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T.Y.B.Sc. Chemistry Syllabus, Pattern – 2015

Inorganic Chemistry (CH-342), Semester-IV,

Chapter -2

METALS, SEMICONDUCTORS and SUPERCONDUCTORS

Metals are generally hard, high melting and boiling point, ductile, malleable, good conductors of heat and electricity, opaque, lustrous, high reflecting power, high coordination number. Chemically there properties depend on cation. Metals have low Ionization potential and by losing their valence electron to form positive charged ion.

Nature of Bonding in Metals (Metallic bonding): -

The atoms in metal are held together by special type of bond. The force that bind metal atom to number of electrons within sphere of influence is called as metallic bond. The metallic bond can explain characteristic properties of metals.

Theories of Metallic bond: -

Characteristics of metallic bond: -

1) It should have ability to bind identical metallic atom.
2) Non-directional character and bond are most of metallic properties are not change when metal is in liquid state.
3) It should have ability to transfer electron from atom to atom.

I) Free Electron Theory: -

Metals have low ionization potential and radially lose their valence electron and form positive ion. These free electrons are delocalized. This theory explains electrical conductivity, malleability and ductility of metals. It fails to explain specific heat and magnetic properties.

II) Valence Bond theory: -

It was explain by Pauling. It was based on the concept of resonance. It considers that there is resonance of electron pair bond between each atom and its nearest neighbors. This theory explains physical proportion of metal. It fails to explain metallic character in solution state.

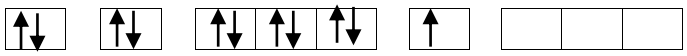
III) Molecular Orbital Theory (Band theory): -

This theory is known as *band model*. It was based on the molecular orbital theory. The MOT approaches to metallic bonding consider delocalization of free electron orbital over all the atoms in metal crystal.

Band theory for sodium metal: -

Consider crystal of metallic sodium. Its structure is with coordination number 8. Each sodium atom possesses the arrangement of electrons in the various energy levels.

Energy level	1s	2s	2p	3s	3p
No. of electron	2	2	6	1	0

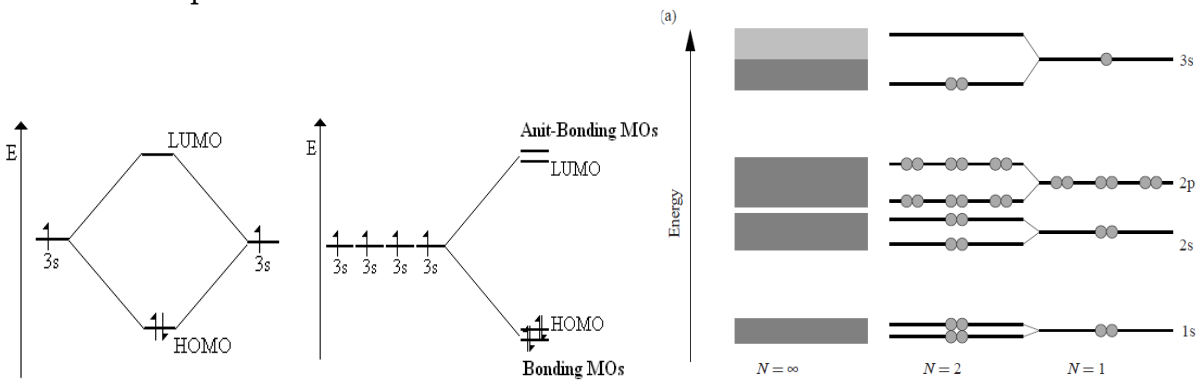


Each electron is occupies particular energy level. There is only one electron in valence level. In 3s level has one electron, while the 3p level ($3p_x$, $3p_y$, $3p_z$) is vacant. The basic requirement for metallic bond is the presence of empty orbital in

valence shell. Here sodium has filled 1s, 2s and 2p orbital, while 3s orbital is incompletely filled.

