SUPERCONDUCTIVTY

The phenomenon by virtue of which certain materials exhibit zero resistivity or infinite conductivity when cooled below a certain temperature is called ‘superconductivity’. The materials which show the property of superconductivity are known as superconductor.

The best known conductors of electricity like silver and copper cannot be come superconductors. Whereas compounds and alloys of some metals, non-metals and ceramics etc., become superconductors when cooled below the critical temperature.

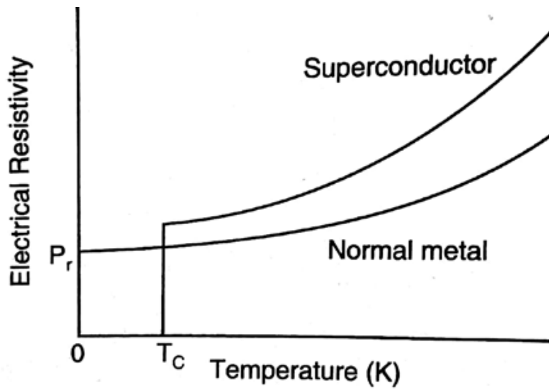
General properties of superconductors:

1) It is a low temperature phenomenon. Below the critical temperature transition from normal state to super conducting state takes place. The transition temperature is different for different materials.
2) Resistance of a superconductor is zero.
3) Superconductivity occurring in metals having valance electrons from 2 to 8. Mono valence metals are not superconductors. E.g. Cu, Ag.
4) Superconducting elements generally lie in the inner columns of the periodic table.
5) Transition metals having odd number of valance electrons i.e. 3, 5, 7 are favorable to exhibit superconductivity more than the metals having even number of valance electrons 2, 4, 6.
6) Ferromagnetic (Fe, Co, Ni) and anti ferromagnetic (Co O, Ni O) materials are not superconductors.
7) Super conductors do not allow magnetic field through them. They are perfectly diamagnetic in nature.
8) Superconductivity vanishes if the current in the superconductor increases beyond the critical current I_C.
9) Superconductivity disappears if the applied magnetic field exceeds the critical field H_C.
10) Thermal conductivity of superconductors is very low which indicates that superconducting electrons has no role in heat transfer.
11) Specific heat of superconductors increase discontinuously.
12) Some elements like Bismuth, Antimony etc., become superconducting under high pressure.

Critical temperature (Tc)

The temperature below which a substance behaves like a superconductor is known as ‘critical temperature’ or ‘transition temperature’ (T_C), it is different for different materials.

If we draw a graph by taking temperature along X-axis and corresponding resistivity along Y-axis the nature of the graph will be like as in the figure.



From the figure it is clear that the resistivity drop suddenly at Tc to zero. If we cool below Tc then the material exist in superconducting state and above Tc the material exist in normal state.

Effect of magnetic field on superconductivity:

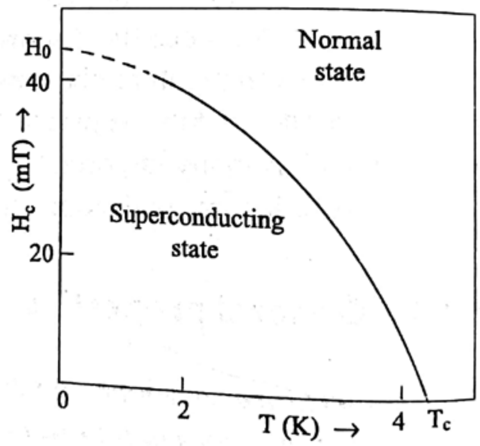
Superconductivity disappears by the application of strong magnetic field. The minimum magnetic field required to destroy superconductivity is called critical field (H_C). The value of critical field depends on the temperature of the material.

At T = Tc, Hc = 0. At temperature below Tc, Hc increases. Thedependance of critical field upon the temperature is given by

$$H_C(T) = H_C(0)(1 - \frac{T^2}{T_C^{\,2}})$$

Where $H_C(0)$ is the critical field at 0^0K

Hc(T) Critical field at T^0C, Tc is the critical temperature



If we draw a graph by taking T along X-axis and H along the Y-axis the nature of the graph will be like in figure. Right to T_C and above $H_C(0)$, the material exists in normal state and below T_C and $H_C(0)$, material in superconducting state.

