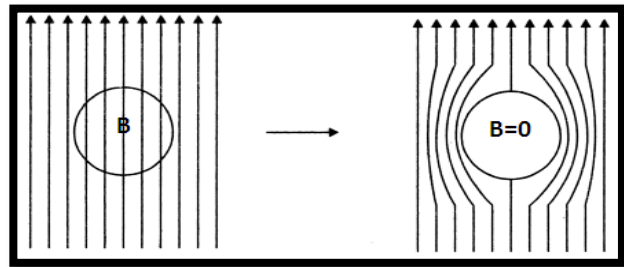
$$\text{Soln: } H_C = H_0 \left[1 - \left(\frac{T}{T_C} \right)^2 \right]$$

$$H_C = 6.5 \times 10^4 \left[1 - \left(\frac{4.2}{7.18} \right)^2 \right] = 42758.55246$$

$$I_C = 2\pi r H_C = 2 \times 3.14 \times 1 \times 42758.55246 = 134.518 \text{ A}$$

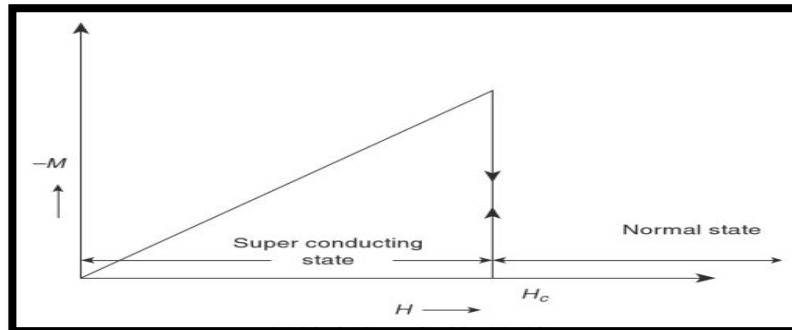
Types of super conductors:

They can be classified as Type-1 & Type-2 depending on the exhibition of meissener effect.

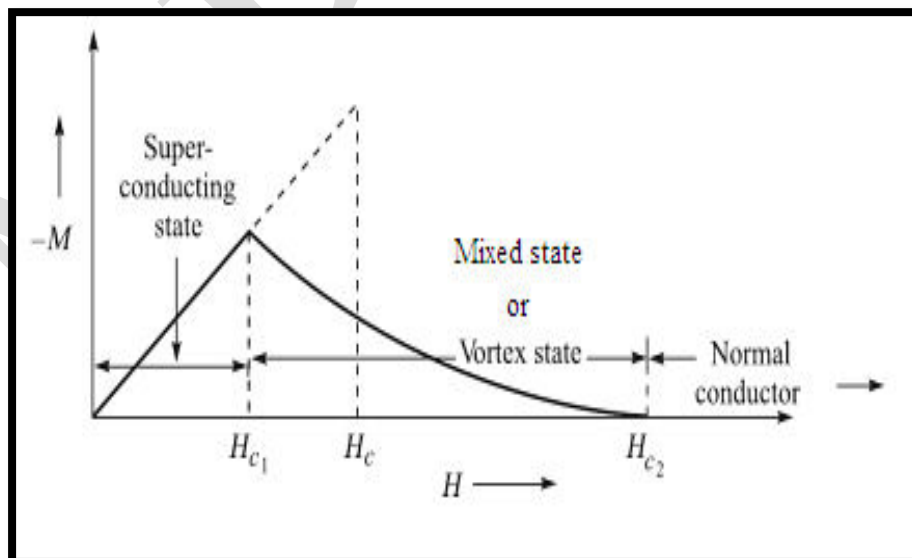


Type-1 Super conductor : They also known as soft super conductors ,when the magnetic field is applied & increased gradually from its initial value $H < H_c$, the diamagnetism disappears abruptly.

Super conducting specimen changes to normal state sharply as shown in fig. Al, zn, Hg are eg, of Type-1 Super conductor.



