Semester –VI
Elective Paper – VII-(B): Materials Science
UNIT-I
MATERIALS AND CRYSTAL BONDING

Syllabus : Materials, Classification, Crystalline, Amorphous, Glasses;Metals, Alloys, Semiconductors, Polymers, Ceramics, Plastics, Bio-materials, Composites, Bulkand nanomaterials. Different types of chemical bonds – Ionic covalent bond or homopolar bond– Metallic bond – Dispersion bond – Dipole bond – Hydrogen bond – Binding energy of a crystal.

Introduction: Elements and their compounds are found in three states.

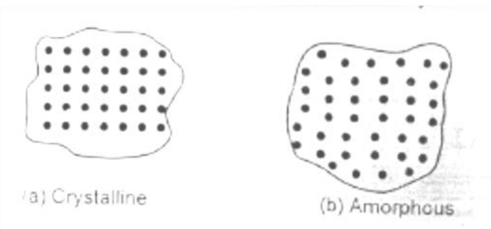
They are 1) Solids 2) Liquids and 3) Gases. We know that some materials are strong, some materials are week and some are good conductors of heat and electricity, some materials are bad conductors of heat and electricity, some materials are magnetic and some are non magnetic and so on.

Solids are divided into two broad categories. They are crystalline solids and amorphous.

Crystalline solids: If the atoms or molecules in a solid are arranged in regular fashion then it is known as crystalline. The atoms are arranged in an orderly three dimensional array that is repeated through the structure.

The metallic crystals are Ag, Cu,Al,Mg etc..

The non metallic crystals are C,Si,Ge etc..



Amorphous solids: When the atoms or molecules in a solid are arranged in an irregular fashion then it is known as amorphous solids.

Ex: Glass, Plastic, Rubber etc..

Distinction between crystalline and amorphous solids:

S.No.	Crystalline solids	Amorphous solids
1	Crystalline solids have a regular arrangement of particles	The amorphous solids have a completely random particle arrangement
2	Crystalline solids have different physical properties in different directions. (Anisotropic)	They have their physical properties same in all directions. (Isotropic)
3	The cooling curve of crystalline substance has breaks	The cooling curve for amorphous substance is smooth
4	All the bonds in crystalline solids are equally strong due to the symmetry	All the bonds in amorphous solids are not equally strong
5	In case of crystalline substance, the melting point is very sharp	The amorphous substance does not have the sharp melting point.

Metallic glasses: We have studied The Crystalline metals in which the atoms are arranged in neat orderly arrays. The bulk of these metals typically consists of small regions of aligned atoms boundaries between them. In case of non-crystalline solids or amorphous solids, the atoms have a lack of symmetric and regular arrangement over relatively large atomic distances. The atomic structure resembles that of a liquid. Therefore, within metallic glass, atoms are packed together in somewhat random fashion, similar to that of liquid. They lack of grain boundaries, which serve as point of weakness.

Metallic glasses are glass or amorphous solid which exhibit metallic properties.

Example: following are few examples of metallic glasses.

i) Alloy of gold and silicon containing 80 atoms% Au and 20 atoms % Si.

A solid may be classified into a number of ways that is on the basis of their mechanical properties, thermal properties, electrical properties, inter atomic bonding etc.The most convenient method is classification of solids in terms of inter atomic bonding.

Classification of materials: Solid materials may be classified into three groups they are

1) **Basic materials:** Metals, ceramics ,polymers
2) **Composites**: Combination of two or more of the basic materials.
3) **Advanced materials**: Semiconductors, biomaterials, smart materials and Nano materials.

Metals: In metals atoms are arranged in an orderly manner. Metallic materials have a large number of free electrons. These electrons are responsible for conduction of electricity.

Some important properties of metals:

(a) Metals are usually good electrical and thermal conductors,

(b) At ordinary temperature metals are usually solid,

(c) To some extent metals are flexible and ductile,

(d) The freshly cut surfaces of metals are shiny,

(e) When struck, metal produce typical sound, and

(f) Most of the metals form alloys

Ex: steel, brass, bronze, etc.

g) Metals may be magnetic, non-magnetic in nature.

h) With regard to mechanical characteristics, these materials are relatively stiff, strong, and ductile.

I) Metallic materials have large numbers of non localized electrons.

j) They are not transparent to visible light.

Example of metals and metal alloys: scissors, coins, a gear, a wedding ring, and a nut and bolt.

Ceramics: Inorganic, non metallic compounds which consist of metallic and non metallic elements are known as ceramics.

Ex:Al_2O_3,SiO_2, Silicates

Ceramics are classified into two groups.

1) traditional ceramics
2) Advanced ceramics

Traditional ceramics: These are made from clay, silicon and feldspar.

Ex: Bricks,

Advanced Ceramic: These are pure compounds such as silicon carbide,Si_3N_4 (Silicon nitride),Al_2O_3

a) **Properties** : With regard to mechanical behavior, ceramic materials are relatively stiff and strong. stiffnesses and strengths are comparable to those of the metals.
b) They are typically very hard and exhibit extreme brittleness (lack of ductility) and are highly subject to fracture.
c) Ceramic materials are typically insulative to the passage of heat and electricity and are more resistant to high temperatures.

Ex: A china teacup, a building brick, a floor tile, and a glass container.

Applications:

1) They are used in higher temperature furnaces.
2) They are used as mechanical cutting tools
3) They are used as wash basins, sinks, tiles etc..
4) They are used as Electrical industry
5) They are used in transformer cores
6) They are used in optical fibers

Polymers: Polymers are organic compounds that are chemically based on Carbon, hydrogen and other non metallic elements. They are prepared by chemically combining simple molecules into long chain molecules which is called as polymerization.

Polymers are classified into two groups.

1) Thermal plastics
2) Thermal setting plastics

Thermal plastics: These materials become soft on heating and hard on cooling. They can be melted reshaped and reformed.

Example: Nylon, polythene, Teflon and polyester.

Thermal setting plastics: These plastics cannot be re melted and reused due to Irreversible chemical reactions. These are used in molding and casting.

Example: Phenol, formaldehyde

Characteristics:

1) Light in weight and soft
2) Poor conductors of heat and electricity
3) Ductile and flammable
4) Dimensionally unstable.

Applications: 1) Used in textile industry

2) Used in synthetic rubber.
3) Used in water pipes
4) Used for storage tanks.
5) Used for Electrical switches.

Composites: Materials which are composed of two or more individual materials from metals ceramics and polymers. Composites exhibit combination of properties that is not displayed by any single material. Most of the composite are synthetic.

Example: Steel reinforced concrete, Vinyl coated Steel, carbon reinforced rubber.

Naturally occurring composites are wood and bone.

Properties: They have better properties than individual components regards to their properties like strength and stiffness, heat resistance etc..

Applications:

1) Used in Fiber glasses.
2) Used in aerospace applications.
3) Used in hi-tech sporting equipments such as bicycle, Tennis rackets etc..
4) Used in automobile bumpers.

Advanced materials:

Materials that are utilised in high Technology applications are called as advanced materials.

They are typically traditional materials whose properties have been enhanced, newly developed and high performance materials.

Ex: Fiber optic Systems, space craft materials, military rocket.

Advanced materials include semiconductor, bio materials, smart materials and Nanomaterials.

Semiconductors: Semiconductors (Ge or Si) have electrical properties that are intermediate between the electrical conductors (i.e., metals and metal alloys) and insulators (i.e., ceramics and polymers). Their resistance decreases as their temperature increases, which is behavior opposite to that of a metal. Their conducting properties may be altered in useful ways by adding impurities (doping) to the crystal structure. A junction is formed by adding different impurity atoms to the same crystal. The behavior of charge carriers at these junctions is the basis of diodes, transistors and all modern electronics. Semiconductors have made possible the advent of integrated circuitry that has totally revolutionized the electronics and computer industries over the past three decades.

Biomaterials: Materials which are used in components implanted into human body to replace damaged body parts. Biomaterials do not produce toxic substances and they are compatible with body tissues.

Applications: 1) used in artificial bones, artificial tissues, stunts etc..

Smart materials: These are the materials which intelligently sense changes in their environment and respond to those changes in predetermined manner. These are latest materials being developed which have significant influence on technology.

Example: Shape Memory alloys, piezoelectric ceramics, magnetostrictive materials. Applications:

1) They are used in sensors.
2) They are used in high-end Technology applications
3) They are used in Paints industry
4) They are used in sophisticated scientific equipments
5) They are used in used in entertainment devices.

Nanomaterials: Nanomaterials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. It is Approximately 100,000 times smaller than the diameter of a human hair. At this scale they exhibit unique optical, magnetic, electrical, and other properties. These materials are useful in electronics, medicine, and other fields.

As early as the 10th century, nanosized particles of gold and silver were used in producing coloured glass and ceramics. Carbon black has been used for a long time in printing materials, rubber tyres and other black rubber products.

Origin of chemical bond: G.N. Lewis (1875-1946) recognized that valence (outmost) electrons are fundamental to chemical bonding. The attraction between electrons of one atom to the nucleus of another atom contributes to what is known as chemical bonds.

Chemical bonding: Atom consists of a positively charge nucleus surrounded by a negatively charged electron cloud. When the two atoms are brought closer, there will be both attractive and repulsive forces acting on them. Therefore, the two atoms take relative positions when there is a balance between these two forces. Chemical bond is defined as inter atomic or inter-molecular or inter-ionic force of attraction which holds the atoms together.

Valence Electrons : Electrons in the outermost occupied energy level.

Types of bonding:

Introduction: We know that the individual atoms are held together in solids by inter atomic forces or bonds. However in addition to these attractive forces, there must be repulsive force because solids are not easily compressed. The attractive forces between the constituent particles in solids are basically electrostatic in origin and the classification of the different types of bonding is strongly dependent on the electronic structure of the atoms concerned. The attractive forces in primary bonds are directly associated with valence electrons in the outer shell which have high energy and hence relatively unstable. If it can acquire more electrons to bring the total up to eight or lose all its electrons to another it can become stable. This is how atomic primary bonds are formed. In fact each bond is a direct consequence of the exchange or sharing of Valence Electrons. There are three strong Principal types of primary bonds. They are ionic, covalent and metallic bonds.

According to strength and directionality, chemical bonds are grouped into primary and secondary.

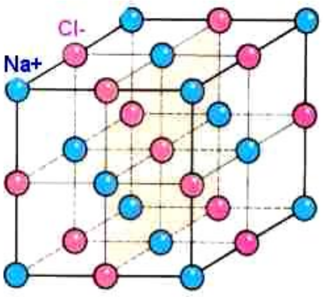
Primary bond : Primary bonds by virtue of their nature are inter-atomic bonds (binding the atoms in a molecule). Primary bonds are formed due to the exchange or sharing of valance electrons.

Examples: ionic, covalent and metallic bonds

secondary bonds: Secondary bonds are intermolecular (binding the molecules in a solid) bonds.

Examples: Van der Waals and hydrogen bonds

(1)Ionic bond:



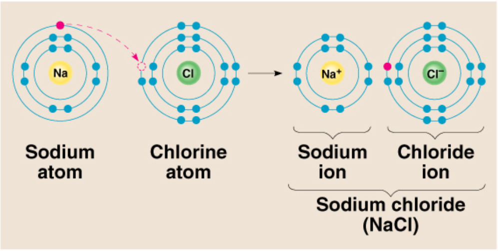
- 1). Ionic bond is formed between two different ions by the transfer of electrons.
- It is the simplest type of chemical bonding to visualize, since it is almost totally electrostatic in nature.
- Ionic bond is the attractive force existing between a positive and negative ion when they are brought closer together.
- These ions are formed when the atoms lose or gain electrons in order to stabilize their outer shell electron configuration.
- Ionic compounds are formed when metals react with nonmetals.

Example: The bond between the Na^+ ion and the Cl^- ion, in NaCl. To obtain the nearest noble gas (Ne) electron configuration Na loses one electron and becomes Na^+ and Chlorine gains one electron from Na and becomes Cl^- to obtain the nearest noble gas (Ar) electron configuration. If these ions are close to each other, ionic bond is formed. In this process 4.5eV energy is released. Here Na^+ ion and Cl^- ion are more stable state than Na and Cl atomic state. The reaction is represented by

$Na^+ + Cl^- \rightarrow NaCl + 4.5eV$

Some other examples: MgO, $MgCl_2$,$CsCl_2$,etc..

Properties of ionic bond:



(1) The strength of the ionic bond is fairly strong.

(2) Ionic crystals have strong binding energy.

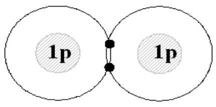
(3) Ionic crystals have high Melting points (M.Ps) and Boiling Points (B.Ps).

(4) The ionic crystals are easily soluble in ionizing solvents such as water.

(5)These bonds are non directional due to spherical charge distribution.

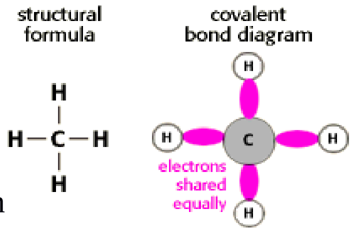
(6) The ionic crystals have electrical conductivity much lower than that of metal.

Covalent bond (Electron pair or homo polar bond):



H_2

- The Covalent bonds are formed by sharing of pair of valence electron between similar or dissimilar atoms.
- The spins of the two electrons in this bond are anti parallel.



Example: Let us consider the hydrogen molecule (H_2), in which the two electrons are shared by two ions. When repulsive forces are balanced by the attractive forces, a molecule forms which has stability greater than that of the two isolated atoms.

It is the common type of bonding in organic molecules and in many inorganic molecules. The balance between the attractive and repulsive forces in hydrogen molecule occurs at a separation of 0.074 nm. The covalent bond strength in hydrogen molecule is about 4.5 eV.

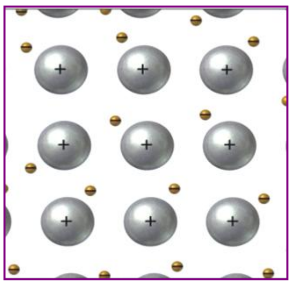
$H + H \rightarrow H_2 + 4.5\text{eV}$

The actual bond is represented as H-H

Properties:

1. Covalent crystals are usually hard and have high binding energies.
2. They have high M.P and B.Ps.
3. They generally dissolve in non- polar solvents such as benzene etc.
4. Basically all covalent crystals are insulators. Because generally no electrons are available for conduction.

Metallic Bond:



- Metallic bonding is found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- Metallic bond is similar to the covalent bond. The metallic bond is weaker than the ionic and the covalent bonds.
- A metal may be described as a low-density cloud of free electrons. Therefore, metals have high electrical and thermal conductivity.

Properties:

(1)Metallic crystals have crystalline structure.

(2) Metallic crystals have high thermal and electrical conductivity.

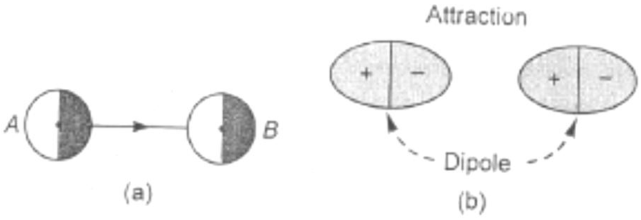
(3) The metallic crystals have high optical reflection and absorption coefficient.

(4) The metallic bond is comparatively weaker than the ionic and covalent bonds.

Molecular Bond (Van der Waals bonding):

- There exists a weak force of attraction between positively charged nucleus of one atom and the negatively charged electrons on the other.
- There also exists a weak repulsive force between negatively charged electrons of one atom to negatively charged electrons of another atom, and also between positively charged nucleus of the other atom.

Def:A bond is formed due to van der waal's force(weak short range forces) of attraction is known as Van der waal' bonding.