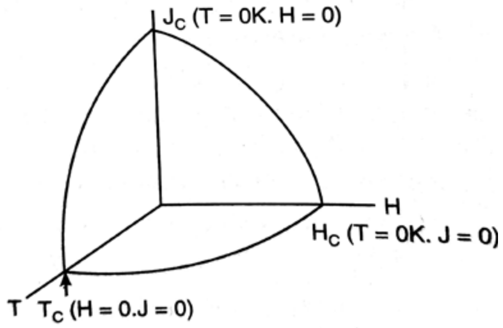
From the figure it is clear that, If H <$H_C(0)$, the material is in superconducting state. And if H> $H_C(0)$, the material is in normal state.

Critical current density

The maximum current density at which the superconductivity disappears is called the critical current density Jc. If the value of J is less than Jc then the current can sustainitself where as if j > Jc the current can not sustain itself.

A superconducting ring of radius r ceases to be a superconductor when the current is

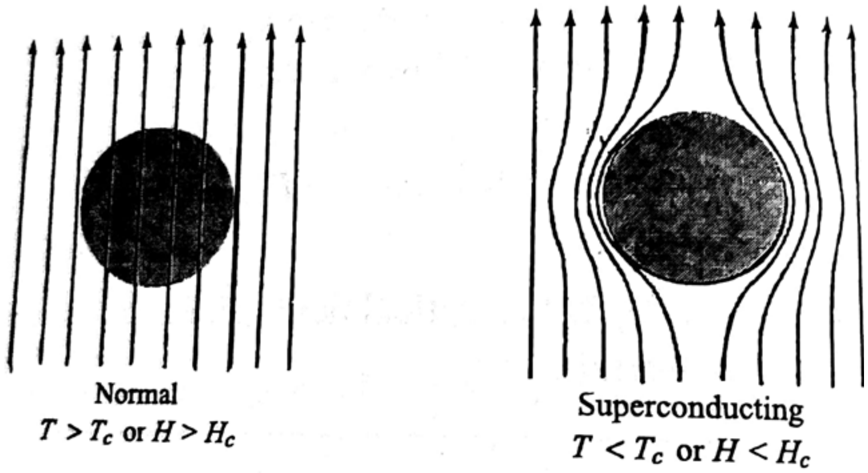
Effect of current $\boldsymbol{I_C = 2\pi r H_C}$



As the temperature of the superconductor increases the current carrying capacity decreases and falls to zero at transition temperature. The variation of critical current Jc, critical magnetic field Hc with temperature is shown in the figure.

Missner Effect:

If a superconducting material is placed in a magnetic field at H < H_C and T < T_C then the magnetic flux inside the material is excluded from the material. This effect is known as 'Missner effect'.



From Missner effect it is clear that magnetic field inside a superconductor is zero i.e. a superconductor is a perfect diamagnetic substance. Because the magnetic induction $\vec{B}$ inside a material medium is given by

$$\vec{B} = \vec{B}_0 + \mu_0 \vec{M} = \mu_0 \vec{H} + \mu_0 \vec{M} = \mu_0 (\vec{H} + \vec{M}) \text{ since} (\vec{B}_0 = \mu_0 \vec{H})$$

Where $\vec{B}_0$ is the magnetic induction in free space. $\vec{H}$ is the applied magnetic field, $\vec{M}$ is the intensity of magnetization.