When two sodium atoms are closed to each other the 3s orbital of one atom is combines with 3s orbital of other atom to form two molecular orbitals i.e. bonding molecular orbital (BMOs) and antibonding molecular orbital (ABMOs). When three sodium atoms are combines together, then these three molecular orbitals will be formed BMOs, ABMOs and non-BMOs. Thus 'n' number of 3s atomic orbitals of 'n' number of sodium atoms on combining will form 'n' number of molecular orbitals in sodium crystal.

The energy levels of these molecular orbitals will be very close together, thus they can consider as continuous and form an **Energy Band**. Hence this theory is called as Band Model. When bringing of two Na atoms together leads to a molecular energy level picture and when adding more and more Na atom leads to the formation of quasi-continuous ***bands***.



MOT of Na_2 *MOT of Na_4* *MOT of Na_∞*

Each Na atom brings with it a single 3s valence electron. Hence, the Na_2 molecule will have 2 valence electrons in these Molecular Orbitals. The electrons will occupy the lowest energy orbital possible according to the Principle of Pauli and the Hunds Rule. If a cluster of 4 Sodium atoms now attempts to bond to form Na4, 4 atomic orbitals (3s) will combine to form 4 molecular orbitals (MO).

When energy levels are close together and form an energy band. This result interaction between various atoms orbital is increases gives broadening of energy band with decrease in interatomic distance. This results increase in width of energy band with decrease in interatomic distance. The lower energy orbital (2s, 2p) interact to form energy band at smaller inter atomic distance.

The formation of energy band in a crystal takes place when…

1) There are large number of atoms,
2) The atoms are sufficiently close to each other,
3) The combining atomic orbitals possess matching symmetry,
4) The atomic orbitals are of the same energy and have sufficient overlapping,
5) The interaction between the atomic orbitals is strong,
6) The energy band covers all atoms and belongs to the whole crystal, i.e. complete dislocation.

The sodium exists in vapour state as free atom. There are absences of energy band. When sodium atoms are brought closer and closer, then interaction between atomic orbitals increases and band width is also increases. The higher energy

orbital (3s, 3p) of sodium will interact to from energy band at great distance i.e. 3.71 Ǻ at which 3s and 3p energy bands overlaps with each other.

In general when there is an overlap of 'n' orbitals in 'n' atoms in structure 'n' molecular orbitals will be obtained. Each molecular orbital in band has two electrons. Thus 'n' electrons of will be filled in n/2 number of BMOs. Therefore, 3s band in sodium metal is half-filled.

Electronic energy bands

The filling of energy levels by electrons was done with following points…

1) The inner electrons of the metal are filled in localized orbitals and not in the bands. The valence electrons are filled in the delocalized energy bands.
2) The valence orbitals and the higher energy empty orbitals merge into the energy band. These bands are delocalized throughout the crystal structure of the metal.
3) As for the free atom, the distribution of the electrons takes place in the MOs or the energy level bands.

n(E) curve:-

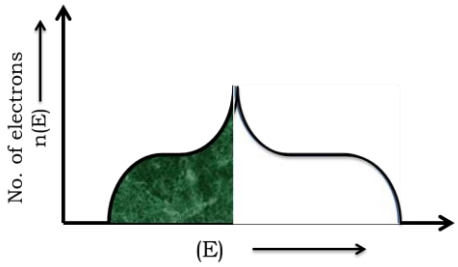
It gives the way in which electron are distributed in energy band between energy levels. The distribution of electron between range of energy level in energy band is given by curve is called a *n(E) curve*. Where n = no of electron in each band and E = energy of band.