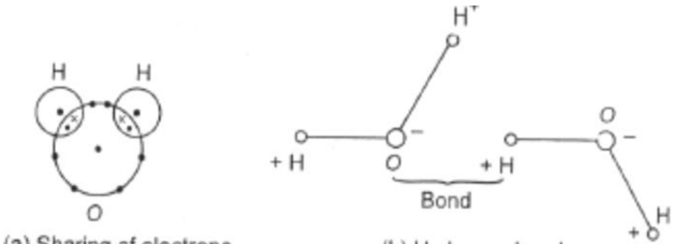
Let us consider two atoms of noble gas argon. Let the electron clouds of two atoms be distributed as shown in the figure (a).The electron cloud of atom A will be attracted by the unprotected nucleus of atom B. We know that the dipoles are formed due to asymmetrical charge distribution around atoms. These dipoles are called oscillating dipole. The van der Waal's bond is formed due to electrostatic attraction between oscillating or permanent dipole as shown in fig. (b)

Characteristics of molecular solids:

1) They have small binding energy.
2) They have low melting point.
3) They are soluble in both polar and non polar solvents.
4) They are good insulators.
5) They are usually transparent to light

Hydrogen bonding:

- A hydrogen atom, having one electron, can be covalently bonded to only one atom.
- However, the hydrogen atom can involve itself in an additional electrostatic bond with a second



(a) Sharing of electrons between hydrogen and oxygen atoms in a water molecule.

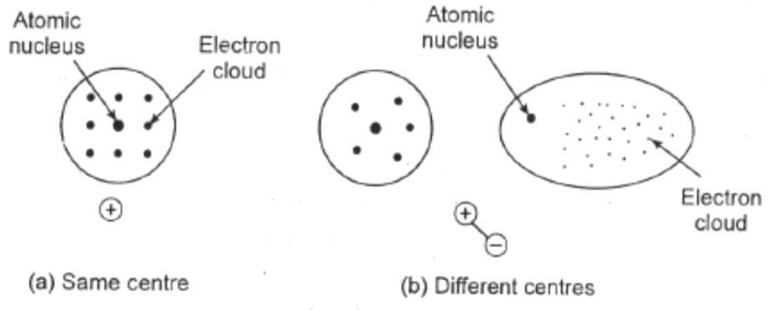
(b) Hydrogen bond between two water molecules.

atom of highly electronegative character such as fluorine or oxygen.

- This second bond permits a ***hydrogen bond*** between two atoms.
- The strength of hydrogen bonding varies from 0.1 to 0.5 ev/atom.
- Hydrogen bonds connect water molecules in ordinary ice.
- Hydrogen bonding is also very important in proteins and nucleic acids and therefore in life processes.

Dispersion bond:

- We know that in a symmetrical molecule, the electrons are distributed uniformly around the nucleus and they are constantly in motion.
- Further, the centre of gravity of positive charges coincides with the centre of gravity of negative charges as shown in the figure (a).
- The molecule is known as non-polar molecule.
- The non-polar molecules have symmetrical structure and zero dipole moment.



(a) Same centre (b) Different centres

Examples: Hydrogen, Nitrogen, Oxygen, carbon dioxide etc..

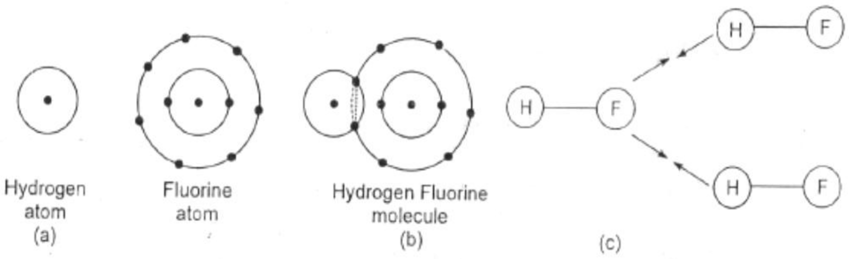
- Sometimes the distribution of electrons in the molecule is not symmetrical around the nucleus in such a case the centre of gravity of nucleus and centre of gravity of electron do not coincide as shown in the figure (b). The molecule is known as polar molecule.

Examples: H_2O, HCl, CO, N_2O NH_3 etc..

- The molecule has some dipole moment.
- There is electronic imbalance of charge which is known as polarization.
- It is important to mention that the nature of polarization is fluctuating and known as dispersion effect.
- Due to dispersion effect there exist a weak force of attraction between the molecules of the same element.
- Due to weak force between the molecules of same element as a result of dispersion effect, a bond is formed which is known as dispersion bond.

Dipole bond:

- We have studied that a covalent bond is formed when the outermost electrons of an atom are shared by two or more electrons.
- Sometimes there is an unequal sharing of electrons between two atoms.



- The unequal sharing of electrons takes place only in those substances in which one of the atoms, in a molecule has high affinity to attract electrons than the other.
- This creates opposite charges on the parent atoms. Now permanent dipoles are produced.
- The permanent dipoles attract each other and a bond is formed which is known as dipole bond.

For example we consider the formation of dipole Bond in case of HCl molecule. The hydrogen atom, with atomic number one, has only one electron in its outermost orbit while the fluorine atom, with atomic number 9 has 7 electrons in outermost orbit as shown in the figure.

It is obvious from figure (a) that hydrogen atom require one more electron to acquire stable configuration where as fluorine atom also require one more electron to acquire stable configuration. So, Hydrogen and Fluorine atoms share a pair of electrons to acquire stable configuration as shown in the figure (b). As a result, a covalent bond is formed.

Here, in this covalent bond, the fluorine atom has high affinity than the hydrogen atom. Therefore, the shared electron pair shifts towards the fluorine atom. This shifting of electron pair produces a dipole and the bond so formed is known as dipole Bond. This is shown in the figure(c).

Cohesive energy or Binding energy: Cohesive energy is that energy evolved when a crystal is formed from individual neutral atoms or the energy needed to break the crystal in to individual atoms.

Expression for Cohesive energy or Binding energy for ionic crystals:

Imagine two ions of opposite charge separated by an infinite distance. Let they be allowed to approach each other. There will be electrostatic attraction between the ions which is described by Coulomb's law. In this case the potential energy will be negative because the work is done by the ions. The variation of Coulomb's attractive potential energy with inter atomic distance is shown in the fig.

The two ions are not expected to approach each other sufficiently close. Because there will be repulsive force between them due to electron cloud of the two ions. The situation is shown in the fig. In this case potential energy is positive because the work is done on the ions.

The potential energy of the system is some of attractive potential energy and repulsive potential energy. At a certain distance of separation the two forces balance each other. If the potential energy is minimum then the solid is stable.

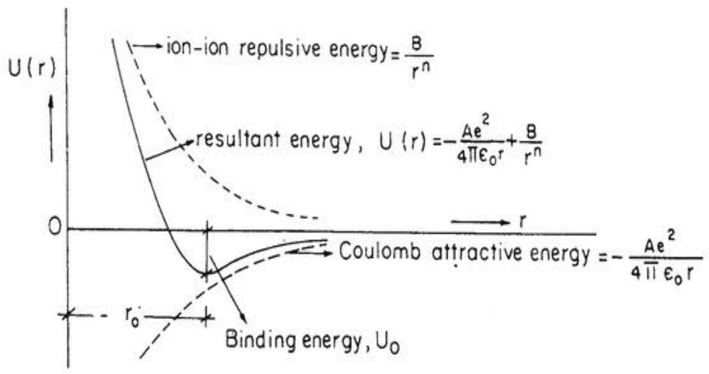


Figure 1. Schematic representation of lattice energy of NaCl as a function of inter atomic spacing

The coulomb energy of attraction between two ions separated by a distance is given by

$$U_a = -\frac{e^2}{4\pi\varepsilon_0\, r}$$

The negative sign shows that the energy is attractive

In the crystal each ion interacts with all its neighboring ions of the same as well as opposite sign. The net energy of attraction per ion pair maybe written as

$$U_a = -A\frac{e^2}{4\pi\varepsilon_0\, r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, the constant A is known as Madelung constant of the crystal.

The two ions cannot continuously approach each other under coulomb attraction but when they are at a certain small distance they begin to repel with each other. The repulsive force arises very rapidly with the decrease in distance.

Born proposed that the repulsive energy can be expressed as

$$U_R = \frac{B}{r^n} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where B is a constant and n is a number ($n \approx 9$)

The total energy is given by

$U_T = U_a + U_R$

$$U_T = -A\frac{e^2}{4\pi\varepsilon_0\, r} + \frac{B}{r^n} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The constant B can be evaluated by recognizing the slope of the potential curve which is zero at the equilibrium distance. Now we can write

$\left(\frac{\partial U_T}{\partial r}\right)_{r=r_0} = 0 \ldots\ldots\ldots\ldots\ldots\ldots (4)$

Applying this condition we have

$$\frac{Ae^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0$$

$$B = \frac{Ae^2}{4\pi\varepsilon_0 n} r_0^{n-1} \dots\dots\dots\dots\dots..(5)$$

Substituting the value of B from the equation (5) in equation (3) we get the value of U_T .

The value of U_T at r = r_o(i.e., U_o)is given by

$$U_0 = -\frac{Ae^2}{4\pi\varepsilon_0 r_o} + \frac{Ae^2}{4\pi\varepsilon_0 n r_o}$$

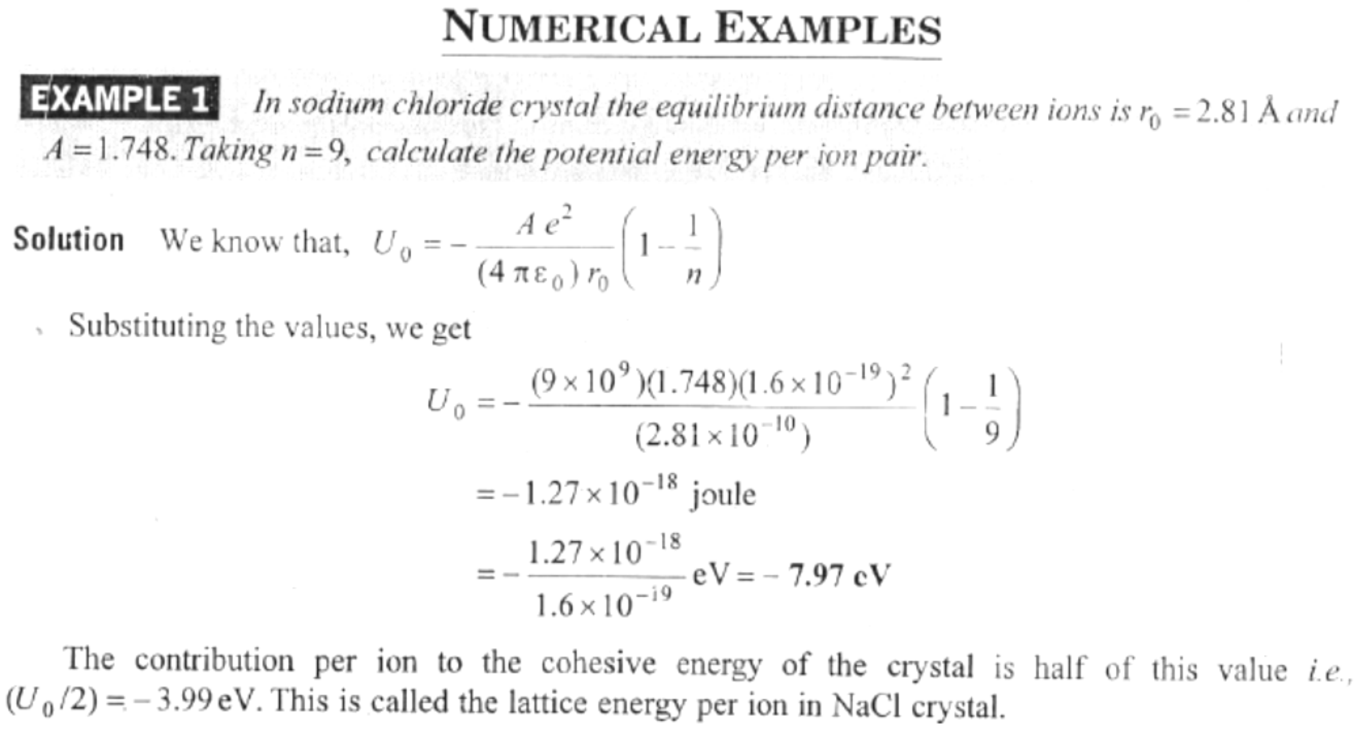
$$U_0 = -\frac{Ae^2}{4\pi\varepsilon_0 r_o}\left[1 - \frac{1}{n}\right]$$

$$U_0 = -\frac{Ae^2}{4\pi\varepsilon_0 r_o}\frac{[n-1]}{n} \dots\dots\dots..(6)$$

The equilibrium energy U_O is called the cohesive energy. This is the amount of energy which is spent to separate the solid ionic crystal into its constituent ions. It is experimentally measured from the Born-Haber crystal data.

Madelung constant: Imagine two ions of opposite charge are allowed to come closer and closer. There will be a coulombian attractive force between them. This force varies inversely as the square of the distance between the two ions. If there would have only attractive force between the two ions, they have finally combined. But due to the electron cloud of the two ions a repulsive force acts between them. The repulsive force increases as the distance decreases. In this way the two ions attract each other when the distance of separation is large and repel each other for small separation. At a certain distance of separation the two forces balance each other. Now the potential energy is minimum and the solid is stable.

The Madelung constant represents the effect of a specific geometrical array of ions on the electrostatic potential energy.



NUMERICAL EXAMPLES

EXAMPLE 1 *In sodium chloride crystal the equilibrium distance between ions is* $r_0 = 2.81$ Å *and* $A = 1.748$. *Taking* $n = 9$, *calculate the potential energy per ion pair.*

Solution We know that, $U_0 = -\frac{A\,e^2}{(4\pi\varepsilon_0)\,r_0}\left(1 - \frac{1}{n}\right)$

Substituting the values, we get

$$U_0 = -\frac{(9\times 10^9)(1.748)(1.6\times 10^{-19})^2}{(2.81\times 10^{-10})}\left(1 - \frac{1}{9}\right)$$

$$= -1.27\times 10^{-18} \text{ joule}$$

$$= -\frac{1.27\times 10^{-18}}{1.6\times 10^{-19}} \text{ eV} = -\mathbf{7.97\ eV}$$

The contribution per ion to the cohesive energy of the crystal is half of this value *i.e.*, $(U_0/2) = -3.99$ eV. This is called the lattice energy per ion in NaCl crystal.

EXAMPLE 2 *Calculate the ionic cohesive energy and the atomic cohesive energy of* CsCl. *The Madelung constant for* CsCl *is* 1.763 *and the separation between adjacent ions is* 3.56 Å. *The non-electrostatic repulsive energy varies as* r^{-n} *where* $n = 10.5$. *The ionisation energy of* Cs = 3.89 eV *and electrons affinity of* Cl = – 3.61 eV.

Solution The ionic cohesive energy of CsCl is given by

$$U_0 = -\frac{A\,e^2}{(4\,\pi\varepsilon_0)\,r_0}\left(1-\frac{1}{n}\right)$$

Substituting the given values, we get

$$U_0 = -\frac{(9\times10^9\ \text{N-m}^2/\text{C}^2)\,(1.763)\,(1.6\times10^{-19}\ \text{C})^2}{(3.56\times10^{-10}\ \text{m})}\times\left(1-\frac{1}{10.5}\right)$$

$$= -10.3\times10^{-19}\ \text{J}$$

$$= -\frac{10.3\times10^{-19}\ \text{J}}{1.6\times10^{-19}\ \text{J/eV}} = -\,\mathbf{6.45\ eV}$$

This amount of energy is needed to remove Cs^+ and Cl^- ions from the crystal. To form Cs^+ from Cs atom requires 3.89 eV and to form Cl^- from neutral Cl atom releases 3.61 eV. Thus, given Cs^+ and Cl^-, we supply 3.61 eV to form Cl and get back 3.89 eV when we form Cs. The energy needed to form the neutral atoms from the crystal is

$$-6.45\ \text{eV} - 3.61\ \text{eV} + 3.89\ \text{eV} = -\,\mathbf{6.17\ eV}$$

This is the atomic cohesive energy.

EXAMPLE 3 *Calculate the binding energy of* NaI *of which the nearest neighbour distance is* 0.324 nm. *Express the energy in* eV *and also in* kJ/kmol. *Madelung constant for* NaI = 1.748 *and* $n = 9.5$.