Type-2 Super conductor: As shown in fig, Type-2 conductors are having two critical fields namely H_{c1} & H_{c2} . Up to the field H_{c1} the specimen is in pure super conducting state rejecting all the magnetic lines. Beyond H_{c1} lower critical field ,magnetic lines starts penetrating the specimen ,up to the second critical field (H_{c2})(upper critical field),the specimen is in mixed state .In other words in this region between (H_{c1}) & (H_{c2}) the meissner effect is in complete .This region is “Vortex-region”. Beyond (H_{c2}) the specimen completely becomes normal from super conducting state. eg : Niobium (Nb) ,Zirconium (Zr) They also known as Hard superconductors, these have large practical applications, since they got very high current density.



UNIT V

NANO-TECHNOLOGY

Introduction:

Nanotechnology is defined as the study and use of structures between 1 nanometer and 100 nanometers in size. Nanotechnology is the engineering of functional systems at the molecular scale. This covers both current work and concepts that are more advanced. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products.

Nanoscience: It deals with the study of properties of materials at nanoscales where properties differ significantly than those at larger scale. The applications of nanoscience emerged as nanotechnology.

Nano science deals with the synthesis, manipulation and the characterization of materials at atomic and molecular level and to study the various properties like electrical, magnetic, optical, mechanical and chemical etc.

Nanoscale:

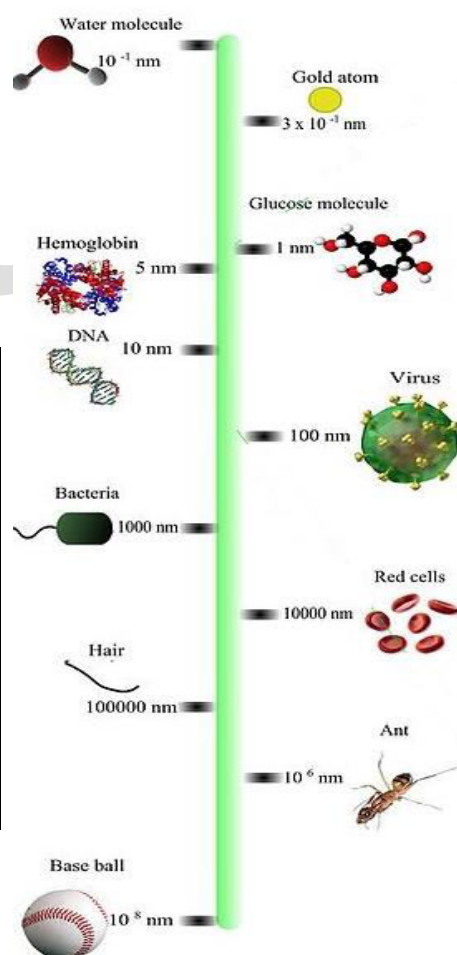
$$1\text{nm} = 10^{-9}\text{m} = 10^{-7}\text{cm}$$

Nano means 10^{-9}m i.e. a billionth part of a meter.

Atoms are extremely small & the diameter of a single atom can vary from 0.1 to 0.5nm depending on the type of the element.

Dimensions of few nanomaterials:

Carbon atom	0.15 in diameter
Water molecule	0.3nm
Red blood cell	7,000nm
Human hair	80,000nm wide
White blood cell	10,000nm
Virus	100nm
Hydrogen atom	0.1nm
Bacteria range	1,000 to 10,000nm
Proteins	5 to 50nm
DNA	2nm Width
Quantum dots	8nm



Nanotechnology: It deals with the design, characterization, production and application of nanostructures, nano-devices and nano-systems.

Nanomaterials:

The materials in which the atoms are arranged in the order of 1 to 100nm in any one of the dimension and these atoms will not move away from each other, called as nano materials. (All materials are composed of grains, which in turn comprise many atoms. The visibility of these grains depends on their size. The materials possessing grains of size ranging from 1 to 100nm, known as nanomaterial's, can be produced with different dimensionalities)

Ex: C, Zn, Cu – Fe alloys, Ni, Pd, Pt etc.