Characteristics:

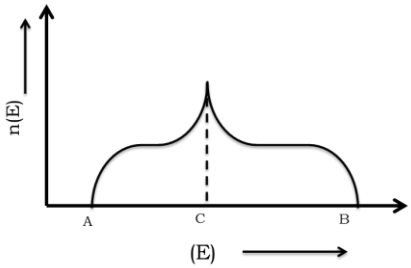
1) This curve represents energy band for particular energy level.
2) The area under curve is proportional to total number of electron.
3) The width of energy band varies from metal to metal. But it is in the range bet 1 to 10 eV.
4) The change in temperature changes filling of electron in available energy levels.

n(E) curve:

It gives the complete distribution of electrons between energy level in the energy band, is given by curve is called as n(E) curve. This curve gives density of energy levels. Here 'n' represent the number of electrons in each energy band and 'E' stands for the energy of the band. The energy distribution of the electrons in a band is given by plotting n(E) Vs. Energy. The dark shaded area in the curve is represents the filled band.



n(E) Vs. Energy curve



n(E) Vs. Energy curve at normal temperature

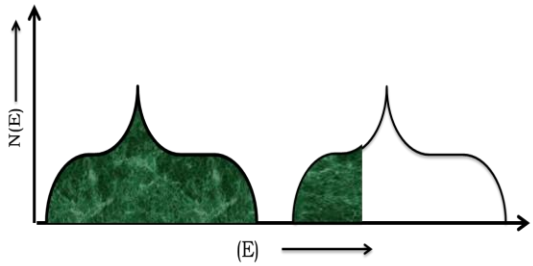
The characteristic of the typical n(E) curve for a metal at normal temperature are …

1) This curve represents an energy band for a particular energy level.

2) The area under the curve is proportional to the total number of electrons in the particular band.
3) The curve shows that 'C' is the most favored energy by electrons.
4) The breadth of the energy band varies from metal to metal, but it is in the range of 1 to 10 eV.
5) The change in temperature changes the filling of the electrons in the available energy levels or state within the bands. It also changes the shape of the curve.

N(E) curve:

This curve gives the density of energy levels. It is define as the curve which gives the number of energy level present in energy bands.



The characteristics of N(E) curves are …

1) 'N' represents total number of energy levels in each energy band and E stands for energy of band.
2) The number of N(E) curves depends on s, p, d, f energy levels. eg. Sodium atom has 1s, 2s, 2p, 3s, 3p energy levels.
3) N(E) curves are separated by energy gap. eq. N(E) curve for 3s is separated from N(E) for 3p.
4) The two N(E) curves may overlap with each other. eq. N(E) curve of 3s is overlaps with N(E) of 3p.
5) The shape of N (E) curve is important to determine electrical conductivity of metals.
6) The electrical conductivity of filled band is zero.

Comparison between the n(E) and N(E) curves: -

Sr. No.	n(E) curves	N(E) curves
1	It gives the energy distribution of the electrons in a band. It gives total number of electrons in the energy band	It gives the total number of energy levels. Each energy level has two electrons.
2	It is used to shows electron distribution between energy levels in band	It indicates actual energy levels in band
3	The area under the n(E) curve gives total number of electrons	The area under the N(E) curve gives total number of energy levels in the energy band
4	The area under the n(E) curve is double than that N(E)	The area under the n(E) curve is double than that N(E)
5	The n(E) curve will not extend at higher temperature	The N(E) curve will extend beyond n(E) curve at higher temperature

Electrical conductivity of metal:

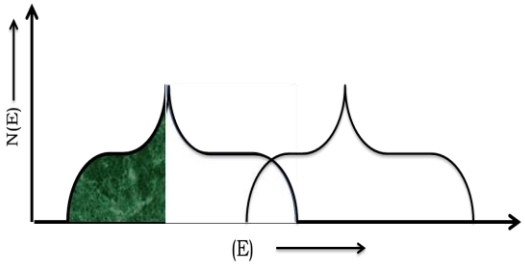
The conductors are material in which large number of free electrons is available for conduction. The mobility of electrons in metal requires delocalized

electron and vacant orbital (hole). According to band theory the energy of metal is depends upon…

1) The filled energy band overlaps with the vacant energy band.
2) The filled energy bands overlaps with incompletely filled band.
3) Incompletely filled bands.
4) The energy gap between the filled band and vacant band should be so small that the electrons from the filled energy band can be promoted at ordinary temperature to vacant band.
5) The filled band is usually called the **valence band** and the vacant or empty band is called **conduction band**.