Since $\vec{B} = 0$ inside a superconductor,

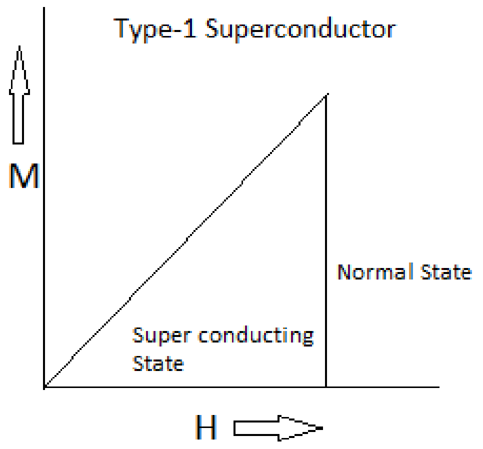
$$(\vec{H} + \vec{M}) = 0$$

$$\vec{H} = -\vec{M}$$

But, $\chi_M = \mu_r - 1 = \frac{\vec{M}}{\vec{H}} = -1, \quad \mu_r = 0$ Hence, a superconductor is perfect diamagnetic.

Type – I superconductors:

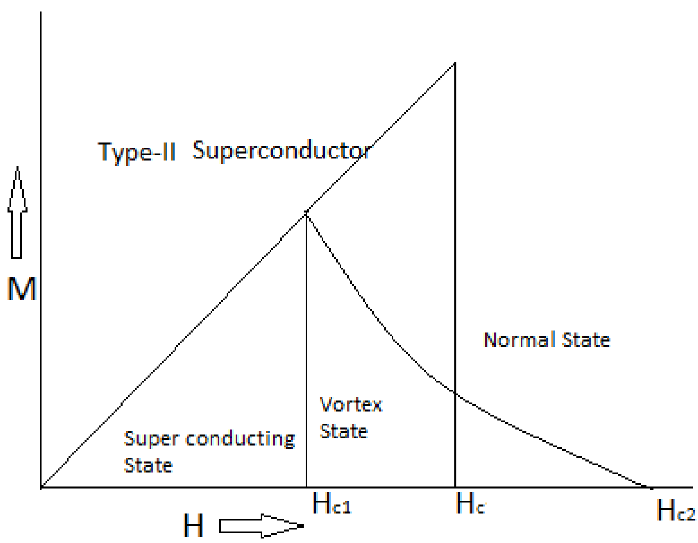
Superconductors which can exhibit complete Missenr effect or perfect diamagnetism are called type-I superconductors. In such case when type –I superconductor is placed in a varying magnetic field H < H_C and on increasing magnetic field the specimen suddenly changes to normal state at H = H_C. i.e. above the critical field (H>H_C) the specimen is in normal state and below the critical field (H<H_C) the specimen in superconducting sate. Type-I superconductors are also known as soft superconductors.



E.g. Zn, Hg, Sn, Ga etc.

Type – II superconductors:

For these superconductors there are two critical fields H_{C1} & H_{C2} when H < H_{C1} the specimen is in superconducting state. When H_{C1} < H < H_{C2} the specimen is in a mixed state i.e. it has both superconducting and normal conducting properties. When H > H_{C2} the specimen lost superconducting properties completely and it is in normal state.



Superconductors which exhibit above phenomenon are called type – II superconductors. Here H_{C1} < H < H_{C2}. These are also called as hard superconductors. These are most useful in commercial purpose.

Comparison between Type-I and Type II Superconductor

Type-I superconductor	Type-II superconductor
1. They exhibit complete meissner effect. 2. They show perfectly diamagnetic behavior. 3. They have only one critical magnetic field Hc. 4. There is no mixed state or intermediate state in case of these materials. 5. The material loses magnetization abruptly 6. Hiest value of Hc is about 0.1 $Wb/m^{2.}$ 7. They are known as soft superconductors, Example- Lead, tin, Mrcury etc	1. They do not exhibit complete meissner effect. 2. They do not show perfectly diamagnetic behavior. 3. They have two critical magnetic field, lower critical magnetic field Hc1 and upper critical magnetic field HC2. 4. Mixed state or intermediate state is present. 5. The material loses magnetization gradually. 6. Upper critical field is of the order of 30Wb/m2. 7. They are known as hard super conductors Example- Nb-Sn, Nb-Ti, Nb-Zr etc

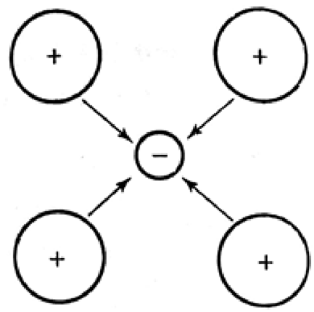
B C S Theory:

This theory is developed by Bardeen, Cooper and Schrieffer. They explained the superconductivity and its properties successfully which involves electron – electron interaction via lattice deformation.