Solution We know that

$$U_0 = -\frac{A\,e^2}{(4\,\pi\varepsilon_0)\,r_0}\left(1-\frac{1}{n}\right)\text{joule}$$

or

$$U_0 = -\frac{A\,e}{(4\,\pi\varepsilon_0)\,r_0}\left(1-\frac{1}{n}\right)\text{eV}$$

$$= -(9\times10^9)\left[\frac{1.748\times(1.6\times10^{-9})^2}{(0.324\times10^{-9})}\right]\left(1-\frac{1}{9.5}\right)$$

$$= \mathbf{-\,6.9\ eV}$$

The binding energy per kmol

$$U_{\text{kmol}} = N_A\,U_0 = (6.02\times10^{26})\times6.9\,\text{eV}$$

$$= (6.02\times10^{26})\times(6.9)\times(1.6\times10^{-19})\ \text{joule}$$

$$= \mathbf{667\times10^3\ kJ/kmol}$$

UNIT II

DEFECTS(IMPERFECTIONS) AND DIFFUSION IN METALS

Syllabus: Introduction – Types of defects - Point defects- Line defects- Surface defects- Volume defects- Production and removal of defects- Deformation- irradiation-quenching- annealing- recovery. Diffusion in solids- Fick's laws of diffusion.

Introduction: we know that a perfect crystal is a periodic arrangement of atoms in the lattice arrays in all directions. Real crystals show deviation from perfect regular lattice structure, that is they have a large number of defects. Any deviation in the Crystal from the perfect atomic periodicity is called lattice defect.

Lattice: a regular repeated three-dimensional arrangement of atoms, ions, or molecules in a metal or other crystalline solid.

Lattice defect: The state in which the lattice arrays of atoms are not continuous throughout the Crystal is known as Lattice defect.

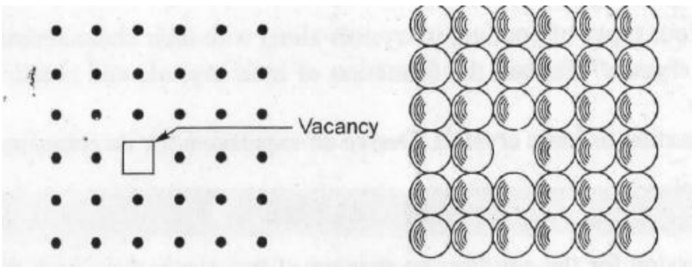
Types of defects: The Crystal defects arise due to the presence of imperfections. Crystal defects can be classified on the basis of their geometry as

1. Point defects
2. Line defects
3. Surface defects
4. Volume defects

(1) **Point defects**: The point defects are imperfect point like region in the Crystal. Their influence extends to only a few atoms diameters beyond their lattice positions.

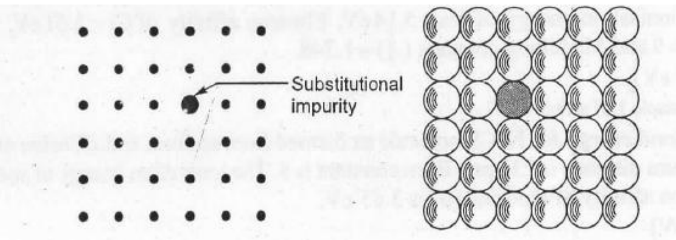
The point defects are

a) Vacancy defect
b) Substitutional impurity defect
c) Interstitial impurity defect

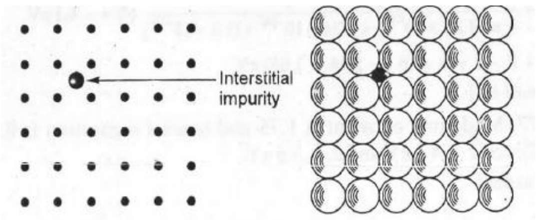


a) **vacancy defect**: When an atom is missing from its normal position, then the defect is called as vacancy point defect. This is shown in the figure.

Vacancies may be single or two or more. In metals, the vacancies are created by thermal excitation. At sufficient high temperatures the atoms of the solid vibrate vigorously about their regular positions. If the atom acquires enough energy, then it leaves its site completely. Now a vacancy is created. This vacancy is called a vacancy defect in a crystal.



b) **Substitutional impurity defect :** A foreign atom may replace a regular atom giving rise to substitution impurity. Pentavalent or trivalent impurity atoms doped in Silicon or Germanium are also substitutional impurity in the Crystal. The substitutional infinity is shown in the figure.



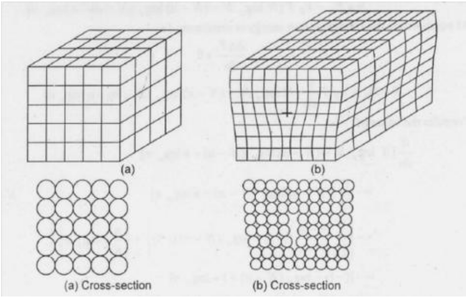
c) **Interstitial impurity defect**: When a foreign atom occupies the void space between the atoms of the crystal, then it is known as interstitial impurity defect. It is shown in the figure

In crystals, there is some empty or void space which is not occupied by the atoms of the crystal. If a small sized atom occupies the void space in the parent crystal without disturbing the parent atoms from their regular sites, then it is known as interstitial impurity defect.

Line defects: The line defects are known as dislocations. In geometrical sense, the line imperfection is a one dimensional defect. These defects take place due to dislocation or distortion of atoms along a line in some direction. A dislocation is defined as a disturbed region between two substantially perfect parts of a crystal.

The two types of dislocations are

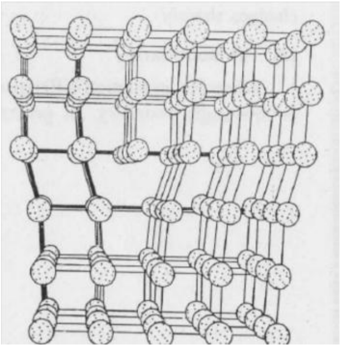
1) Edge dislocation and
2) screw dislocation



Edge dislocation : In a perfect crystal, the atoms are arranged in both vertical and horizontal plane parallel to the side faces as shown in the figure (a).If one of these vertical planes does not extend to full length but ends in between within the Crystal as shown in figure (b). Then it is called edge dislocation. Therefore in this defect, a line of atoms is not in proper position or part of vertical layer of atoms is removed.

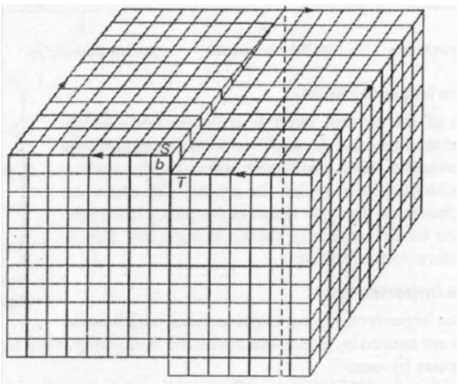
The following points are observed.

1) In the perfect crystal, the atoms are in equilibrium position.
2) In the imperfect crystal, just above the discontinuity the atoms are pressed hard and are in a state of compression.
3) Just below the discontinuity, the atoms are pulled apart and are in a state of tension.
4) This distorted configuration extends all along the edge inside the Crystal perpendicular to the cross-section.
5) Edge dislocations are represented by ⊥ or T depending on whether the incomplete plane starts from the top or from the bottom of the Crystal. These two configurations for referred to as positive or negative edge dislocations respectively. A three-dimensional picture of Edge dislocations is shown in the figure.

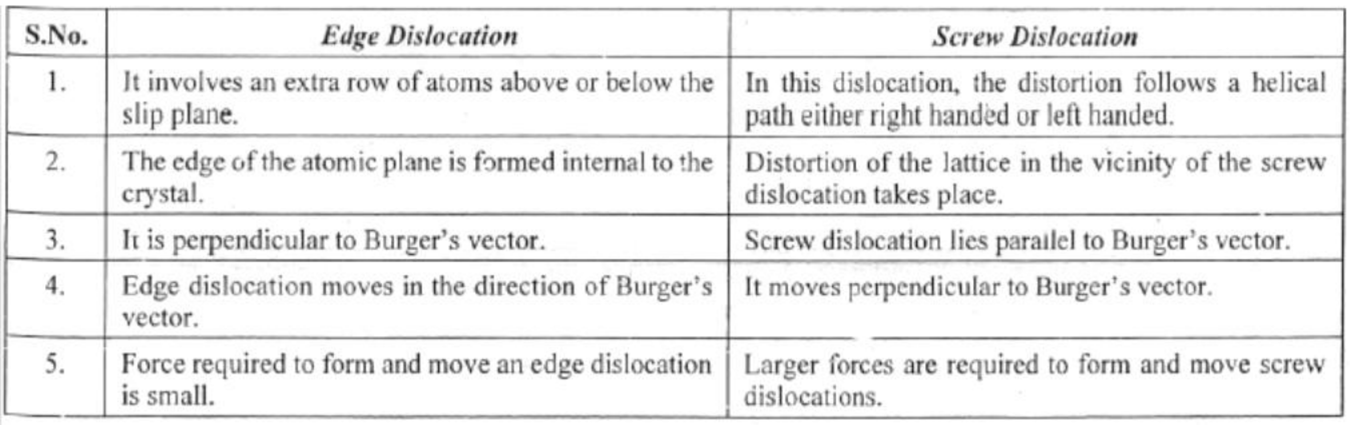


Screw dislocation: As shown in the Figure, when a part of a crystal is displaced relative to the rest of the Crystal it is important to mention here that the displacement terminates within the Crystal.

Screw dislocation is defined as a displacement of the atoms in one part of a Crystal relative to the rest of the Crystal. The screw dislocation forms a ramp around the dislocation line.



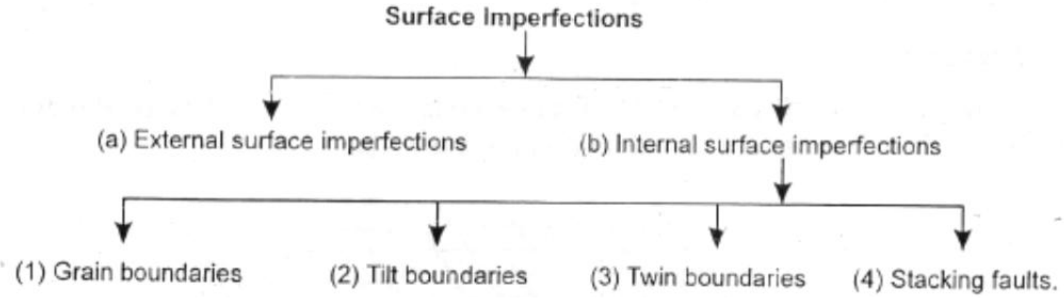
distinction between edge and screw dislocation

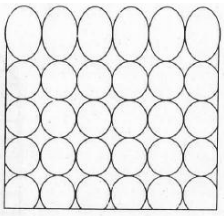


S.No.	*Edge Dislocation*	*Screw Dislocation*
1.	It involves an extra row of atoms above or below the slip plane.	In this dislocation, the distortion follows a helical path either right handed or left handed.
2.	The edge of the atomic plane is formed internal to the crystal.	Distortion of the lattice in the vicinity of the screw dislocation takes place.
3.	It is perpendicular to Burger's vector.	Screw dislocation lies parallel to Burger's vector.
4.	Edge dislocation moves in the direction of Burger's vector.	It moves perpendicular to Burger's vector.
5.	Force required to form and move an edge dislocation is small.	Larger forces are required to form and move screw dislocations.

surface imperfections: Surface imperfections arise from a change in the stacking of atomic planes on or across a boundary.

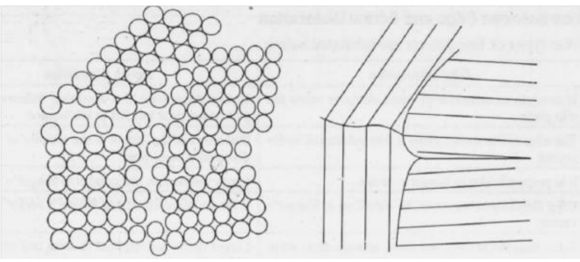
The classification is as follows:





External surface imperfections: The atomic bonds do not extend beyond the surface. At the boundary, the atomic bonds are terminated. As a result, the atoms on the surface cannot be compared with the atoms within the Crystal. The atoms of the surface have neighbors on one side where as the atoms inside the Crystal have neighbors on either side as shown in the figure. This is shown as external surface imperfection.

Internal surface imperfections: The internal surface imperfections are imperfections which occur inside the crystal. They are caused by grain boundaries, tilt boundaries, twin boundaries and stacking faults.



Grain boundary: This is two dimensional defects. When a piece of iron or copper solidifies or recrystallizes, new crystals form in different part. They grow and encroach on each other. The atoms held in between are attracted by crystals on either side and depending on the forces, the atoms occupy equilibrium positions. These positions at the boundary region between two crystals are distorted. The boundary region is called a crystal boundary or grain boundary. The Grain boundary is shown in the figure. The Crystal orientation changes sharply.

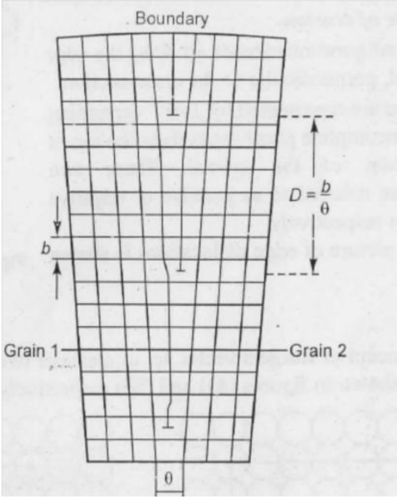
Tilt boundaries: when the orientation difference between two neighboring crystal is less than 10^0 then it is called as low angle boundary. In general low angle boundaries can be described by suitable arrays of dislocation. Figure shows a low angle tilt boundary. The neighboring crystals are tilted with respect to each other by only a small angle.

The angle of tilt is given by

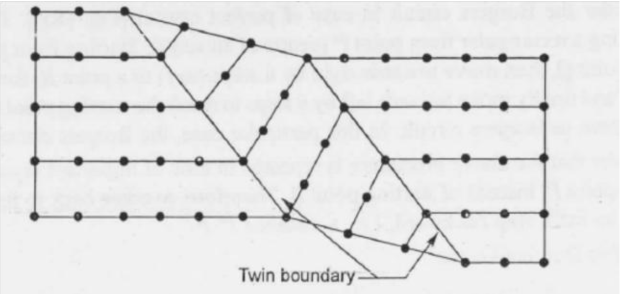
$$\theta = \frac{b}{D}$$

Where b = burgers vector

D= average vertical distance between dislocations.

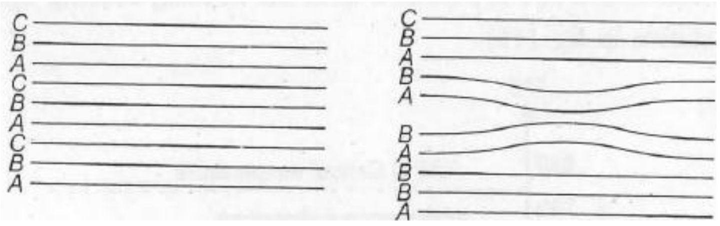


Twin boundaries: When the atomic arrangement on one side of a boundary is mirror reflection of the arrangement on the other side, then it is called as Twin boundary. the Twin boundary is shown in the figure. As they occur in pair, they are called twin boundaries. The region between the pair boundaries is called the twinned region.



Stacking faults: When the staking of atomic planes is not in a proper sequence throughout the Crystal, the fault caused is known as stacking fault. Figure shows a stacking fault.

For example, the stacking sequence in fcc crystal is described by A-B-C- A-B-C- A-B-C. But the stacking fault may change the sequence A-B-C- A-B-A-B-C . The region in which the stacking fault occurs (A-B-A-B) forms a thin region and it becomes HCP. This thin region is a surface in perfection and is called stacking fault.



Volume defects: The volume defects such as cracks may arise in crystals when they are grown or while they are used. In growing a crystal, it is possible that a small electrostatic dissimilarity between the stacking Layers may result in a track.

Presence of large vacancy or void space, when cluster of atoms are missed is also considered as volume imperfection.

While growing a crystal, there is every possibility of inclusions foreign particles and non-crystalline regions which have the dimensions of the order of 0.2nm. These are also called volume imperfections.

The cracks may also generate when the Crystal is used in some device application and is subjected to sudden thermal waves.