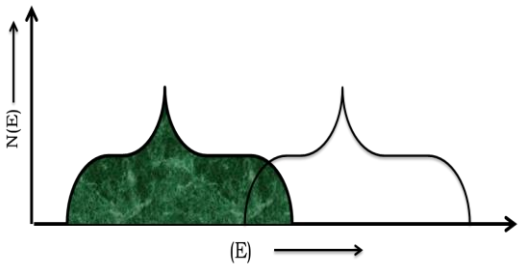
a) Electrical conductivity of univalent metals:

Univalent metals are Li, Na, K, Ag, etc. There metal has single electron in valence shell (ns^1). Example: ^{11}Na - $1s^2$, $2s^2$, $2p^6$, $3s^1$, $3p^0$. The capacity of 3s band is two electron. Here 3s band is half filled. The 3s band is overlaps with empty 3p band which gives greater number of energy levels for the movements of free electrons. Only half 3s band is filled by electrons and other half band remains vacant. This filled 3s band is overlaps with vacant 3p band. As a result electrons can moves from filled energy level to empty energy level gives to conductivity. It result into Sodium metal is good conductor of electricity.



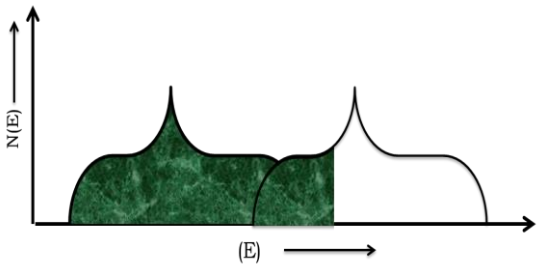
b) Electrical conductivity of divalent metals:

Divalent metals are Be, Mg, Co, Sr, Ba, etc. These metals have two valences electron (ns^2). Example: ^{12}Mg - $1s^2$, $2s^2$, $2p^6$, $3s^2$. The 3s level contain two electrons i.e. full filled level. We expect Mg metal is non-conductor, but 3s band is overlap with empty 3p band. It results electrons can move from filled to empty energy level shows electrical conductivity.



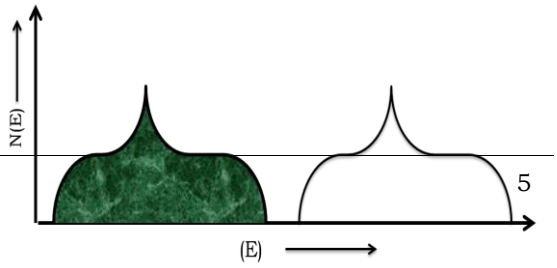
c) Electrical conductivity of trivalent metals: -

The most common example of the trivalent metal is Aluminum. ^{13}Al - $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$. The 3p orbital is incompetently filled. The Al metal contains filled 3s and incompletely filled 3p band. There is partial overlap of 3p band with 3s band. It results electrons can moves from filled to vacant energy levels gives electrical conductivity.



Insulator: -

The Diamond is insulator, i.e. nonconductor. In case of diamond, each carbon atom possesses four valence



electrons, ^{6}C - $1s^2$, $2s^2$, $2p^2$. Both 2s and 2p bands are separated by some gap. There are gap between filled band and empty band. Thus electrons cannot promote, result there is no flow of electrons. Example: Si, Ge, etc.

Effect of temperature and impurity on conductivity: -

1) **Effect of temperature: -**

As number of energy levels are increases in energy band, greater the free movement of electrons and hence higher the conductivity is observed. The expansion of metal on heating gives more space for electrons. Thus it is expected that the conductivity is increases with temperature. But actually conductivity decreases with increasing the temperature. This is because heating produces more atomic vibration, which disturbs crystal structure of metal and lattice energy. It result on free movement of electrons and thus decreases conductivity.