According to BCS theory superconductivity is due to the domination of attractive interaction between two electrons by means of phonon exchange over usual repulsive interaction.

Electron – electron interaction:

Let us consider an electron approaching the lattice of positive ions. Positive ions attract towards the electron and form a positive ion core. The electron is screened by the positive ion core by which the charge of the electron reduces. Due to the attraction between the charge and the positive ion core the lattice is deformed.

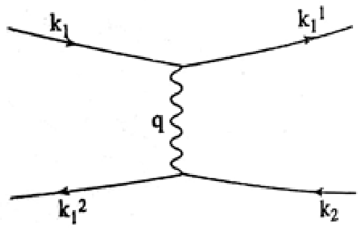


Positive ions attracted towards an electron forming a positive ion core

Suppose another electron approaches the assembly of the electron and the ion core, it is attracted towards the assembly and interacts with the first electron via lattice deformation. This interaction is due to exchange of virtual phonon 'q' between two electrons. In terms of wave vector the interaction may be expressed as

$K_1 - q = K_1'$ And $K_1 + q = K_2'$

$\Rightarrow K_1 + K_2 = K_1' + K_2'$ i.e. the net wave vector is conserved.



The exchange of virtual phonons between the two electrons (Cooper pair)

The pair of electrons called 'Cooper pair' and the electrons are known as 'Cooper electrons'.

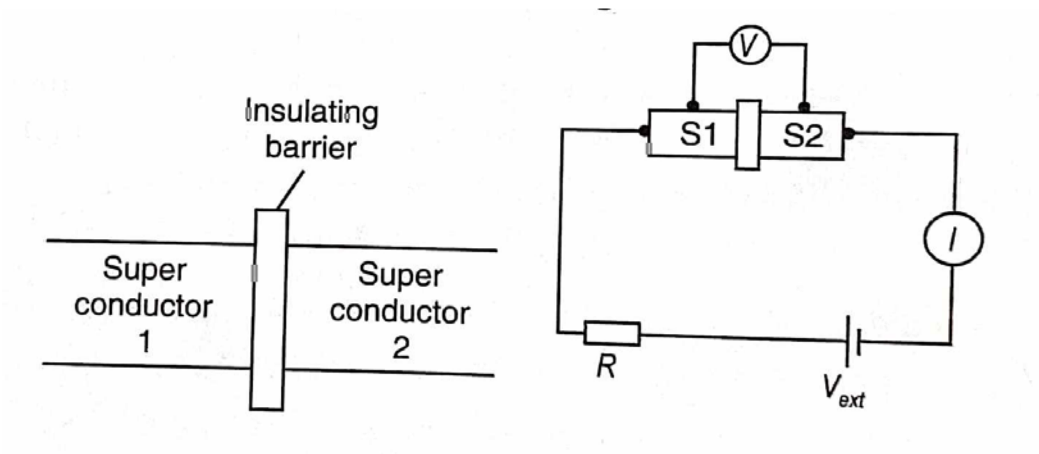
According to Fermi Dirac distribution

$$F(E) = \frac{1}{1 + \exp((E - E_F)/KT)}$$

At T = 0^oK and E < E_F all the energy states below the Fermi level are filled and all the energy states above the Fermi level are empty. So due to the addition of cooper electron they are forced to occupy the energy states above the Fermi level. Due to attraction between the electrons they form a bounded state whose total energy is less than the energy of the pair in the Free State i.e. less than $2E_F$. The difference in the two energy states is the binding energy of the cooper pair. To break cooper pair in to two separate electrons the energy equivalent to binding energy of the cooper pair should be supplied. The binding energy of cooper pair is strongest when the electrons forming the pair have opposite moment and opposite spins i.e. $K\uparrow, K\downarrow$. The cooper electrons are the super electrons which are responsible for the superconductivity.