Using optical microscope, presence of volume defects can be detected.

Production and removal of defects*:* Following are two main sources of production of dislocations.

1) Mechanical deformation and
2) Mishandling during grain growth.

Mechanical deformation: When crystals are subjected to various kinds of situations during manufacturing and fabrications, they are deformed. The deformations may be geometrically linear, angular or complex. As a result the dislocations enter into the crystal.

Mishandling during grain growth:We know that crystals are obtained by the process of crystallization. In doing so, the molten metal is solidified. It is almost impossible to achieve perfection in the process of grain growth and control on the size and orientation of grains. Therefore, defects are produced.

Effect of dislocations: Effect of dislocations are harmful to the properties of crystalline materials. They are

i) Dislocations are responsible for reduced the electrical conduction.
ii) They influence the surface-sensitive properties.
iii) The mechanical strength is lowered.
iv) Thermal, magnetic, chemical, optical etc.. properties are changed.

Remedies: Following few remedies are used to avoid or minimize the occurrence of dislocations.

i) Care full control on crystallization.
ii) Prevention of undesired mechanical deformation.

iii) Use of thermal energy.
iv) Use of whisker form of material.

Introduction to heat treatment: The properties of metals, alloys, ceramics materials can be changed by heat treatment. Heat treatment refers to the heating and cooling operation under definite conditions to make metal and alloys for specific applications. For various fabrication and manufacturing operations, heat treatment is very important process. Heat treatment not only increases the hardness but also increases the tensile strength and toughness. The rate of cooling and the manner of cooling are the controlling factors in heating treatment process.

Purpose of heat treatment: The heat treatment processes serve the following purposes:

1) To change the chemical composition.
2) To produce hard surfaces and tough interior portions.
3) To relieve the internal stresses produced during cold working and other operations.
4) To improve magnetization property, especially of steels for producing permanent magnets.
5) To improve electrical properties.
6) To refine grain structure after hot working of a metal.
7) To improve mechanical properties such as tensile strength, ductility etc..
8) To soften a metal to improve its machinability.

Classification of heat treatment processes:

a) Quenching or hardening:

- In this process, the heated steel is suddenly dipped into a cooling medium.
- The cooling material may be cold water, oil, air fused salt etc..
- The salt may be sodium chloride, calcium chloride etc.
- The hardness in steel depends essentially on its quenching rate.
- A very Rapid quenching is necessary to harden low and medium plain carbon steel.
- quenching in water bath is commonly employed. For high carbon and alloy Steel, oil is generally used as quenching medium.
- Different oils are used for this purpose. The different oils have different cooling effects.
- As a result, they impart different hardness on quenching accordingly .
- For example cooling brine or water spray is most effective.

The final structures obtained with different rates of cooling have different properties and appearance. The properties like tensile strength, hardness, yield point etc. can be changed by different cooling rate. It is important to mention here that the faster the cooling rate, the greater will be the hardness of Steel. Different structures of Steel are obtained when the quenching is done in water or oil or air.

Annealing: This is a kind of heat treatment after which a metal or alloy acquires a structure close to the equilibrium one. Annealing involves the following three processes

i) Heating to a desired temperature
ii) Holding at that temperature for specific time.
iii) Cooling, usually to room temperature.

In annealing process time is an important parameter.\

Annealing of steel is done to impart softness to it. In this process, the Steel is heated above its critical temperature. After this, this is hold at this temperature for about 1 hour. Finally it is cooled slowly in the furnace at a rate of about 30^o to 15^o C/hour. After cooling, the Steel is changed into different forms.

Annealing serves the following objectives.

i) Soften the steel
ii) Refines the Grain structure
iii) Improves ductility of steel
iv) Enhances the machinability

Types of annealing process : The various types of annealing operations are

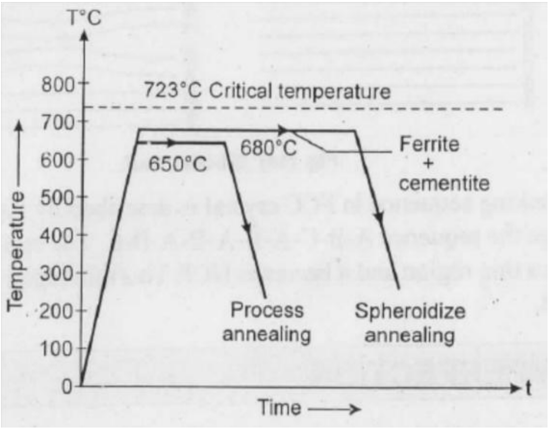
1) full annealing
2) partial anneling
3) Spheroidise annealing
4) Diffusion annealing

1) **full annealing**:

- This operation removes all structural imperfections by complete recrystallization. This operation is often utilised in low and medium Carbon Steels.
- The process consists of heating Steel to about 50 to 70^o C its critical temperature until equilibrium is achieved.
- This is hold at this temperature for the considerable time. Finally, heating-furnace is turned off and both furnace and steel are allowed to cool to room temperature slowly.
- The process takes several hours.
- After this process, the steel structure becomes chemically homogeneous and gets soft.

2) **partial annealing**:

- In this process, the steel is heated to 550 to 650 ^{o}C which is a little below the critical temperature.
- It is held there for a prolonged duration.
- After this, it is slowly cooled. This results in formation of pearlite.
- New crystals of the same structure are formed after the heating-cooling operation.
- The process is shown in the figure.
- Obviously, annealing time and temperature control is very essential for proper process annealing.



3) This process is carried-out on low carbon steel. **Spheroidise annealing**:

- This process is normally applied to high carbon steel by heating below lower critical temperature approximately 680^{o}C .
- It is hold for a long time at this temperature.
- Finally, cooled slowly below 600 ^{o}C.
- Obviously this is a time consuming process. this is shown in figure. Cutting tools, measuring instruments are produced by this process.
- This type of heat treatment produces carbide in the form of round or globular(Spheroids) instead of plates.
- Due to this fact, the process is known as Spheroidise annealing.

4) **Diffusion annealing :** For the jobs above critical temperature, the diffusion annealing is employed. This is followed by full annealing to obtain fine grained structure. This process is used to heavy casting to make austenitic grain homogeneous.

Recovery: The term recovery implies all the changes in fine structure and properties of a metal that take place during heat treatment. They are

1) Some of the internal Strain energy relieved by virtue of dislocation motion without any externally applied stress.
2) Internal stresses are relieved.
3) Some reduction in number of dislocations and dislocation configurations.
4) Microstructure remains unaffected.
5) Physical properties such as electrical and thermal conductivities are recovered to their precold worked states.

Recovery is further subdivided into the following Two States.

i) **Strain relief crystallization**: This is a stage at which the number of point defects, mainly vacancies diminishesin a number of metals such as aluminum and iron.
ii) **Polygonization**: This is a kind of recovery involving formation of new long angle boundaries within each grain. These boundaries can form by slip and climb of dislocations; as a result, a grain is divided into sub grains, or polygons which the free of dislocations.

The process of recovery is also called as stress- relieving Annel.

The recovery process is adopted in boiler tube, cartridge cases and components made by welding etc..

Introduction to diffusion:

- Diffusion is a phenomenon of material transport by atomic motion.
- The diffusion may be defined as a flow process which governs the movement of atoms and molecules in solids.
- The atoms and molecules change their positions under the influence of thermal energy, electric and magnetic field gradients, concentration gradient, etc..
- Diffusion processes play an important role in many solid state phenomena.
- Atomic vibrations in solids are inherent phenomena.
- Thermal energy derived from these atomic vibrations is responsible for diffusion of atoms.
- The knowledge of diffusion phenomenon is essential for the introduction of a very small concentration of an impurity in a solid state device.

Types of Diffusion:

The process of diffusion is broadly classified as follows:

1) Microscopic diffusion
2) Macroscopic diffusion.

1) Microscopic diffusion: This Diffusion concerns with the movement of individual atoms and molecules. This is a random process i.e. each atom or molecule follows a random path. Microscopic view considers the system on atomic or molecular level.

Microscopic diffusion is further classified into following types:

i) Self diffusion: In this case, thermally excited atom from from site of crystal lattice jumps to an adjacent site.

ii) Inter – diffusion: This is observed in binary metal - alloys such as Cu-Ni system.

iii) Volume diffusion: In this case, the atomic movement takes place throughout the volume of solid.

iv) Surface diffusion: In this type of diffusion, the atomic movement takes place along the surface of the system.

v) Grain boundary diffusion: In this type of diffusion, the atoms diffuse along the grain boundaries.

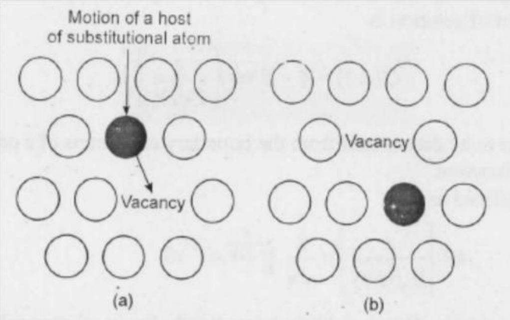
vi) Pipe diffusion: This diffusion takes place along the dislocation edge.

2) **Macroscopic diffusion**: This is a mass flow process, i.e.a large number of atoms and molecules take part in the diffusion process. It is important to mention that the process takes part in a pre-defined direction and not in a random direction.

Microscopic view means a total view. This view analyses the system as a hole in bulk nature

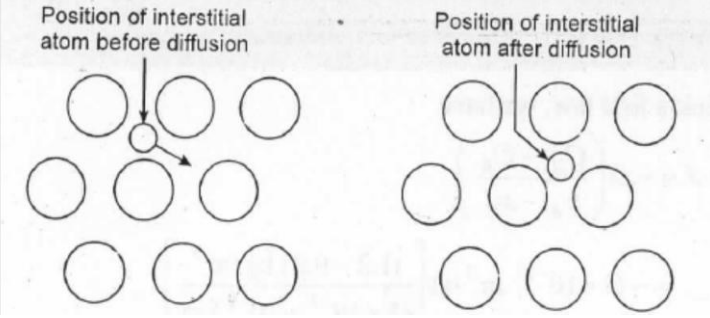
Diffusion Mechanisms: Almost all the mechanisms are based on vibrational energy of atoms in a solid. The important mechanisms are

1. Vacancy mechanism
2. Interstitial mechanism
3. Direct interchange diffusion mechanism



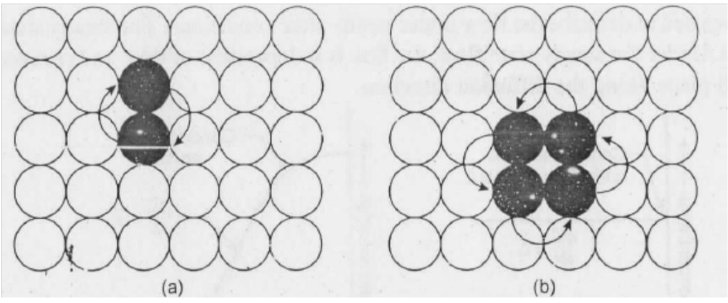
1. **Vacancy mechanism**:
   - We know that vacancies are vacant atomic states.
   - The vacancy mechanism involves the shifting of an atom from its normal lattice position to adjacent lattice site or vacancy. This is shown in the figure. This is known as vacancy diffusion.
   - At the position of shifted atom a new vacancy is created as shown in the figure.
   - For this diffusion process vacancy is necessary.
   - The vacancies are continually being created and destroyed,
   - i.e. Vacancies move through the lattice and produce random shift of atoms from one lattice position to another lattice position.
   - Vacancy diffusion is responsible for the phenomenon of creep in materials.
   - It is bulk diffusion process. If a solid is composed of single element, i.e. pure metal, the movement of thermally excited atom from one side of crystal lattice to an adjacent site is called self diffusion.
   - The process of self diffusion in gold and silver occurs by vacancy mechanism.

2. **Interstitial mechanism:**
   - when a solid is composed of two or more elements whose atomic radii differ significantly, interstitial diffusion may take place.
   - The large size atoms occupy lattice sites where as smaller size atoms fit into interstics created by the large atoms.



   - This diffusion is smaller in vacancy diffusion except the interstitial atoms stay on interstitial sites.
   - Therefore, this diffusion mechanism involves atoms that migrate from an interstitial position to neighbouring one which is empty as shown in the figure.
   - This diffusion mechanism is found for inter diffusion of impurities such as hydrogen, carbon Nitrogen, Oxygen etc.. which have small atoms.

3) **Direct interchange mechanism**:



- In this mechanism the atoms exchange places through rotation about a mid-point.
- Two or more atoms jump past each other and exchange positions but the number of sites remain constant as shown in the figure.

Fick's law of diffusion:

- Diffusion is a mass flow process i.e. quantity of element that transported within another.
- This is a macroscopic view and a time dependent process.
- Diffusion can occur under the influence of concentration gradient, an electric or magnetic field gradient or a stress gradient.
- Here, we shall consider diffusion or rate of mass transfer under concentration gradient in one dimensional case.
- Regarding the rate of mass transfer, Fick gave two laws known as Fick's laws.
- They are

1) Fick's first law
2) Fick's second law

Fick's first law of diffusion: Considered two material systems in which their atoms move in one direction under the influence of concentration gradient. Concentration gradient means a change in mass per unit volume or weight per unit volume.

This law describes the rate at which diffusion occurs. This law states that the quantity(dn) of a substance diffusing per unit time(dt) through the surface area(A) is proportional to (i)concentration gradiant(dC/dx) and (ii)the coefficient of diffusion (D). The law can be expressed as

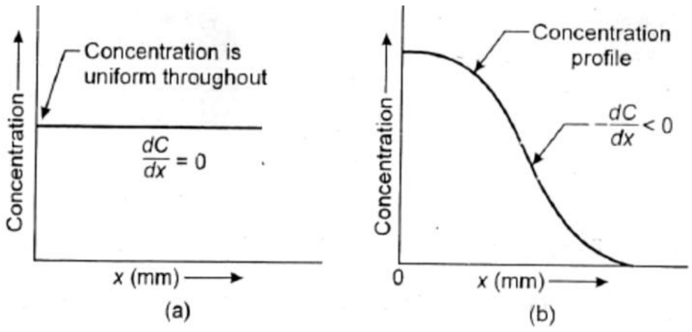
$$dn = -D\frac{dC}{dx}Adt \ldots\ldots\ldots\ldots\ldots (1)$$

The negative sign implies that the diffusion occurs in the reverse direction of concentration gradient vector. Equation (1) can be written as

$$\frac{dn}{dt} = -DA\frac{dC}{dx} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

If J be the diffusion flux per unit cross- sectional per unit time, then equation (2) can be expressed as

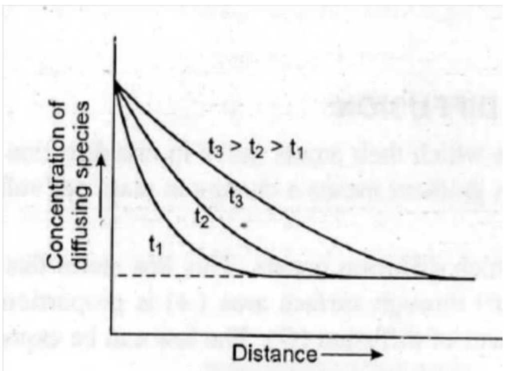
$$J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dC}{dx} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$



The term D is more popular and is known as diffusivity.

This law can be used to describe the flow under steady state conditions. The steady condition is shown in the figure. Under steady state flow, the flux is independent of time and remains the same at any cross- sectional plane along the diffusion direction.

The profile will be non -linear when D is a function of C as shown in the figure. This law does not provide about the time dependence of the concentration.



Fick's second law : This law is an extension of Fick's first law to non-steady flow. If the concentration gradient varies in time and the diffusion coefficient is taken to be independent of concentration, the diffusion process is described by Fick's second law. Figure shows the concentration profiles at three different diffusion times.