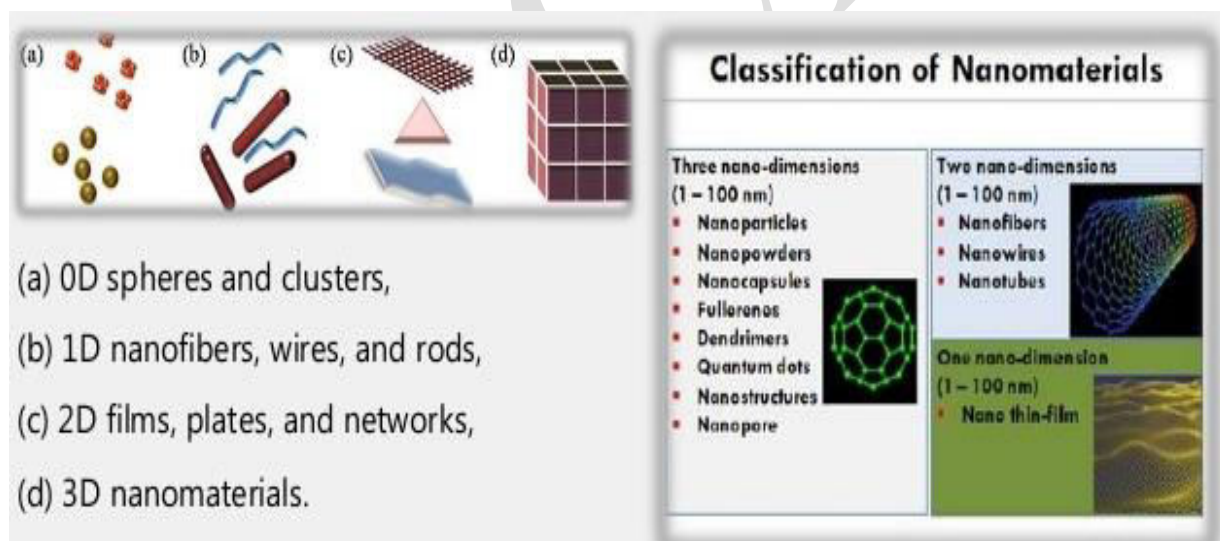
Zero-dimensional nanomaterials: Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials are nanoparticles.

One dimensional nanomaterial: Materials that are nanoscale in one dimension called as one dimensional nano materials (nano layers). Examples: Nano tubes and nano wires.

Two dimensional nanomaterials: Materials having two of its dimension in nano scale is called two dimensional nano materials. Examples: Nano thin films, nano plates

Three dimensional nanomaterials: Materials having three of its dimension in nano scale is called three dimensional nano materials.

Examples: 3D particles of precipitates, Colloids, quantum dots, tiny particles of semiconductor materials.



Basic principles /properties of Nanomaterials:

When the material size of the object is reduced to nanoscale, then it exhibits different properties than the same material in bulk form. The factors that differentiates the nanomaterials from bulk material is

They are

- Increase in surface area to volume ratio
- Quantum confinement

Increase in surface area to volume ratio: Nano materials have a large surface area to volume ratio when compared to bulk material and it is a great measure for efficiency of nanotechnology.

Example: Let us consider a sphere of radius 'r'

$$\text{Its surface area} = 4\pi r^2$$

$$\text{Its volume (atom)} = \frac{4}{3}\pi r^3$$

$$\text{Surface area (S.A.) to volume ratio} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

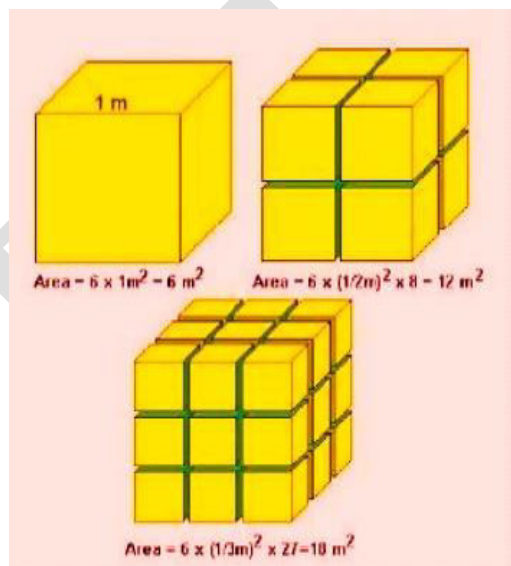
Therefore when the radius of the sphere decreases, its surface area to volume ratio increases.

Example: Let us consider a cubic volume shown in figure.