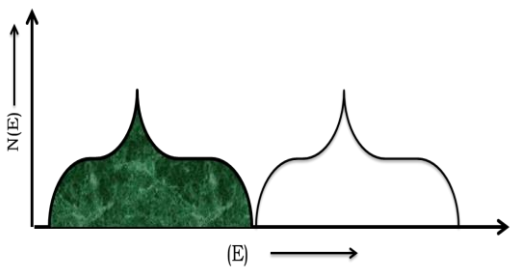
2) **Effect of impurity: -**

The regular atomic arrangement of crystal is disturbed by the addition of impurity. It produces defect in structure which result into decreases of conductivity of metal with addition of impurity.

Semiconductor: -

It is the material whose electrical conductivity is less than that of metal but greater than insulator is called as semiconductor. The semiconductor has both properties, i.e. insulator at low temperature and conductors at higher temperature. They shows very small energy gap between filled band and empty band. The electrical conductivity is increases with increasing in temperature and impurities. There are two types of semiconductors – intrinsic semiconductor and extrinsic semiconductors.

1) **Intrinsic semiconductor:-**



This material is insulator at absolute zero temperature and in pure form, while conductor at high temperature. Example: - graphite. There is small energy gap between filled band and empty band. When temperature increases electrons from filled band are excited and promoted into next higher empty band. This results conductivity in material. The conductivity of intrinsic semiconductors is increases with increasing in temperature. This is due to increase in number of excited electrons with increase in temperature.

2) **Extrinsic semiconductors: -**

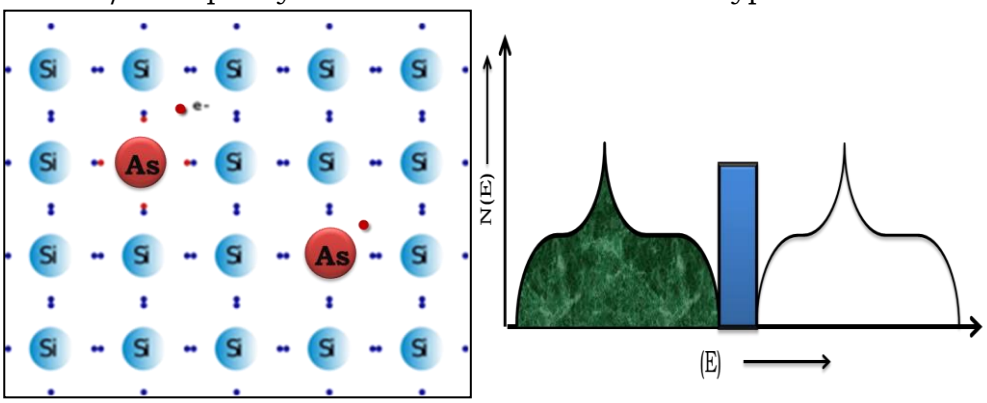
If impurities are added to normally insulator, the material becomes semiconductor called as impurity or extrinsic semiconductors. There are two types on the basis of nature of impurity added, a) n–type, and b) p–type semiconductors.

a) n-type semiconductors: -

Here 'n' is stands for negatively charged electrons. When an negative impurity atom was added; it has more valence electrons than insulator which creates n-type semiconductor.

Example:- Phosphorous/Arsenic (contains 5 electron – ns^2, np^3) are added to pure Silicon/Germanium (contain 4 electron - ns^2, np^2). Each 'As' atom was forms 4 covalent bonds with surrounding 4 Si; while 5th electron is remaining unused.

This extra electron is just below impunity band and it can be excited into empty band by heat or electric field. Crystal of pure Si/Ge becomes negatively charged due to donor P/As impurity atom. Hence it is called as n-type semiconductor.