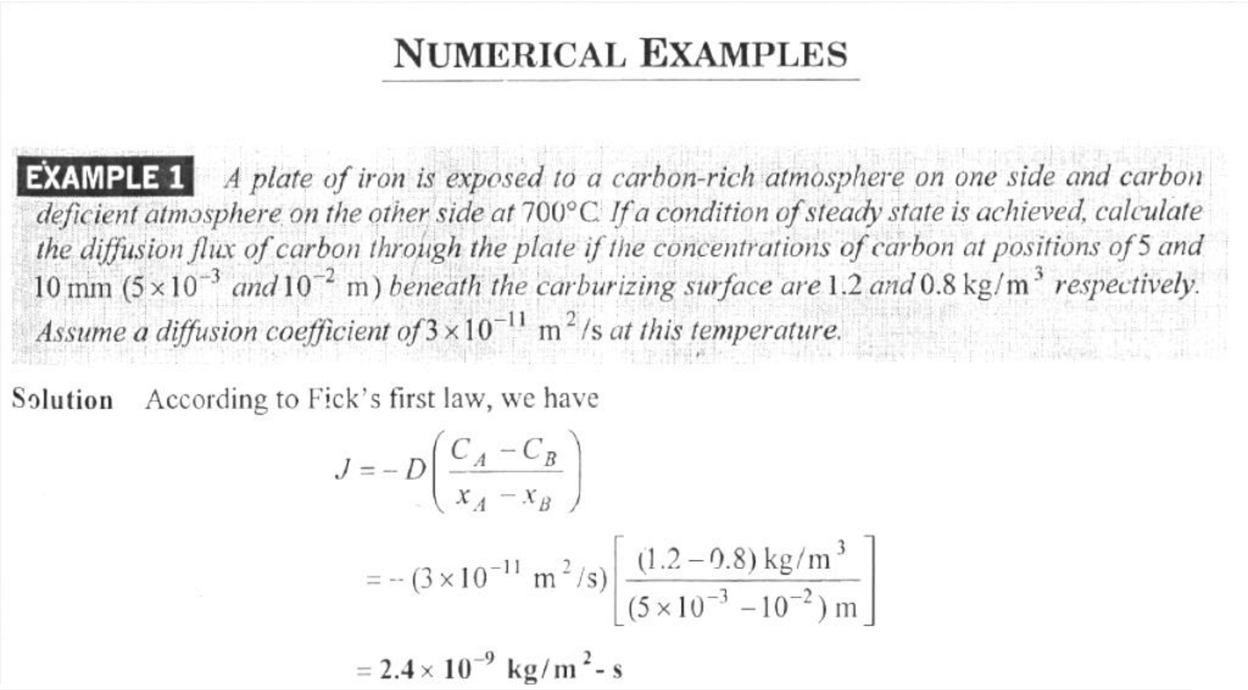
The Fick's second law for unidirectional flow under non-steady conditions can be expressed by the following partial differential equation.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \ldots\ldots.. (4)$$

Eq. (4) can be written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \ldots\ldots.. (5)$$

The solutions to differential equation (5) are commonly used for practical problems due to its relative simplicity.



NUMERICAL EXAMPLES

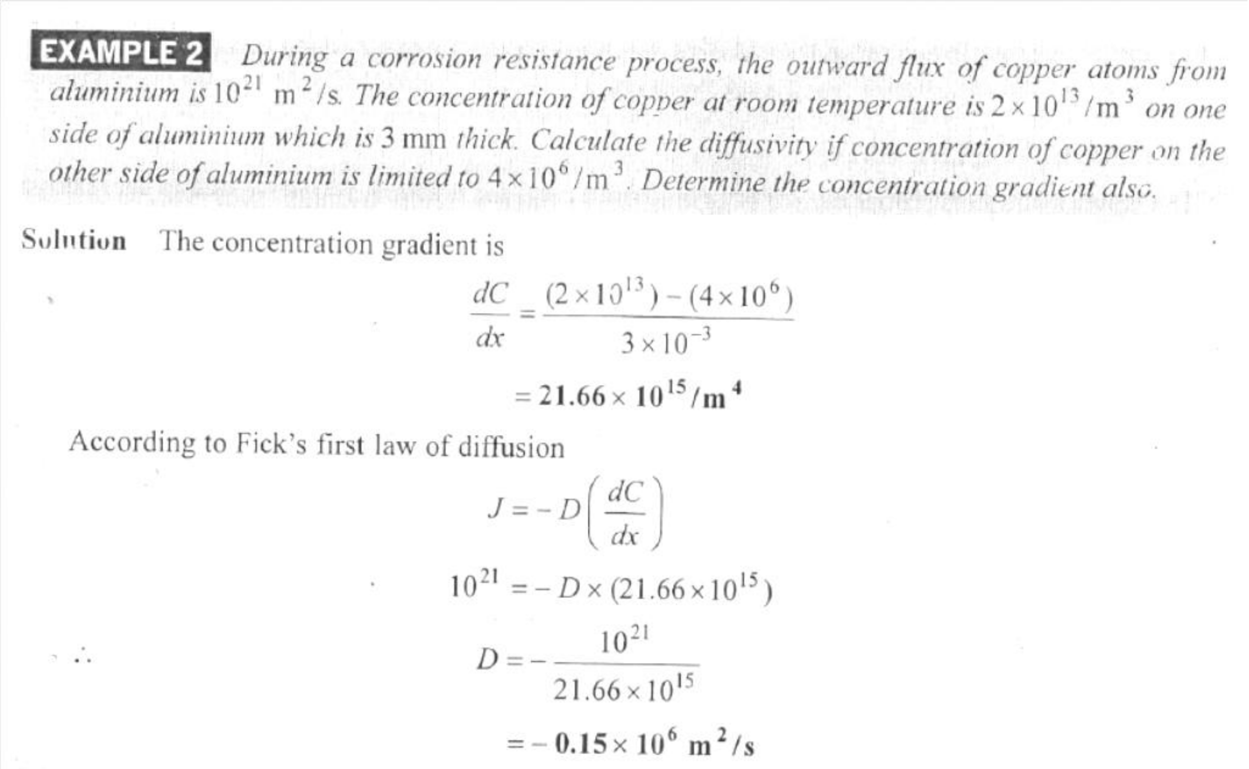
EXAMPLE 1 *A plate of iron is exposed to a carbon-rich atmosphere on one side and carbon deficient atmosphere on the other side at* 700°C*. If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of* 5 *and* 10 mm (5×10^{-3} *and* 10^{-2} m) *beneath the carburizing surface are* 1.2 *and* 0.8 kg/m^3 *respectively. Assume a diffusion coefficient of* 3×10^{-11} m^2/s *at this temperature.*

Solution According to Fick's first law, we have

$$J = -D\left(\frac{C_A - C_B}{x_A - x_B}\right)$$

$$= -(3 \times 10^{-11}\ \text{m}^2/\text{s})\left[\frac{(1.2 - 0.8)\ \text{kg/m}^3}{(5 \times 10^{-3} - 10^{-2})\ \text{m}}\right]$$

$$= \mathbf{2.4 \times 10^{-9}\ kg/m^2\text{-}s}$$



EXAMPLE 2 *During a corrosion resistance process, the outward flux of copper atoms from aluminium is* 10^{21} m^2/s*. The concentration of copper at room temperature is* 2×10^{13}/m^3 *on one side of aluminium which is* 3 mm *thick. Calculate the diffusivity if concentration of copper on the other side of aluminium is limited to* 4×10^6/m^3*. Determine the concentration gradient also.*

Solution The concentration gradient is

$$\frac{dC}{dx} = \frac{(2 \times 10^{13}) - (4 \times 10^6)}{3 \times 10^{-3}}$$

$$= \mathbf{21.66 \times 10^{15}/m^4}$$

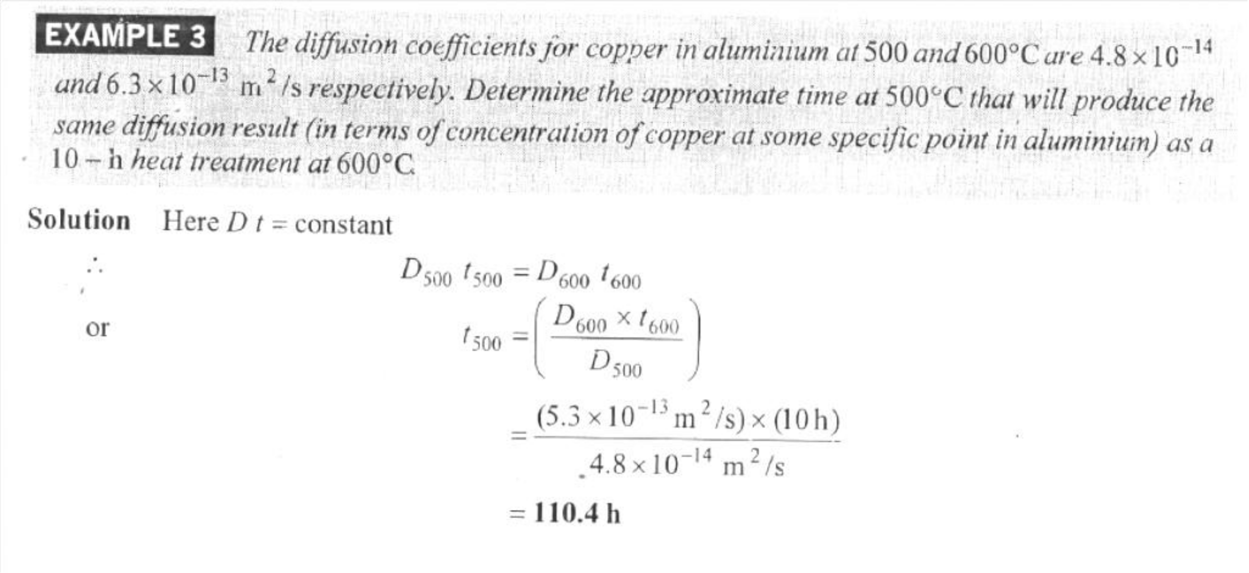
According to Fick's first law of diffusion

$$J = -D\left(\frac{dC}{dx}\right)$$

$$10^{21} = -D \times (21.66 \times 10^{15})$$

$$\therefore \quad D = -\frac{10^{21}}{21.66 \times 10^{15}}$$

$$= \mathbf{-0.15 \times 10^6\ m^2/s}$$



EXAMPLE 3 *The diffusion coefficients for copper in aluminium at* 500 *and* 600°C *are* 4.8×10^{-14} *and* 6.3×10^{-13} m^2/s *respectively. Determine the approximate time at* 500°C *that will produce the same diffusion result (in terms of concentration of copper at some specific point in aluminium) as a* 10 – h *heat treatment at* 600°C*.*

Solution Here $D\,t$ = constant

$$\therefore \quad D_{500}\, t_{500} = D_{600}\, t_{600}$$

$$\text{or} \quad t_{500} = \left(\frac{D_{600} \times t_{600}}{D_{500}}\right)$$

$$= \frac{(5.3 \times 10^{-13}\ \text{m}^2/\text{s}) \times (10\ \text{h})}{4.8 \times 10^{-14}\ \text{m}^2/\text{s}}$$

$$= \mathbf{110.4\ h}$$

UNIT-IV

MAGNETIC MATERIALS

Syllabus: Dia-, Para-, Ferri- and Ferromagnetic materials, Classical Langevintheory of dia magnetism. Curie's law, Weiss's theory of ferromagnetism, Ferromagnetic domains. Discussion of B-H Curve. Hysteresis and energy Loss.

Introduction:

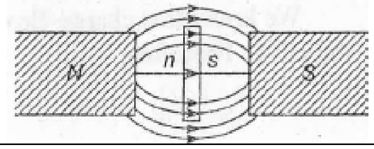
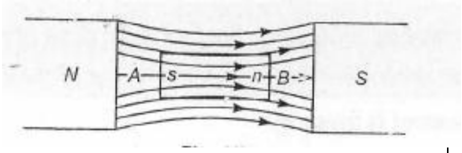
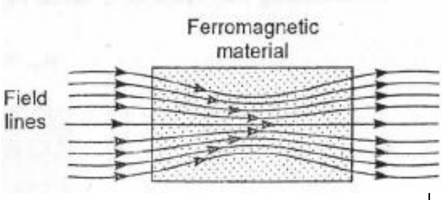
Magnetic materials are those substances which get magnetised when placed in a magnetic field. So, the substance develops magnetization which may be parallel or anti parallel to the applied field. The response may be strong or weak. Depending upon the magnitude and sign of response to the applied magnetic field, and also on the basis of temperature on the magnetic properties, all magnetic, all materials are classified broadly under the following three categories

1. Diamagnetic materials
2. Paramagnetic materials
3. Ferromagnetic materials

Two more classes of materials have structures very close to ferromagnetic materials but they have quite different magnetic effects. They are

4. antiferromagnetic materials
5. Ferrimagnetic materials.

Para dia, and ferromagnetic substances

S.No.	Diamagnetic materials	Paramagnetic materials	Ferromagnetic materials
1	The substances which when placed in a magnetic field, acquire feeble magnetism opposite to the direction of magnetic field are known as paramagnetic substances	The substances which when placed in a magnetic field, acquire feeble magnetism in the direction of magnetic field are known as paramagnetic substances	The substances which when placed in a magnetic field, become strongly magnetised in the direction of magnetic field are known as ferromagnetic substances
2	Ex: Bismuth, Zink, Copper silver, gold, H_2O,Hg etc.	Ex: Aluminium, Platinum, Manganese, Copper chloride, oxygen, etc.	Ex: Iron, Nickel, Cobalt etc.
3	when a bar of dia magnetic substance is suspended between two magnetic poles, then the axis of bar becomes perpendicular to the magnetic field as shown in the figure 	when a bar of magnetic substance AB is placed in a magnetic field, it tries to concentrate the lines of force into it as shown in the figure 	when a bar of magnetic substance is placed in a magnetic field, it tries to concentrate the lines of force into it as shown in the figure 

4	. They are weakly repelled by a magnet	They are weakly attracted by a magnet	They are strongly attracted by a magnet.
5	The permeability little less than unity	The permeability ($\mu=B/H$) is little greater than one.	The permeability is very high
6	**Susceptibility** is little less than unity and negative	**Susceptibility** is little greater than unity and positive	**Susceptibility** is very high and positive
7	-	-	Above certain temperature , called Curie temperature, ferromagnetic substances changes paramagnetic substance $\chi \propto \frac{\mathbf{1}}{\boldsymbol{T}}$
			A few materials have their atomic moments arranged in such a way that the net magnetization is zero such materials are called antiferromagnetic

(d) Ferrimagnetic materials:

(i) It is a special case of antiferromagnetic in which antiparallel moments are of different magnitudes and a large magnetization arises.

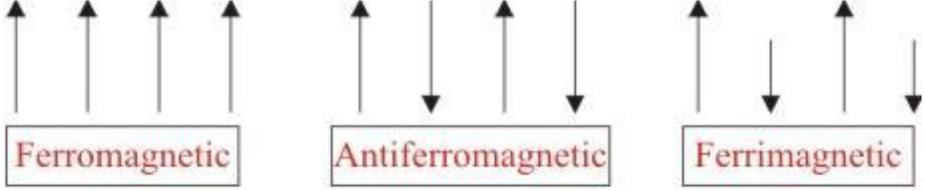
Examples : Ferrous Ferrite (FeO.Fe2O3) and Nickel ferrite (NiFe2O4)

(ii) Magnitude of susceptibility is very large and positive.

(iii) These materials also follow a temperature dependence of magnetization and susceptibility near Curie transition in a similar manner as shown by the ferromagnetic materials.

(iv) These materials, like ferromagnetic materials, show significantly large magnetization below the magnetic transition temperature and hence, often the temperature dependent behavior is clubbed with that of ferromagnetic materials.

A schematic representation of this inequality in the neighbouring magnetic moment can be like this:



Langevin's theory of diamagnetism:

An atom is made up of central positive nucleus and number of electrons revolving around it in discrete orbits. This will result in the production of magnetic field perpendicular to the plane of the orbit. Thus, the electronic orbits are associated with a magnetic moment. Most of the orbital planes are not parallel to each other and sense of rotation is not essentially the same. Hence, the vector sum of magnetic moments is zero and so there is no resultant magnetic moment for each atom.

But, in the presence of external magnetic field it causes a rotation action on the individual electronic orbits. This action produces an induced magnetic moment, which according to Lenz's Law will be in direction opposite to the field and hence tend to decrease the magnetic induction. This action is called diamagnetic action and the substances belonging to this action are called diamagnetic substances.