If a given sample its surface area is 6m^2 . When it is divided into 8 pieces its surface area becomes 12m^2 . When the volume is divided into 27 pieces its surface area becomes 18m^2 .

Thus, when the given volume is divided into smaller pieces, the surface area increases.

Due to increase in surface area, more number of atoms will appear at the surface. This makes nano materials more chemically reactive. Reducing the dimensions of material affects reactivity, optical properties, electrical properties, magnetic properties.



(ii) Quantum Confinement: The properties of materials can be studied based on the energy levels. When atoms are isolated, their energy levels are discrete. When very large no of atoms are closely packed to form a solid, the energy levels split & form bands. Nano materials represent intermediate stage. As a result, the energy levels change.

When we apply the problems of particles in a potential well as well as in a potential box. The dimensions of such wells or boxes are of the order of deBroglie wavelength of electrons, energy levels of electrons change. This effect is called Quantum confinement.

This affects the optical, electrical, magnetic properties of nanomaterials.

When the electrons are confined, the particles will have more oscillations and this will result in colour change of the materials. For examples, nano gold colloids are dispersed in ruby glass, the ruby glass exhibits red hue.

Synthesis (or) Fabrication of nanomaterials:

The production of nano materials or nano crystalline materials requires precise methods. There are various techniques that are capable of creating nano structures. In general there are two approaches that are classified as

- 1) Top-down approach (or) technique

2) Bottom-up approach (or) technique

Top-down approach: Top down techniques involves starting with a block of individual material, etching (removing the surface by dissolution) or convert it down to the desired size. The challenge here is to produce smaller and smaller structures. Nano material particle can be made through this method.

In this method, the nanomaterials are synthesized by assembling or arranging the bulk materials into nanosizes.

Top –down processing has been and will be the dominant process in semiconductor manufacturing.

Examples: (i) Sol-gel method.

(ii) Ball-milling method.

(iii) Lithography.

(iv) Mechanical grinding.

Bottom-up approach: Bottom-up technique involves the assembly of smaller sub unit (atoms or molecules) to make larger structure.

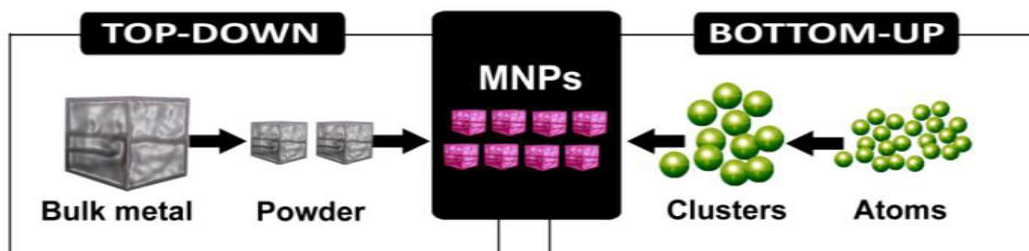
In this method, the nano materials are synthesized by assembling (or) arranging the atoms or molecules together to form the nano materials.

Examples: (i) physical vapour deposition method

(ii) Chemical vapour deposition method

(iii) Plasma arcing and

(iv) Electro deposition



Sol-Gel Method:

The sol-gel method is a wet chemical method or chemical solution deposition method. This technique is used to generate nanoparticles & nanopowders.