Josephson Effect:

The tunneling of cooper pairs between two superconductors separated by a thin insulating layer is known as 'Josephson Effect'. The tunneling current is very less since the two superconductors are weakly coupled to thin insulating layer. Tunneling of cooper pairs take place even in the absence of applied voltage as well as when a voltage is applied to the super conductors.



D.C Josephson Effect:

According to this effect a d c current flows across the junction of two superconductors separated by a thin insulating layer in the absence of any external electric or magnetic field. The tunneling current is

$I = I_0 \sin(\phi_0)$,

I_0 is the maximum current flow through the junction. It depends up on the thickness of the junction and temperature. Φ_0 is the phase difference between the two parts of the junction. The magnitude of the current varies from $+I_0$ to $-I_0$

A.C Josephson Effect:

According to this effect when a d c voltage is applied across the junction of the two superconductors separated by a thin insulating layer, R.F current oscillations are generated across the junction.

The expression for R.F current is given by

$$I = I_0 \sin(\varphi_0 + \omega t) = I_0 \sin(\varphi_0 + \Delta\varphi)$$

Where $\Delta\varphi = 2\pi t\left(\frac{2eV}{h}\right)$

So $I = I_0 \sin\left[\varphi_0 + 2\pi t\left(\frac{2eV}{h}\right)\right]$

The current represents an alternating current with frequency

$$F = \frac{2eV}{h}$$

Applications of Josephson Effect:

1. It is used to generate microwave of frequency $F = \frac{2eV}{h}$
2. It is used to define standard volt by national Bureau of Standards.
3. It is used to measure very low temperature. For this A C Josephson effect is used.
4. It is used as a switching device with a switching time of 1 Pico second.

High T_C Superconductors

Based on transition temperature superconductors are divided into two categories as low $\mathbf{T_C}$ and high $\mathbf{T_C}$ superconductors. The materials having $\mathbf{T_C}$ below 24K are regarded as low $\mathbf{T_C}$ superconductors and those having $\mathbf{T_C}$ above 27K are regarded as high $\mathbf{T_C}$ superconductors.

Examples

1. **LBCO-** Mixed metallic oxide of lanthanum-barium-copper ($La_1Ba_2Cu_3O_7$ exhibited super conductivity at about 30K.
2. **YBCO-**Mixed metallic oxide of Yittrium-barium-copper ($Y_1Ba_2Cu_3O_7$ exhibited super conductivity at about 95K.
3. **BSCCO-** Mixed metallic oxide of Bismuth, strontium, calcium and copper ($Bi_2CaSr_2Cu_2O_{10+x}$ exhibited super conductivity at about 110K.

The oxygen vacancies are found to play a key role in the superconducting behavior of ceramic oxide. When the cell contains one atom f rare earth metal, two barium atoms, three copper atoms have seven oxygen atoms then such compounds are called 1-2-3 superconductors.