Theory:

Consider a circular orbit of radius 'r_0' in which an electron revolves with an angular velocity 'ω_0'. This constitutes a current of magnitude $\frac{e\omega_0}{2\pi}$ where $\frac{\omega_0}{2\pi}$ frequency and e is the charge of electron.

Therefore, the magnetic moment associated with this electron,

$$\mu_e = iA = \frac{e\omega_0 \pi {r_0}^2}{2\pi} = \frac{e\omega_0 {r_0}^2}{2}$$

where A = area of cross section of the circular orbit.

The angular momentum of the electron due to rotation of the electron of mass m

$= m{\omega_0}^2 \, {r_0}^2 = L$

Hence $\mu_e = \frac{eL}{2m}$

From Bohr's theory, L= nħ where n is an integral number.

Therefore, the magnetic moment of the electron is multiple of $\frac{e\hbar}{2m}$

i.e., where, $\mu_e = \frac{ne\hbar}{2m}$ $\frac{e\hbar}{2m}$ is called Bohr Magneton.

Here $\hbar = \frac{h}{2\pi}$ where 'h' is called the Planck's constant.

The total magnetic moment of the atom will be given by the vector sum of the moments of each orbit.

According to Larmor, the external field causes the 'Precession' of the orbits and velocity of the precession is given by,

$$\omega = \frac{-eB}{2m}$$

This produces a variation in the magnetic moment of the electron. The variation magnetic moment is given by

$$\Delta\mu_e = \mu_e(final) - \mu_e(initial)$$

$$\Delta\mu_e = \frac{1}{2}e(\omega + \omega_o){r_0}^2 - \frac{1}{2}e\omega_o{r_0}^2 = \frac{1}{2}e{r_0}^2[(\omega + \omega_o) - \omega_o]$$

$\frac{1}{2}e{r_0}^2\omega = -\frac{e^2B{r_0}^2}{4m}$ $\quad\quad\quad\quad$ $\because \omega = \frac{-eB}{2m}$

The negative sign shows that an increasing magnetic field tends to induce currents which produce a field opposite in direction to the applied field.

The above expression is only for an electronic orbit. Since complex atoms have electrons, the ${r_0}^2$ term is replaced by$\sum \vec{r}_0^{\,2}$ an appropriate average value since all the orbits are neither equal nor circular.

$$\Delta\mu_e = -\frac{e^2B}{4m}\sum \vec{r}_0^{\,2}$$

In a plane, $\vec{r}_0^{\,2} = \vec{r}_x^{\,2} + \vec{r}_y^{\,2}$

For a spherically symmetric atom, $\vec{r}_x^{\,2} = \vec{r}_y^{\,2} = \vec{r}_z^{\,2} = \frac{1}{3}\vec{r}^{\,2}$

where the bars indicate the average value for all the electrons. The magnetic moment per kilogram atom,

$$\Delta\mu = -\frac{Ne^2B}{4m}\frac{2}{3}\sum \vec{r}^{\,2} \quad\quad\quad \because \mu_0 = \frac{B}{H}$$

where N is the Avogadro number. If the atom possesses no intrinsic moment, the kilogram atomic susceptibility,

$$\chi = \frac{\Delta\mu}{H} = -\frac{Ne^2B}{6mH} = -\frac{\mu_0 Ne^2}{6m}\sum \vec{r}^{\,2}$$

$$\chi = -\frac{\mu_0 Ne^2}{6m}\sum \vec{r}^{\,2}$$

Results:

1. Diamagnetic susceptibility arises from the Larmor precession of the electronic orbits and it is determined by the charge distribution in the atom. It is independent of temperature.

2. The diamagnetism is the inherent property of all atoms and rnolecules. Only if the atom possesses an initial magnetic moment then it behaves as para or ferromagnetic.

Drawbacks:

1. In most of the diamagnetic materials the susceptibility varies with temperature at very low temperatures. But according to classical theory it is independent of temperature.

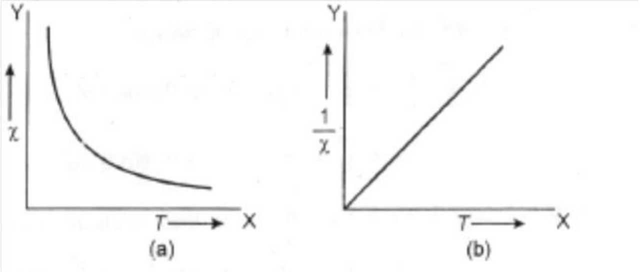
2. Further, the value of the susceptibility depends upon the physical nature of the material. But it is not indicated in this theory.

4.3 Curie’s law:

The gram molecular susceptibility of a paramagnetic gas varies inversely as absolute temperature. This is known as Curie's law.

$$\chi \propto \frac{1}{T}$$

The variation of susceptibility with temperature is shown in fig.



Weiss theory of ferromagnetism:

The transition metals Fe, Co and Ni exhibit magnetization even when the magnetizing field is removed. This phenomenon is called Ferromagnetism. Weiss postulated the existence of an internal molecular field ‘H_i’ which favours spontaneous magnetization of a ferromagnetic material and is proportional to the magnetization □ of the material. This magnetization ‘I’ is called spontaneous magnetization (i.e., the spontaneous magnetization is arisen in the absence of any applied field)

∴ $H_i = \lambda I$ where λ is molecular field coefficient or Weiss constant. The net effective magnetic field is then equal to $H + H_i$.

∴ $H_e = H + H_i = H + \lambda I$

$$I = \frac{\mu_0 \mu^2 N \lambda H_e}{3kT} = \frac{\mu_0 \mu^2 N \lambda}{3kT}[H + \lambda I]$$

$$I\left[1 - \frac{\mu_0 \mu^2 N \lambda}{3kT}\right] = \frac{\mu_0 \mu^2 N H}{3kT}$$

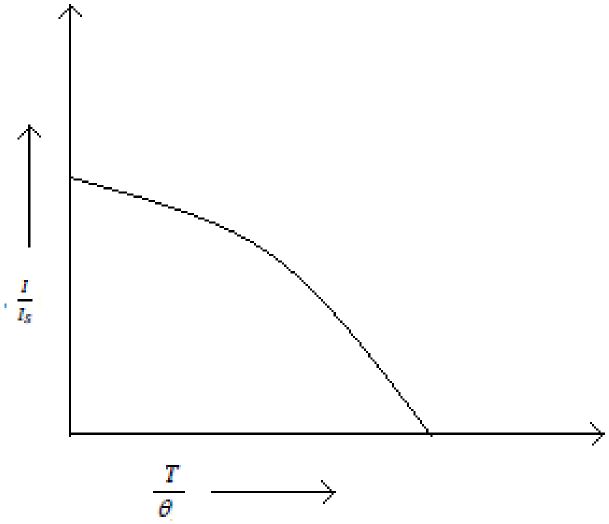
Put $\frac{\mu_0 \mu^2 N}{3k} = C$, and $\theta = C\lambda$, we get

$$I\left[1 - \frac{\theta}{T}\right] = \frac{CH}{T}$$

$$X = \frac{I}{H} = \left[\frac{C}{T\left(T\left[1 - \frac{\theta}{T}\right]\right)}\right] = \frac{C}{T - \theta}$$

This is called Curie - Weiss Law and θ is called curie temperature. *When* $T = \theta$, $\chi \longrightarrow \infty$ and for temperatures less than θ, the relation does not signify any meaning. This means field there exists a spontaneous magnetization even in the absence of external magnetic field. The material is ferromagnetic below Curie temperature, ‘θ" and becomes paramagnetic above curie temperature. Thermal agitation opposes the tendency of Weiss molecular field to align the molecular magnets. But below curie temperature Weiss field energy overcomes thermal energy. Consequently alignment of most molecular magnets results giving rise to magnetization of the material even in the absence of applied field - the so called phenomenon of spontaneous magnetization.

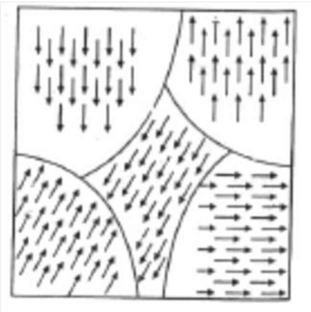
emperature dependence of spontaneous magnetization



Referring the experimental curve, when T= 0, $\frac{I}{I_s} = 1$. That is the spontaneous magnetization is maximum. Here I = spontaneous magnetization and Is = saturation magnetization; When T= θ and $\frac{I}{I_s} = 0$ the spontaneous magnetization vanishes.

When temperature is low, Weiss field overcomes the thermal energy and at T = 0 gives rise to maximum magnetization. But as the temperature increases thermal energy increases which randomises more and more of the parallel spins and at Curie temperature, the parallel alignment of all spins vanishes resulting in the zero value of spontaneous magnetization. The substance becomes paramagnetic.

4.5 Domain theory of ferromagnetism:



Weiss proposed this concept of Domains in 1907 to explain the hysteresis effect observed in Ferromagnetic materials as well as to explain the properties of Ferromagnetic materials. A region in a ferro or ferri-magnetic material where all the magnetic moments ate aligned in the same direction is called a domain. So a ferromagnetic material is divided up into these small regions, called domains, each of which is at all times completely magnetized. The direction of magnetization, however, varies from domain to domain and thus the net macroscopic magnetization is zero in a virgin specimen in the absence of external magnetic field. But when the ferromagnetic material is in the magnetic field, in the initial stages of magnetization in the material, the domains having moments parallel to the magnetic field increases in area; in the final saturation stage the other domains are rotated parallel to the field. Similarly if we demagnetize the material the regular domain arrangement is changes and it is different from the original state. This creates the hysteresis in the ferromagnetic substances.

Further, this theory can explain the following

i. If a magnet is broken into pieces, each piece will be a magnet with a north and a south pole. This is because the domains continue to remain in broken pieces.

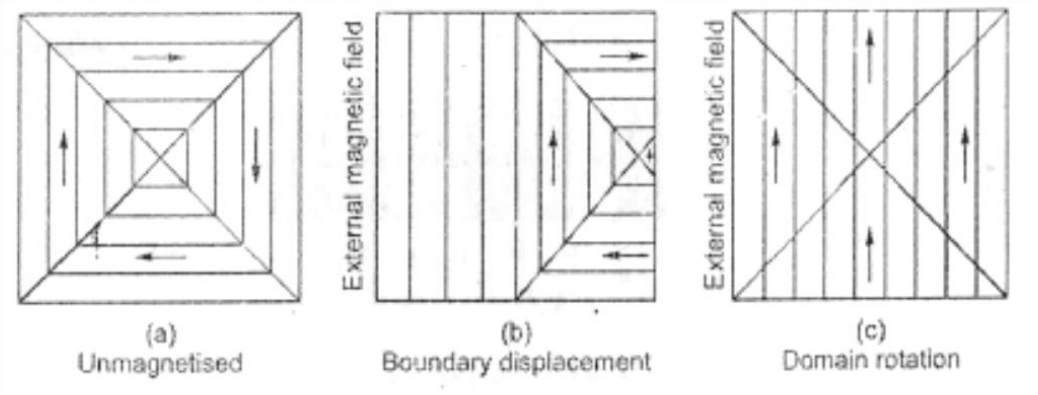
ii. A magnet heated or roughly handled tends to lose its magnetism. This is because the alignment of the domains in the magnet is likely to be disturbed during heating and rough handling. Hence, magnetism is reduced or lost.

iii. Domains of soft iron are easily rotated with a comparatively small magnetizing force and hence they are very easily magnetized or demagnetized. In the case of steel a large force is required for rotating the domains which explains the high retentivity of that material.

iv. A specimen when magnetized suddenly experiences a slight change in its length which is due to rearrangement of domains inside. This is called magnetostriction.

There are two possible ways to align a random domain structure by applying an external magnetic field.

i.By the displacement of the boundaries of the domains**:** Consider an unmagnetised specimen in which each domain is spontaneously magnetised. The direction of magnetisation is shown by arrow mark (fig. a). When substance is placed in magnetic field (fig. b), the domains which are oriented favourable with respect the to the external field increase in size field while those oriented opposite to the external domains are reduced.



(a) Unmagnetised (b) Boundary displacement (c) Domain rotation

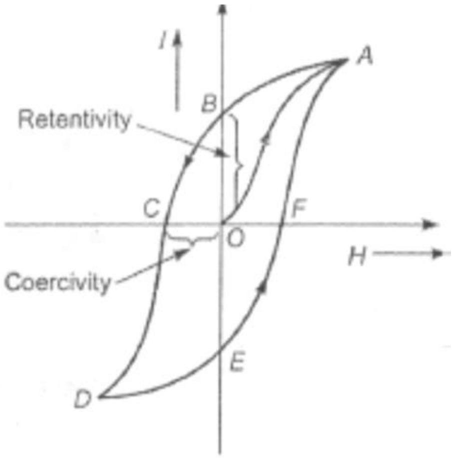
ii.By the rotation of domains**:**

The domains rotate until their magnetic momenta aligned more or less in the direction of external magnetic field (fig. c).

When the external field is weak, the substance is magnetised mostly by the boundary displacement. On the other hand, in strong magnetic fields, the magnetisation takes place mostly by the rotation of domains. When the domain vectors are oriented parallel to the direction of field, the stage is called as saturation limit. On the removal of external field, the boundaries do not move completely back to their original position and hence, the substance is not completely demagnetised, i.e., there still remains some residual magnetism. At high temperature, the domains are broken up and the ferromagnetic substance becomes paramagnetic.

B.H. CURVE:

Consider an unmagnetised ferromagnetic substance (say iron bar) in a magnetising field. The ferromagnetic materials show a relation between intensity of magnetization and strength of magnetic field. This property is called hysteresis. The literal meaning of hysteresis is retardation or lagging of an effect behind the cause of the effect. When the bar is slowly magnetised, the variation of intensity of magnetisation *I* is shown in fig. The curve so obtained is known as hysteresis curve.



Significant Features of Hysteresis Curve:

(i) When substance is slowly magnetised, the intensity of magnetisation I increases with field H. Part OA of the curve shows that I increases with H. At point A, the intensity of magnetisation I becomes constant, i.e., it has acquired its saturation value. Now we say that bar has acquired a state of magnetic saturation.

(ii) Now consider that the magnetising field H is decreased. It is obvious from the figure that intensity of magnetisation also decreases without following path AO. It follows the path AB. At B, the intensity of magnetisation has some value while magnetising field H is zero. The value of intensity of magnetisation for which H = 0 is called retentivity or residual magnetism. Hence, the retentivity or remanence is defined as the intensity of magnetisation remaining in the substance when the magnetic field has been reduced to zero.

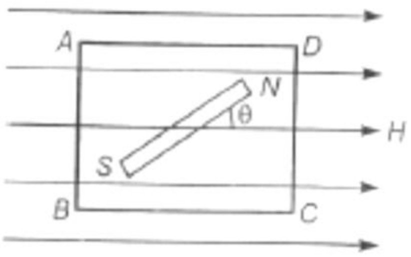
(iii) Further, consider that direction of H is reversed. In this case, the curve BCD is obtained. For the part BC, the value of I decreases as the value of H is increased in reverse direction upto a point C where I is zero. This shows that a magnetising force OC is required to reduce the residual magnetism. The value of magnetising force is called coercive force or coercivity. So the coercivity is a measure of the magnetising field required to destroy the residual magnetism in the specimen. Further increasing of H in reverse direction gives a saturation point D. The point D is symmetrical to A.

(iv) If now the field is increased in steps, a curve DEFA is obtained.

It can be observed from the figure that throughout the cycle ABCDEFA, the intensity of magnetisation I lags behind the magnetising field H. Thus, the lagging of intensity of magnetisation behind the magnetic field is called hysteresis and the path ABCDEFA as hysteresis loop. So, a closed curve in H-I plane is called as hysteresis loop.

4.7 Hysteresis loss:

When a ferromagnetic substance is taken through a cycle of magnetisation, the energy is expended. The energy is utilized in aligning the molecular magnets in the direction of magnetic field. When the magnetising field is removed, the energy required to magnetise a specimen is not completely recovered. The reason is that the magnetisation does not fall to zero. In this way, there is a loss of energy in taking a ferromagnetic substance through a cycle of magnetisation. The loss of energy can be calculated in the following way:



Consider unit volume ABCD of a magnetic substance containing N elementary magnets placed in a magnetising field of intensity H as shown in fig. Let at any instant, during the process of magnetisation, an elementary magnet NS make an angle ‘θ’ with the direction of magnetising field H. Suppose ‘M’ be the magnetic moment of each elementary magnet. Then, the component of M parallel to the direction of the field will be M cos □ while the component of M perpendicular to the direction of field will be M sin θ.