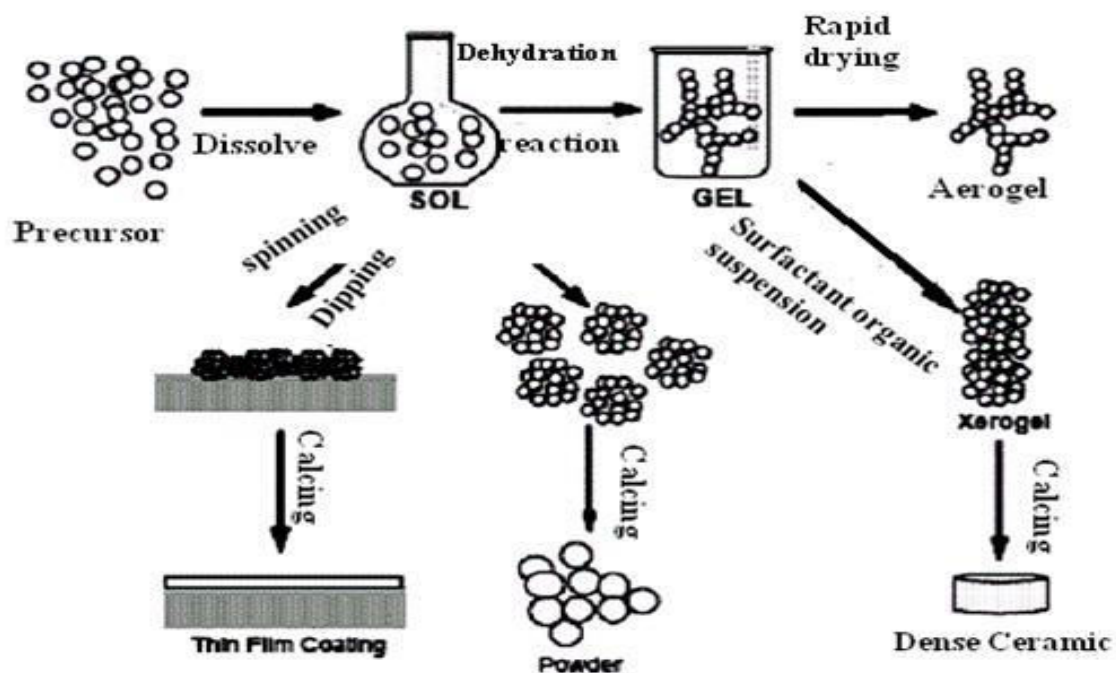
A given material converted into colloids & dissolved in water or in acids, then forms a solution (Sol). A colloid suspended in a liquid is called as “Sol”. A suspension that keeps its shape is called Gelatin or “Gel”. The sol-gel formation occurs in different stages. They are

1) Hydrolysis of precursors.

2) Condensation and polymerization of monomers to form particles.

3) Growth of particles and development of particles. (Agglomeration)

The schematic representation of the synthesis of nano particles using the Sol-Gel method is shown in fig.



This method takes place in following steps.

- (i) Take a material & convert it into liquid precursors (inorganic salts or organic species such as metal –alkoxide) & dissolved in water or in other solvents. It forms colloidal suspensions known as “Sol”.
- (ii) This solution is kept at a suitable temperature and some amounts of gelling agents are added to it. This will produce a gel. (By dehydration reaction with Sol forms Gel)
- (iii) Rapid drying of the gel, under super critical conditions an aero-gel.
- (iv) Drying of the “Gel” i.e. water & other liquids are removed from the gel forms a Xerogel. By calcination xerogel forms ceramics.
- (V) The solution further proceed through spinning & finally by calcination forms thin films & nanopowder respectively.

Advantages:

- (i) This method is used to prepare thin films, nanopowder, glasses, glass ceramics etc at very low temperatures.
- (ii) To prepare mono-sized nanoparticles.
- (iii) Very high purity in synthesized materials can be obtained.

Disadvantages:

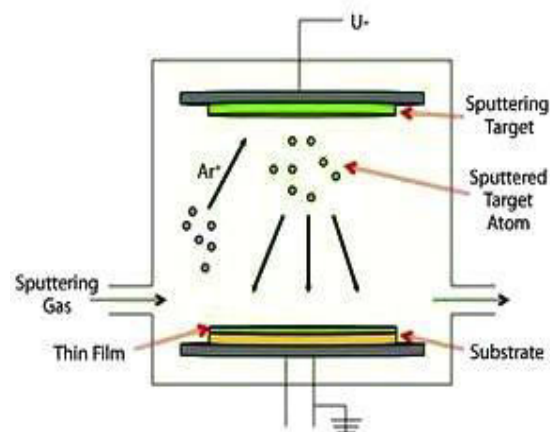
- (i) The raw materials are very costly.
- (ii) The synthesis reaction requires relatively longer time.
- (iii) Organic solvents used are harmful to the environment.

PVD(Physical vapour deposition technique):

Physical Vapour Deposition (PVD) is a collective set of processes used to deposit thin layers of material, typically in the range of few nanometers to several micrometers. PVD processes are environmentally friendly vacuum deposition techniques consisting of three fundamental steps :

- Vaporization of the material from a solid source assisted by high temperature vacuum or gaseous plasma.
- Transportation of the vapor in vacuum or partial vacuum to the substrate surface.
- Condensation onto the substrate to generate thin films.