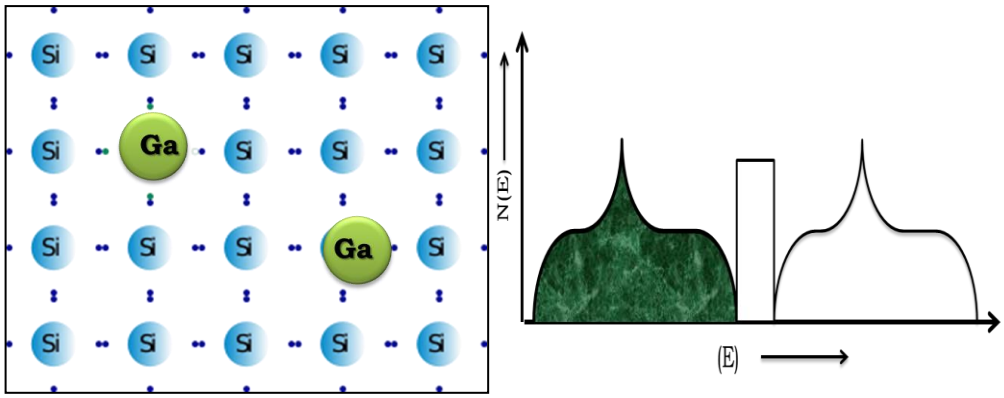


The impurity energy level is just below vacant band of the electron from empty conduction band. The electrons from impurity level can excite into empty conduction level. The conductivity of n-type semiconductor increases with increasing temp, but if large increase in temp, conductivity is decreases.

b) p-type semiconductors: -

Here 'p' stands for positive holes in pure element. When positive impurity atom was added; it has less number of valence electrons than insulator atom.

Example; - Ga/In (contain 3 valence electrons) are added to pure Si/Ge (contain '4' valence electrons). The 3 valence electrons from each Ga form were three covalent bonds with 3 Si. The 4th Si atom are linked with Ga atom by incomplete bond contain only one electron from Si. In this bond there is electron deficiency in lattice. This creates positive holes. The numbers of holes are equal to the number of Ga atom. The electron from neighbors moves into positive hole. The conductivity is due to movement of positive holes. Hence it is called as p-type semiconductor.



The impurity energy level is just above filled band of the valence band. The electrons from valence band are excited into empty impurity level and then into conduction band. Conductivity of p-type semiconductor increases with increasing temperature and impurity added.

Non-stoichiometry and Semiconductivity: -

Compounds in which constituent ions (cation and anion) are not in exactly same ratio as indicated by chemical formula such compound are called as Non–Stoichiometric crystals. Eq. FeO, ZnO, NiO, etc.

In FeO should be Fe_1O_1 but actual composition is $Fe_{0.95}O_1$, similarly ZnO is found $Zn_{1.08}O_{1.0}$ and in NiO is found $Ni_{0.98}O_{1.0}$

In FeO possess slightly less Fe^{2+} ions than O^{2-} ions, while ZnO possess slightly more Zn^{2+} ions than O^{2-} ions. Thus these compounds are non-stoichiometric. The number of +ve and -ve ions present are less or more than those expected but overall charge is neural in crystal.

There are two types of defect in crystal - Schottky defect, and Frankel defect

Schottky defect:

When there is excess of metal i.e. $Zn_{1.08}O_{1.0}$ compound, the excess electrons free to move in crystal and gives conduction. Such crystal is called as ***n–type semiconductor.***

Zn^{2+}	O^{2-}	Zn^{2+}	O^{2-}	Zn^{2+}
O^{2-}	Zn^{2+}	e^-	Zn^{2+}	O^{2-}
Zn^{2+}	O^{2-}	Zn^{2+}	O^{2-}	Zn^{2+}
O^{2-}	Zn^{2+}	O^{2-}	Zn^{2+}	O^{2-}
Zn^{2+}	e^-	Zn^{2+}	O^{2-}	Zn^{2+}

Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}
O^{2-}	Ni^{3+}	O^{2-}	Ni^{2+}	O^{2-}
Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}	Ni^{3+}
O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}
Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}

Frenkel defect:

When there is deficiency of metal, $Ni_{0.98}O$ In such compound, positive ion is absent from its normal lattice site. To balance this charge adjacent cation gets oxidized to higher oxidation state. In this crystal electron transfer takes place from Ni^{2+} to Ni^{3+}. This Ni^{3+} ion appears to moves through crystal since charge carries are positive center and crystal is called ***p-type semiconductor***.

COMPARISSION between conductor, semiconductor and insulator: -

	Conductor	**Semiconductor**	**Insulator**
Valence electron	Metals having 1/2 electron	Nonmetals 4 electron	Nonmetals – more than 4 electron
Energy gap betⁿ V.B. and C.B.	Absent or very small	Very small	Very large
Valence band	Half-filled / partially filled	Completely filled	Completely filled
Temperature.	High conductivity at R.T., at high temp conductivity is decreases.	Insulator at low temp, conductor at high at high temp	No conductivity by change in temp
Impurity	Conductivity decreases with addition of impurity.	Conductivity increases with addition of impurity.	No change in Conductivity

Applications of semiconductors:

1) In the preparation of thermostats and photocells - The thermostats are used to control temperature in heating device. The photocell is used for long distance signaling and automation.
2) The semiconductors are used in making thermocouples - which are used to produce electricity.
3) In rectification of an A.C. current - used to convert A.C. into D.C. by p–n junction diodes.
4) In transistors, in electronics, p–n–p junction serves as device of amplification. Used to control current intensity and voltage.
5) Used to convert heat energy to electrical energy.

6) Used in television, radio, mobile set, etc.

Super conductivity:

The scientist Lord Kelvin in 1848 first proposed that there is an absolute zero temperature i.e. limit to coldness. This absolute zero is known as *Kelvin.* The Van-deer-Walls have done further study about absolute zero in 1873. The K. Onnes in 1911 firstly liquefies Helium at 4.2 °k temperature at atmospheric pressure. He was awarded Noble Prize in 1913 for investigation of properties of matter at low temperate.

Definition of superconductivity:

A substance that has no electrical resistance below certain characteristic temperature, (T_c) called as the ***Critical Temperature***.

Properties:

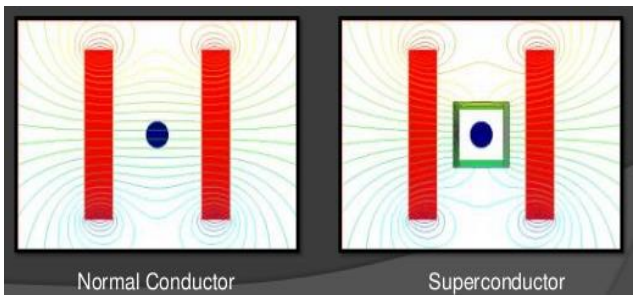
The superconductor is the absence of electrical resistance. The zero electric resistance below temperature called the Critical Temperature (T_c). There are two types of semiconductors.

Type – I: The super conductors, which includes magnetic field completely, until critical field (H_c) is reached, show loss of superconductivity.

Type – II: The superconductor, which includes high temperature material, show gradual magnetic field penetration above lower critical field (H_{c1}) and gradual loss of superconductivity. This lost completely above an upper critical field (H_{c2}).

Meissner effect: -

The magnetic field below critical field does not affect superconductivity. Above the critical fields i.e. lower critical field (H_{c1}) and upper critical field (H_{c2}), the magnetic flux will penetrate most of the superconductor and destroys superconductivity. In short when superconductor is place near magnet, the magnetic field get repelled by the superconductor because it does not allow the field to penetrate its surface is called Meissner Effect.