Now, the magnetic moment per unit volume (i.e., intensity of magnetisation I) parallel to the field is

I=$\sum M \cos\theta$ ……….......(1)

The magnetic moment per unit volume perpendicular to the field is

I=$\sum M \sin\ \theta$……………...(2)

(∵ There can be no magnetisation perpendicular to H)

When I is increased by an amount dl, then

dI = d$\sum M\cos\theta = \sum Md(\cos\theta) = -\sum M \sin\ \theta\ d\theta$ … …….(3)

The negative sign shows that I decreases as θ increases.

The torque due to the field acting on the dipole of moment ‘M’ when it is inclined at an angle θ to the field is given by

$$\tau = \mu_0 MH\ sin\theta d\theta$$

So, the work done when it moves through a small angle +dθ is $-\mu_0 MH\ sin\theta d\theta$. Here we have used negative sign because the work has to be done against the magnetic field in increasing θ by dθ. Hence, the work done per unit volume of the material is

dW=$-\Sigma\mu_0 MH\ sin\theta d\theta$ ……….. ...(4)

Substituting eq. (3) in eq. (4), we get the work done per unit volume in turning the elementary magnets through a small angle dθ.

W=$\mu_0 HdI$ … … ....(5)

Thus, work done by the magnetising field per unit volume of the material for completing a cycle is

$W = \oint \mu_0 HdI$...................(6)

= area of I - H loop

This is known as Warburg's law.

Since, the magnetic induction B is related to magnetisation I by the relation

$$B = (H + I) or\ dB = \mu_0(dH + dI)$$

$dI = \left(\frac{dB}{\mu_0} - dH\right)$ … .....(7)

Substituting the value of dI in eq. (6), we get

$$W = \oint \mu_0 H \left(\frac{dB}{\mu_0} - dH\right) = \oint HdB - \mu_0 \oint HdH = \oint HdB - 0$$

$\oint HdH = 0$, because the plot of H against H is a straight line and area enclosed by it is zero.

W=$\oint HdB$ =area of B−H loop

So, the work done per unit volume of the material per cycle is equal to μ_0 times the area of I-H loop or area of B-H loop. The work is measured in joule/m per cycle and is dissipated in the form of heat. In this way, the area enclosed by a complete hysteresis loop on I-H curve or B-H curve denotes the energy dissipated of the material during each magnetic cycle.

UNIT-V

Dielectric Materials

Introduction: Dielectrics are the substances which do not contain free electrons or the number of such electrons is too low to constitute the electric current. In dielectrics, the electrons are tightly bound to the nucleus of the atom.

Examples: Mica, glass, plastic, etc.

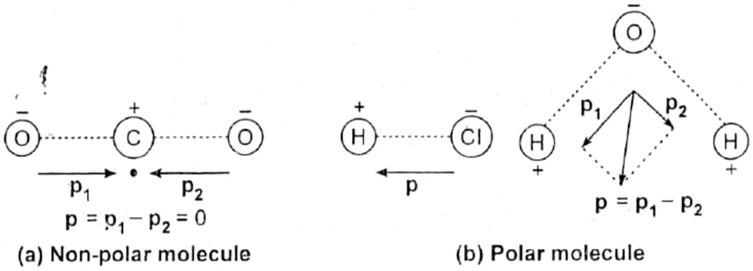
A non conducting material acts as a source of storage of electrical charges. Therefore, they are known as dielectrics. So to be a good dielectric, the material must be an insulator.

Differences between dielectrics and conductors:

S.No.	Dielectrics	Conductors
1	Dielectrics do not contain free electrons	Conductors contain free electrons.
2	They do not conduct electricity below its critical field.	They conduct Electricity
3	Above critical field strength, they lose insulation property.	They always conducts electricity.
4	Electrons are tightly bound to the nucleus.	Electrons are loosely bound to the nucleus.
5	Ex: Mica, glass, plastic	Ex: gold, silver, copper, iron

Uses of dielectric:

1) It helps to maintain two large metal plates at very small separation.
2) It helps to increase potential difference across a condenser.
3) It helps to increase capacitance of a capacitor.



(a) Non-polar molecule (b) Polar molecule

Non-Polar dielectric: We known that atom consists of positive and negative charges in equal magnitudes. The positive charge of the nucleus is concentrated at centre of gravity of the positive charge. Similarly, the negative charge of electron is concentrated at the centre of gravity of negative charges. When these two centers of gravity coincide, the molecule is known as non-polar molecule. The non-polar molecules have symmetrical structure and zero dipole moment.

Examples: H_2, O_2, N_2 etc..

Polar dielectric : When the positive and negative charge centers of gravity do not coincide, the molecule is called as polar molecule. Such molecule has un-symmetrical structure and a permanent dipole moment.

Examples: H_2O, HCl, NH_3 etc..

Dielectric constant or Relative permittivity(k) : We define dielectric constant as follows

1) Def: The ratio of the capacitance of a condenser with dielectric to the capacitance of the same condenser without dielectric is defined as dielectric constant.

$$k = \frac{C}{C_0}$$

   We have studied that when dielectric is placed between the plates of a conductor its capacity is increased.

2) Instead of maintaining the two capacitors at the same potential difference, we can give the same charge to each capacitor. It has been observed that the potential difference V_d between the plates of the capacitor filled with dielectric is smaller than the potential difference V_0 without dielectric.

Def: The ratio of potential difference without dielectric to the potential difference with dielectric is defined as dielectric constant (k).

$$k = \frac{V_0}{V_d}$$

3) According to Coulomb's law the force of attraction or repulsion between two electric charges q_1 and q_2 separated at a distance r in free space is given by

$$F_0 = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}$$

When the charges are placed in some other medium, then

$$F = \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r^2}$$

Where $\in$ = permitivity of the medium

$$\therefore \frac{F}{F_0} = \frac{\varepsilon_0}{\varepsilon} = \frac{1}{k}$$

$\therefore k = \frac{\varepsilon}{\varepsilon_0}$

Def: The ratio of permittivity of medium to the permittivity of free space is defined as dielectric constant(k)

.

$$And\ also \quad k = \frac{F_0}{F}$$

Def: The ratio of force between two charges in air or vacuum to the force between the same charges in a medium is known as dielectric constant (k).

Dielectric strength:

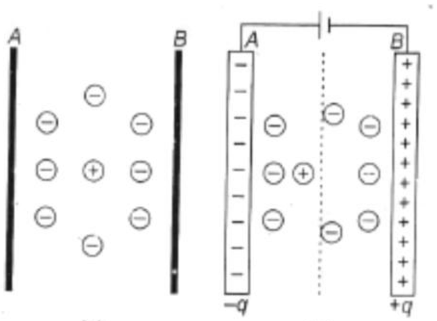
Def: The maximum electric field that it can maintain without electric breakdown is known as dielectric strength.

Let us consider that a dielectric is placed between the plates of a parallel plate capacitor and a potential difference is maintained between the plates. As the potential difference is increased, the strength of electric field increases. Now, the molecules of the dielectric feel more and more stretched. If the dielectric field is further increased by increasing the potential difference gradually, a stage is reached when the electrons break- up from the molecules of dielectric. As a result, the electrons become conducting.

The dielectric strength of a dielectric may also be defined as the critical value of electric field intensity below which the dielectric behaves as an insulator and above which the dielectric behaves as conductor.

The dielectric strength depends on the thickness of the insulating material and the duration for which the dielectric is subjected to an electric field. Moisture, surface irregularities, impurities are also responsible for dielectric strength.

Polarisation of dielectric material and Polarizability: Let a dielectric slab be placed between the two metallic plates which can be given to equal and opposite charges. The figure (a) shows the electronic structure of an atom when the two plates are not charged. When the plates are charged, that is an electrostatic field is established between the two plates as shown in the figure (b), the electrons are slightly displaced towards the positively charged plate while the positively charged nucleus towards the negatively charged plate. The electronic displacement is a function of the magnitude of the charges on plates and the nature of dielectric. In this way, the dielectric is acted upon by the forces and is said to be polarized. Now the distorted atom is called as electric dipole.



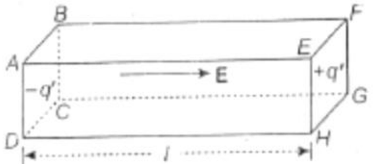
(a) (b)

The process of producing electric dipoles which are oriented along the field direction is called polarization in dielectric.

Expression for dielectric polarization: we have studied that an electric dipole has an electric dipole moment.

The electric dipole moment per unit volume is called as dielectric polarization P.

Suppose a dielectric slab of area cross section A and length l is placed in an electric field as shown in the figure. Let the induced charges on faces A B C D and E F G H be $-q'$ and $+q'$ respectively. The dipole moment P will be $q'l$. As volume of the slab is Al , hence the electric dipole moment per unit volume that is electric polarization P is given by



$$P = \frac{q'l}{Al} = \frac{q'}{A}$$

Hence dielectric polarization is numerically equal to the surface charge density.

Polarizability(α): when the strength of electric field is increased, the induced dipole moment μ also increases. The induced dipole moment is proportional to the intensity of electric field.

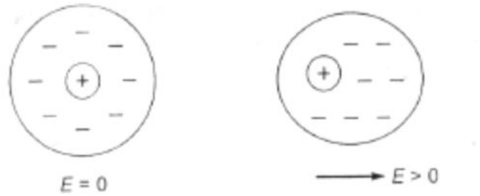
$$\therefore \mu = \alpha E$$

Here α is a constant of proportionality and is called polarizability.

Mechanism of polarization (polarizability): There are four different mechanisms by which electrical polarization can occur in dielectric materials when they are subjected to an external electric field. They are

1) Electronic polarization
2) Ionic polarization
3) Orientational polarization
4) Space charge polarization

1) **Electronic polarization**: The electronic polarization occurs due to the displacement of positive and negative charges in a dielectric material when an external electric field is applied. Figure(a) shows the charge distribution of an atom in the absence of the field while figure(b) shows the charge distribution in presence of applied electric field. This process occurs throughout the material and the material as a whole is polarized.



(a) Charge distribution in absence of field

(b) Charge distribution when field is applied

The displacement of positively charged nucleus and negatively charged electrons of an atom in opposite directions, on application of electric field is called electronic polarization.

As the nucleus and the centre of electron cloud are separated by a certain distance, dipole moment is created in each atom. The induced dipole moment P_e is proportional to field strength(E)

i.e., $P_e \propto E$

If there are N atoms in the dielectric then $P_e \propto NE$

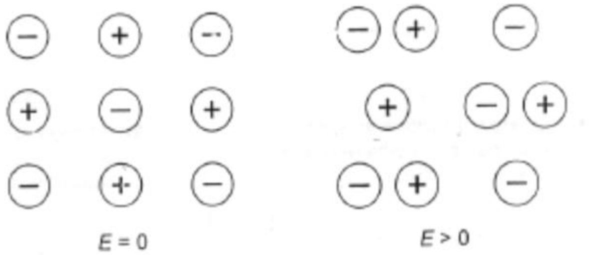
$$P_e = \alpha_e NE$$

Here α_e is Electronic polarizability. The electronic polarizability is independent of temperature.

2) **Ionic polarization**: Ionic polarization occurs only in those dielectric materials which possess ionic bonds such as NaCl as shown in figure (a). When such a material is subjected to an external electric field, the adjacent ions of opposite signs undergo displacement as shown in the figure (b).

The displacement causes an increase or decrease in the distance separation between the atoms depending upon the location of ion pair. This leads to a net dipole moment. This polarization is also independent of temperature.

Therefore ionic polarization is due to displacement of cations and anions in opposite directions and occurs in ionic solids.

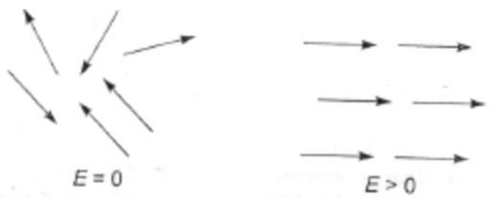


(a) Ion placement in absence of field

(b) Ion displacement in presence of field

3) **<u>Orientational polarization:</u>** Polar dielectrics exhibit orientational or dipolar polarizability. When in the absence of external electric field, the polar dielectrics exhibit dipole moment. The orientations of the molecule are random and hence the net dipole moment is zero. The dipole orientation is shown in the figure (a).

Def: When an external field is applied, the field tries to align these dipoles along the direction of field as shown in figure (b). This type of polarization is known as orientational polarization.



(a) Dipole orientation in absence of field

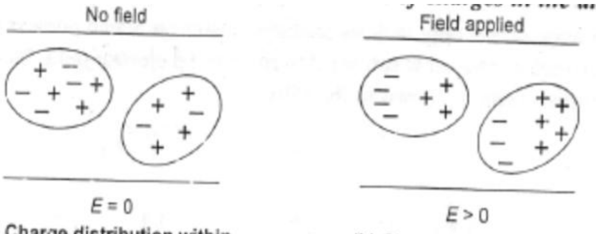
(b) Dipole alignment due to applied field

The orientation polarization is strongly temperature dependent. This decreases with increase of temperature.

4) **<u>Space charge polarization:</u>** Space charge polarization occurs due to the accumulation of charges at the electrodes or at the interfaces in a multiphase material. As shown in fig.(a) the ions diffuse over appreciable distance in response to the applied field. This gives rise to redistribution of charges in the dielectric medium.

The Space charge polarization is not an important factor in most common dielectrics.

The total polarization of a material is sum of electronic, ionic, and orientational polarization.



(a) Charge distribution within low resistivity phase in the absence of field

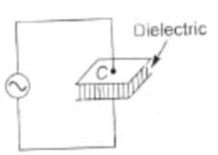
(b) Charge accumulation at the interface due to applied field

<u>Dielectric loss</u>: In order to understand the dielectric loss, let us consider the charging and discharging of a condenser. When a condenser is charged to a potential V, an amount of energy $\frac{1}{2}cV^2$ is supplied. This energy is stored as the electrostatic potential energy of the condenser. This energy resides in the dielectric medium. When the condenser is discharged, the same amount of energy should be released. In practice only a part of energy is released. The rest of energy is dissipated as heat. This is called as dielectric loss.

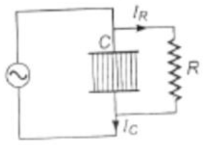
When the capacitor is charged, the dielectric medium comes under the influence of applied AC field. As a result, the molecules are polarized. Due to the polarization, the molecules come into a state of electrostatics stress. The molecules behave as electric dipoles. When the capacitor is discharged, the molecules should return to their normal unstressed state immediately. But to return to their normal state, the dipoles required some sort of internal friction. This involves the loss of energy. This energy is dissipated as heat by the dielectric to the surroundings.

The dielectric loss may be defined as the loss of energy in the form of heat by dielectric medium due to internal friction developed in switching of dipoles to their normal state under the action of charging and discharging.

Expression for dielectric loss: Let a dielectric material be placed between the plates of a capacitor which is subjected to an alternating electric field as shown in the figure(a). As a result, the dipoles of the material are engaged in switching action. Now, the movements of dipole is opposed by internal friction. This action is equivalent to the presence of a resistance accompanying the capacitor as shown in the figure(b). We know that, when an alternating current flows through a resistor, the current I_R and applied voltage V are in phase as shown in the figure (c). When an alternator voltage is applied to a capacitor, the current I_C flowing through the capacitor leads the applied voltage by a phase angle 90^0 as shown in the figure (d).



(a) A dielectric is an alternating field



(b) A resistance accompanying the capacitor

Fig C

For pure resistance, I_R & V are in phase

Fig D

For a capacitor, I_C leads V by 90°

Consider the equivalent circuit of figure (b). Let a current I_R be flowing through the equivalent resistance R and I_C be the current through the capacitor. I_R will be in the direction of V while I_C will lead V by phase angle 90^0 as shown in the figure (E). the resultant of I_C and I_R is I. The angle between I and I_C is denoted by δ is called as dielectric loss angle. The tangent of this angle δ, that is $\tan\delta$ is called as loss tangent. This is taken as a measure of electrical loss.