Different PVD technologies utilize the same three fundamental steps but differ in the methods used to generate and deposit material.



The two most common PVD processes are **thermal evaporation** and **sputtering**.

Thermal evaporation is a deposition technique that relies on vaporization of source material by heating the material using appropriate methods in vacuum.

Sputtering is a plasma-assisted technique that creates a vapor from the source target through bombardment with accelerated gaseous ions (typically Argon).

In both evaporation and sputtering, the resulting vapor phase is subsequently deposited onto the desired substrate through a condensation mechanism to give nanofilms(thin-films).

Applications:

PVD is used in a variety of applications, & used in

- including fabrication of microelectronic devices,
- interconnects, battery and fuel cell electrodes,
- diffusion barriers,
- optical and conductive coatings,
- surface modifications.

Advantages:

- This method consists good strength and durability
- It is environment friendly vapor deposition technique.

Disadvantages:

- Cooling systems are required, to get nanomaterials.
- Mostly high temperature and vacuum control needs skill and experience.

Characterization of Nano-particles:

Characterization refers to the study of material features such as its composition, structure and its properties like physical, electrical, magnetic etc.

For characterization of nano particles both X-ray diffraction (XRD) & electron microscope are the most widely used techniques. They are

1. XRD
2. Electron microscope.

2) Electron microscope: It is an instrument by using we can study & analysis of small particles & crystal structures. It's magnification is high i.e. 10^6 times greater than the size of given particle (or) object. In electron microscopes, current carrying coils produce magnetic fields that act as lenses to focus an electron beam on a specimen.

They are two types of electron microscope

- (1) SEM (Scanning electron microscope)
- (2) TEM (Transmission electron microscope)

SEM (Scanning electron microscope):

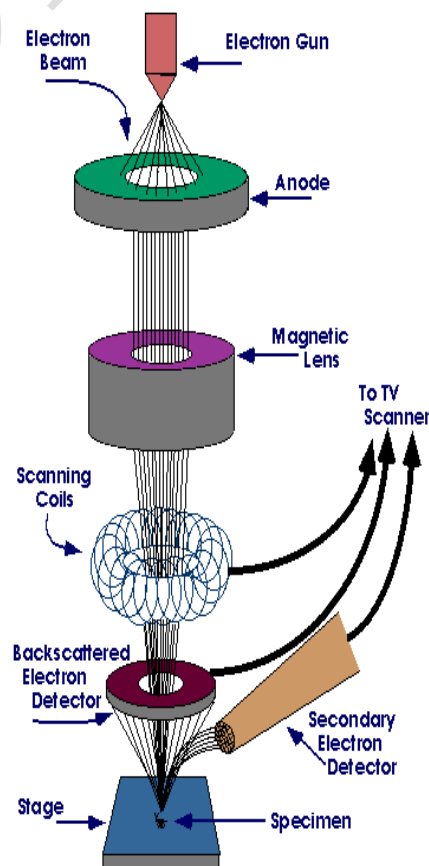
Scanning electron microscope is an electron microscope that images the sample surface by it with a high energy beam of electrons.

Principle: The surface of a sample is scanned using a high energy beam of electrons.

This gives rise to secondary electrons, back scattered electrons, and characteristic X-rays. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. while the SEM Creates magnified images by using electrons instead of Light waves.

SEM consists of

1. Electron gun.
2. Anode.
3. Magnetic lens (consists of two condensed lens)
4. Scanning coils.
5. TV scanner.
6. Detectors.
7. Specimen stage.



Construction and working:

1. The virtual source at the top represents the electron-gun which produces a stream of high energy monochromatic electrons.
2. Electrons are attracted and travel through anode thereby attains directionality.
3. Two magnetic lenses are used as condenser lenses to convert the diverging electron beam into a fine pencil beam and condenser lens eliminated the high angled electrons from the beam so electron –beam becomes thin and coherent.
4. A scanning coil is used to deflect the electron beam to scan the sample.
5. The objective lens is used to focus the scanning beam on a desired spot on the sample.
6. When the high energy electron beam strikes the sample, some electrons scattered due to elastic scattering (due to back scattering) called back scattered electrons, some electrons are knocked off from the surface called secondary electrons and some electrons penetrate deep into the inner shells of the sample atoms to knockoff inner shell electrons due to which X-rays (wavelength matches) are produced.
7. The intensities of secondary electrons, back scattered electrons and X-rays recorded using detectors and the signals are amplified and the images are then displayed on a TV scanner (monitor).
8. This process is repeated several times i.e. 30 times/sec to get accurate results.