Two fluid models:

The scientists Gorter and Casmir sequester that the conduction electrons were either in normal or standard or superconducting state. The quantity of heat required to raise the temperature of system from lower to higher temperature divided by temperature difference is called as *heat capacity of a system*.

$$C\ (T_2\ T_1) = q\ /(T_2 - T_1)$$

Where C = heat capacity,

T_2 and T_1 = two temperatures of a system.

q = quantity of heat absorbed.

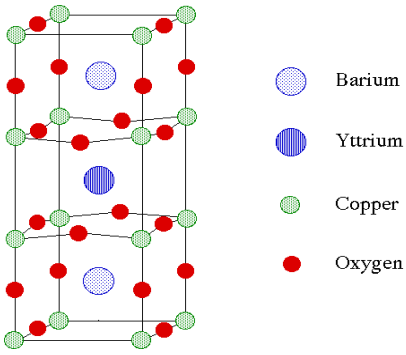
Above critical temperature all conduction electrons are in normal state, while at 0°k all conduction electrons are proposed to be in the superconducting state. From 0°k to T_c very small numbers of electrons are in the normal state i.e.

$$n_n / n = (T/T_c)^4$$

This model is known as two fluid models. It is similar to the model for super fluidity in ^4He.

Structure of superconductors: -

In 1986, Bednorz and Muller found that La_2CuO_4 in which Lanthanum is partially replaced by Barium shows superconductivity around 3°k. The oxide La–Ba–Cu–O is metallic and probably magnetic. Thus it is unlikely material for superconductor. In 1987, several groups reported that compound of the type $YBa_2Cu_3O_7$ become super conducting at 77°k. This compound is also called as '123' (i.e. one atom of Yttrium, two atom of Barium and three atoms of Copper).



Synthesis and processing:

Method –1:

The precursor metal oxides are directly sintered or calcined in air or O_2. It is then annealed in air or O_2.

$$\tfrac{1}{2} Y_2O_3 + 2BaCO_3 + 3CuO \xrightarrow{950-960°C} YBa_2Cu_3O_{6.5} + 2CO_2$$

$$YBa_2Cu_3O_{6.5} + 0.2O_2 \xrightarrow{400-500°C} YBa_2Cu_3O_{6.9}$$

After heating this mixture at 960°C, material is then cooled to 500°C in the stream of O_2 for several hours and then cooled slowly to room temp.

Method –2: - Sol-Gel method –

The sol-gel method is used for the preparation of 123 compounds. First dispersion of various metal compounds is converted into homogeneous gel by adding organic solvent such as alcohol. The gel is then decomposed at low temperature to get expected oxide. The material prepared by this method is very fine particle size material which further need annealing or heating under suitable condition to get desired oxygen stoichiometry and characteristic material.

Applications:

1) Magnets – used in High field magnet, NMR, medical diagnostic, refining by magnetic separation, magnetic shielding.
2) Energy related – production by magnetic fusion and magneto-hydrodynamics, energy storage and electrical power transmission.
3) Transportation – high speed trains, ship drive system.
4) Electronics – bolometer, electromagnetic shielding.
5) Computers and information technology – semiconductor-superconductor hybrid, active super conducting element, voltage standard, Opto-electronics.

Low temperature Super conductors (Liquid Helium):

The applications based on low temperature liquid helium super conductors are

1) High field magnet, electronics and radio frequency devices.
2) NMR spectrometers,
3) NMR imaging which is better than CATSCAN.
4) Useful in high Q – cavities.
5) Used in Josephson junction – used in digital computers in detectors for high frequency electromagnetic radiation, used in SQUID (Superconducting Quantum Interference Devices.)

High temperature Superconductors:

The applications banned on high temperature Superconductors are –

1) For low current applications - LASER ablation, election beam evaporators
2) In SQUIDS – used in medical diagnostics i. e. checking the heart and the brain, under sea communication, submarine detection, etc.