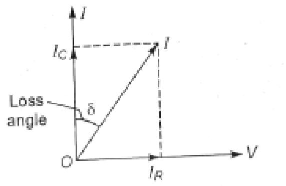


Fig. E Showing current through resistance and capacitor.

Dielectric loss = $V I_R = VI \cos(90-\delta)$

$= VI \sin\delta$………..(1)

(Dielectric loss is due to Joule heating=VI)

From Fig.(E) $I_C = I\cos\delta$ or $I = \frac{I_c}{Cos\delta}$……………..(2)

Substituting the value of I from equation (2) in Eq (1) we get

Dielectric loss=$V \times \frac{I_c}{\cos\delta} \times \sin\delta$

$= V I_C \tan\delta$……………(3)

Let X_C be the reactance of the capacitor then

$$X_c = \frac{1}{2\pi f c}$$

Where f is the frequency of a.c applied and c is the capacity of the capacitor.

Now, the current I_C is given by

$I_c = \frac{V}{X_c} = V \times 2\pi f c$……..(4)

Substituting tha value of I_C in eq.(3)we get

Dielectric loss = $V \times (V \times 2\pi f c)\tan\delta = V^2\ 2\pi f c \tan\delta$

Dielectric loss =$2\pi f c \tan\delta$

This expression shows that power loss depends on $\tan\delta$ provided factor like voltage, frequency and capacitance are constants. From figure (E), it is clear that for a given value of I_C, $\tan\delta$ is large when I_R is large. But large I_R means higher joule heating and hence large dielectric loss. Thus large $\tan\delta$ indicates higher dielectric loss.

Classification of dielectric material: Dielectric materials have forbidden energy gap greater than 3eV. The dielectric materials can be classified into the following two types:

1) Active dielectrics and
2) Passive dielectrics

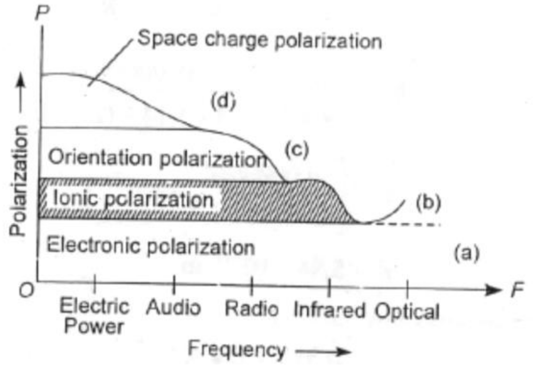
1) Active dielectrics: Consider a dielectric material kept in an external magnetic field. If it actively accepts the electricity, then it is known as active dielectric material. Therefore, active dielectrics or the dielectrics which can easily adapt themselves to store the electrical energy in it.
   Examples: Piezo- electrics, Ferro- electrics etc.
2) Passive dielectrics: Passive dielectrics are the dielectrics which restrict the flow of electrical energy in them. So, these dielectrics act as insulators.
   Example: All insulating materials such as mica, rubber, glass, etc.

Factors affecting polarization:

1) **Temperature dependence**: The electronic and ionic polarizations are almost independent of temperature. But at slightly higher temperatures, they show an increasing trend.

   The orientation and space charge polarization are temperature dependent.

   The orientation polarization is inversely proportional to temperature that is, it decreases with increase of temperature. At high temperatures, the orientational polarization contribution is very small because it becomes difficult for the dipoles to align themselves along the field direction against the thermal agitation. However, in space polarization, when the temperature is increased the ions can easily overcome the activation barrier and hence they diffuse through inter-atomic distances. So, Ɛ will increase with the increase of temperature.
2) **Frequency dependence**:
   i) **Electronic polarization** : This is very rapid and will complete at the instant the voltage is applied. The reason is that electrons are very light elementary particles than ions. Therefore, they follow alternations of electric field up to very high frequencies. This kind of polarization occurs during every cycle of the applied voltage. This is shown in the figure (a).



   ii) **Ionic polarization**: This is slower than electronic polarization. In this case, ions are heavier than electron cloud. In addition, the frequency of applied electric field with which the ions will be displaced is equal to the frequency of the lattice vibration (nearly equal to 10^{13} Hz). At optical frequencies, there is no ionic polarization. If the applied voltage is less than 10^{13} Hz as shown in the figure(b), the ions have enough time to respond during each cycle of the applied field.
   iii) **Orientational polarization:** This is even slower than ionic polarization. The relaxation time for this case varies with respect to the dielectric materials used. The molecules in the liquid easily re-orient themselves as compared to solids. This type of polarization occurs at audio or radio frequency ranges as shown in the figure(c).
   iv) **Space charge polarization**: This is the slowest process. This occurs at very low frequencies as shown in the figure(d). In this case, a whole body of charges has to be moved through the electric.

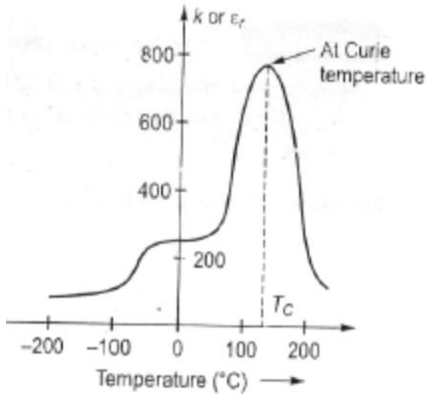
   So, we observe that at low frequencies, all the four types of polarizations occur and the total polarization is maximum.

Polarization curve and hysteresis loop:

Ferroelectrics: So far, we have considered the dielectric materials whose polarization depends directly on the applied field. A plot of polarization P verses field gives a straight line, that is varies linearly. Therefore, the ordinary dielectrics are often called linear dielectrics. These dielectrics do not possess polarization in absence of field.

However, there is a class of dielectric materials (Ferro electrics) which possess the following characteristics:

1) The relationship between polarization P and applied field E is complex in nature and therefore they are nonlinear.
2) The dielectric constant of ordinary dielectrics does not change much with temperature. However, in case of ferroelectrics, the dielectric constant depends on temperature.



The variation of dielectric ε_r or k as a function of temperature is shown in the figure(a).

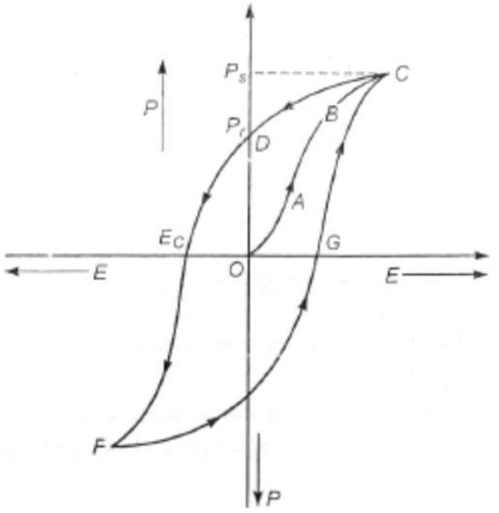
It is clear from the figure(a) that initially ε_r increases linearly with temperature and then it exhibits one sharp maximum where the dielectric constant ε_r reaches to its maximum value. Finally, the dielectric constant drops significantly above a critical temperature. This temperature is called Curie temperature.

3) The most important feature of these dielectrics is that they exhibit the electrical hysteresis for the variation of polarization with the applied field. This is analogous to the way in which ferromagnetic materials exhibit magnetic hysteresis for the variation of B with H. Due to this feature, these dielectrics are named as ferroelectrics.

Therefore, Ferro electric materials are that class of dielectric materials which possess electrical properties which are analogous to the magnetic properties of a ferromagnetic material.

Examples of ferromagnetic materials are barium titanate ($BaTiO_3$), potassium dihydrogen phosphate (KH_2PO_4), Rochelle salt, etc.

Ferro electricity: **The intrinsic Ferro-electric property is the possibility of change of orientation of the polarization direction by an electric field**. This leads to hysteresis curve in polarization P and electric field E.



When a ferroelectric specimen is subjected to electric field, the polarization P versus electric field E describes a closed loop called as hysteresis loop as shown in the figure. Let initially, the specimen has polarization equal to zero. When the electric field is applied to the specimen, the polarization increases along the curve OABC. After the point C, the polarization will not increase even if E is increased. The interaction of point C on polarization axis represents the saturation polarization (P_S).

When E is reduced gradually such that E=0, the curve traces the path CD. It is observed that certain amount of polarization called remnant (remain) polarization (P_r) is still present. This is the polarization that exists in the absence of external field. Therefore, it is called as spontaneous polarization.

In order to reduce the polarization to zero, a field in reverse direction must be applied. This is denoted by E_C called as coercive field.

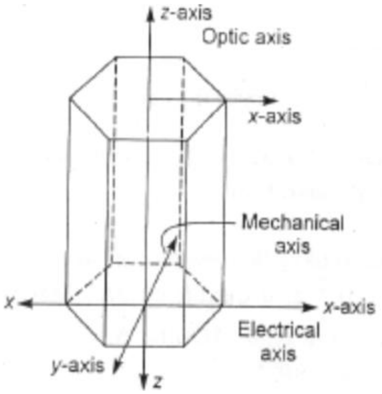
Further increase of field brings the specimen to saturation state.

When the field is brought to zero and increased in the positive direction, a curve FGC is traced. Now the hysteresis cycle is completed.

The area bounded within the curve represents the loss of electrical energy /cycle.

Applications: The following are the applications of ferroelectrics

1) Due to high value of dielectric constant, they are used to manufacture small sized capacitors of large capacitances.
2) Piezoelectric transducer to produce and detect sound waves.
3) Using the hysteresis curve, they can be used as memory device in computers.
4) They are used to detect infrared radiation.
5) They are used in electromechanical filters.

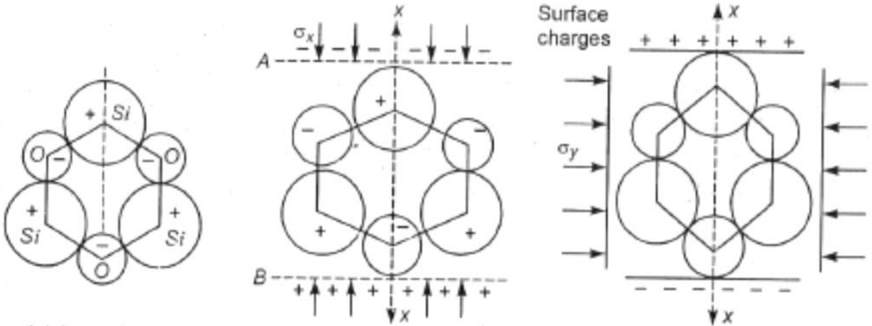


Piezoelectricity : Piezoelectric effect was discovered by Curie brothers in 1880, when compressed or stretched in a certain direction become polarized and depolarization charges appear on its surface, that is a potential difference is produced along a perpendicular axis. **The polarization of dielectric as a result of mechanical deformation is called as Piezoelectric effect**. The Crystals that exhibit the piezoelectric effect are called piezoelectrics. These materials also exhibit inverse piezoelectric effect, i.e., when an electric stress is applied, the material becomes strained. The strain is directly proportional to the applied field. It is important to mention here that all ferroelectrics are piezoelectric but all piezoelectric materials need not necessarily be ferroelectric. The quartz crystal is only piezoelectric while barium titanate exhibits both ferroelectricity and piezoelectricity.

Piezoelectricity in quartz:

The atoms are arranged in the hexagonal form in the plane of paper. The hexagonal prism is shown in the figure. The hexagonal prism has three major Axes.

i) Optic axis or z-axis
ii) The electric axis or x-axis. The axis passes through any set of opposite corners.
iii) The mechanical axis or y-axis. This axis passes through the opposite faces.



(a) Arrangement of atoms

(b) Crystal under stress (longitudinal)

(c) Crystal under stress (transverse)

When the Crystal is not under stress, all the charges are balanced as shown in the fig.(a). When the Crystal is stressed fig (b), the equilibrium is disturbed. In this case, the crystal is polarized. As a result, the electric charge is developed on faces A and B. This is known as longitudinal effect. Similarly, a transverse effect is shown in fig (c).

The charge developed on a given area on the Crystal face is proportional to the area affected by the pressure. Therefore, it is proportional to the force acting normally on the surface. This explains the piezoelectricity in a quartz crystal.

Pyroelectricity: When the temperature of the specimen is changed, there is a change in spontaneous polarization. This effect is known as pyroelectric effect. This branch of physics is known as pyroelectricity.

The pyroelectric coefficient λ is defined as the change in polarization per unit temperature change of specimen. Therefore,

$$\lambda = \frac{dP}{dT}$$

Due to the change in polarization, there will be a corresponding change in external field. This results in a change of charge on the surface. It is possible to detect a charge of 10^{-16}C using a suitable electrometer. Therefore, a temperature change as small as 10^{-6} ^{0}C can be measured using pyroelectric effect. The pyroelectric materials such as barium titanate, $LiNiBO_3$ etc. are used to make very good infrared detectors which can operate at room temperature.

<u>Clausius- Mossotti equation</u>: The molecules of non-polar dielectrics do not possess permanent dipole moment. However, when an external electric field is applied, dipole moment is induced. The polarization p_i is proportional to local electric field E_i

$P_i = \alpha_e E_i$…………..(1)

Here α_e *is the* electronic polarizability per atom.

If there are N molecules per unit volume of the dielectric, then polarization P is given by

$$P = \sum_i P_i = N\alpha_e E_i \quad \text{or} \quad \alpha_e = \frac{P}{NE_i}\text{…..(2)}$$

$Here\ E_i = lorentz\ field = E + \frac{P}{3\epsilon_0}$…………..(3)

Substitute the value of E_i in equation (2) we get

$\alpha_e = \frac{P}{N\left(E+\frac{P}{3\epsilon_0}\right)}$…..(4)

$But\ P = \epsilon_0\ (\epsilon_r - 1)E$

$\therefore E = \frac{P}{\epsilon_0(\epsilon_r-1)}$…………………..(5)

$From\ eqs\ (4)\ \&\ (5)$, we get

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

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

$$\frac{N\alpha_e}{\epsilon_0} = \frac{1}{\left(\frac{1}{(\epsilon_r-1)}+\frac{1}{3}\right)} = \frac{1}{\frac{3+(\epsilon_r-1)}{3(\epsilon_r-1)}} = \frac{3(\epsilon_r-1)}{\epsilon_r+2} =$$

$$\frac{(\epsilon_r-1)}{\epsilon_r+2} = \frac{N\alpha_e}{3\epsilon_0}$$

This is known as Clausius-Mossotti equation

In general $\frac{(\epsilon_r-1)}{\epsilon_r+2} = \frac{N\alpha}{3\epsilon_0}$

$Here\ \alpha\ = Total\ polarizability$

<u>Clausius-Mossotti equation in terms of refractive index:</u> According to Maxwell, the velocity of propagation of electromagnetic waves for an unbounded medium is given by

$$v = \frac{1}{\sqrt{\mu\epsilon}}$$

Here μ is the magnetic permeability and ϵ is the absolute permeability of the medium.

Let μ_0 be the permeability of non magnetic medium, then the velocity in such a medium is given by

$$v = \frac{1}{\sqrt{\mu_0 \epsilon}}$$

The refractive index of the medium is given by

$$n = \frac{velocity\ of\ \ in\ wave\ vacuum}{velocity\ of\ \ wave\ in\ medium}$$

$$n = \frac{1/\sqrt{\mu_0 \epsilon_0}}{1/\mu_0 \epsilon} = \sqrt{\frac{\epsilon}{\epsilon_0}} = \sqrt{\epsilon_r}$$

$$n^2 = \epsilon_r$$

This relation is known as Maxwell's equation.

Substitute the value of ϵ_r in Clausius-Mossotti equation we get

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha_e}{3 \in_0}$$

Specific polarization of dielectric: According to Clausius-Mossotti equation, we have

$$\frac{(\in_r - 1)}{\in_r + 2} = \frac{N\alpha_e}{3 \in_0}$$

The dielectric constant $\in = \frac{\in}{\in_0}$

$$\frac{(\in - \in_0)}{(\in + 2 \in_0)} = \frac{N\alpha_e}{3 \in_0}$$

$\frac{(\in - \in_0)}{(\in + 2\in_0)}$ is known as Specific polarization of dielectric.