Applications:

1. Topography: To study the surface features of an object and its texture.
2. Morphology: To study the shape, size, arrangement of particles.
3. Composition: To study the elements and compound ratio in a sample.
4. Crystallography: Arrangement of atoms, and their order in the crystal.
5. SEM shows very detailed 3D images at much high magnifications as compared to light microscopes.
6. The surface structure of polymer nano composites, fracture surfaces, nano fibres, nano particles and nano coating can be imaged through SEM with great clarity.

TEM (Transmission electron microscope):

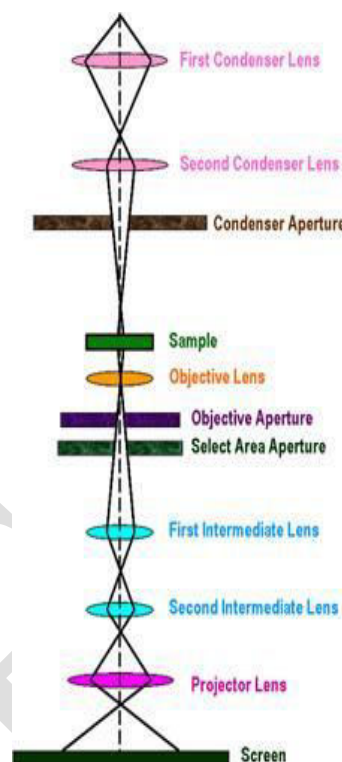
TEM is a powerful tool to investigate the lattice structure and defects on materials directly. The first TEM invented by Ruska in April 1932 could hardly compete with optical microscope with only 14.4 (3.6×4.8) magnification. The basic components in TEM are:

- Electron gun
- Condenser system
- Objective lens (most important lens in TEM which determines the final resolution)
- Diffraction lens
- Projective lens (all lens are inside the equipment column, between apertures)
- Image recording system (used to be negative films, now is CCD cameras)

- Vacuum system

Working:

1. The virtual source at the top represents the electron gun which produces of high energy monochromatic electron beam.
2. The beam strikes the ultra thin specimen(usually thinner than 10 nm) and parts of it are transmitted.
3. The image formed from the interaction of the electrons with the sample is magnified and focused onto an imaging device, such as photographic film, a fluorescent screen, or detected by CCD camera.
4. The darker areas of the image represents those areas of the sample that fewer electrons were transmitted through (they are thicker or denser).
5. The lighter areas of the image represents those areas of the sample that more electrons were transmitted through(they are thinner or less dense).



Applications: TEM gives the following useful information:

1. **Morphology:** The size, shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.
2. **Crystallographic information:** The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects a few nanometers in diameter.
3. **Composition:** To study the elements & compound ratio in a sample.

Applications of Nano materials or Nano technology:

Nano materials are ‘small materials with big future’ because of their extremely small size, they have many applications and advantages.

1. Material technology:

- Nano materials used in cutting tools made up of nano crystalline materials which are much harder, much more wear-resistant and last longer.
- Nano materials used as sensors.
- They are used as smoke detectors, ice-detectors on air craft wings.

2. Information-technology:

- Nanoparticles are used for information storage.
- Nan photonic crystals are used in chemical/l computers.
- Nano thickness –controlled coating are used in optoelectronic devices.
- Nanoscale-fabricated magnetic materials are used in data storage.
- Used in opto electronic devices, mobiles and laptops etc.

3. Electronic industry:

Nano materials used in

- Glass fibres.
- Used to prepare laser diodes.
- Optical switches
- data memory

4. Medical field:

- Nano materials used in drug delivery systems.
- Used as agents in cancer therapy.
- Used as active agents.
- Used to reproduce or repair damaged tissues.