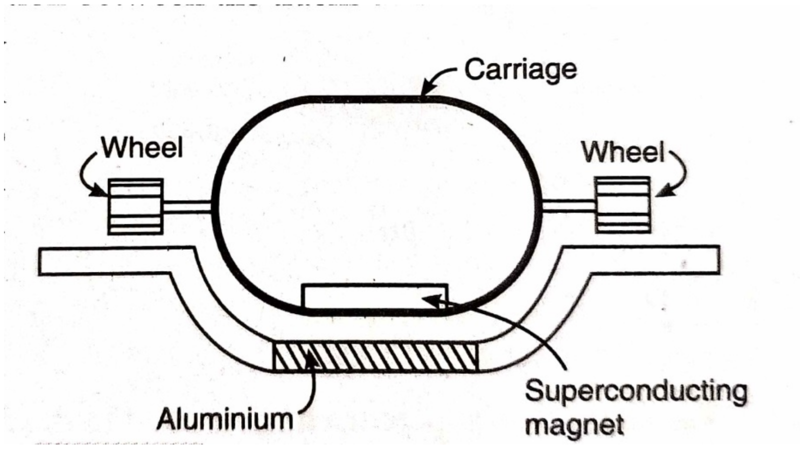
Properties of High T_C Superconductors

1. High T_C Superconductors are brittle in nature.
2. The properties of the normal state of these materials are highly anisotropic.
3. The Hall coefficient is positive indicating that the charge carriers are holes.
4. Their behavior can not be explained by BCS theory.
5. The isotope effect is almost absent in these materials.
6. The magnetic properties of these materials are highly anisotropic.

Applications of superconductors:

1. **Transformers and electrical Machines**
   The transformers and electrical machines with superconducting coils generate stronger magnetic field hence the size of the motors and generators will be drastically reduced. In this case the eddy current loss is very less therefore they are having 99% efficiency.

2. **Magnetic levitation: (MagLev Trains)**
   Since superconductors are diamagnetic substances and magnetic field inside them is zero, therefore hey can be suspended in air against the repulsive force from a permanent magnet. This effect is known as 'magnetic levitation'. It can be used to construct high speed train with minimum expenditure.



Operation-

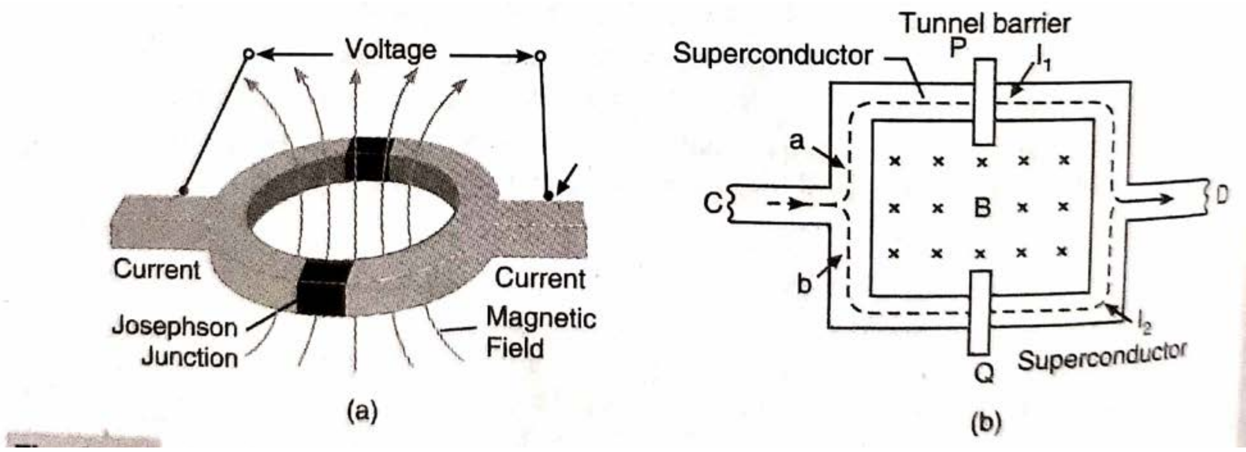
In case of MagLev train, the train has superconducting magnets built into the base of its carriages. An aluminium guide-way is laid on the ground and carries electric current. The repulsion between the two powerful magnetic fields, namely the field produced by electric current in the aluminum guide-way causes magnetic levitation of the train. A levitation of about 10 to 15cm is achieved so that the train floats in air.

3. **SQUIDS** (Super conducting quantum interference devices)- SQUID is a device used to measure extremely weak magnetic flux.

There are two main types of SQUIDS. DC SQUID AND AC SQUID.

Fabrication.

SQUIDS arefabricated by depositing a thin niobium layer on an alloy having 10% gold or indium. It act as the basic electrode of the SQUID and the tunnel barrier is oxidized onto this neiobium surface. The top electrod is a layer of lead alloy deposited on top of the other two. The entire device is cooled to nearly absolute zero with liquid helium.



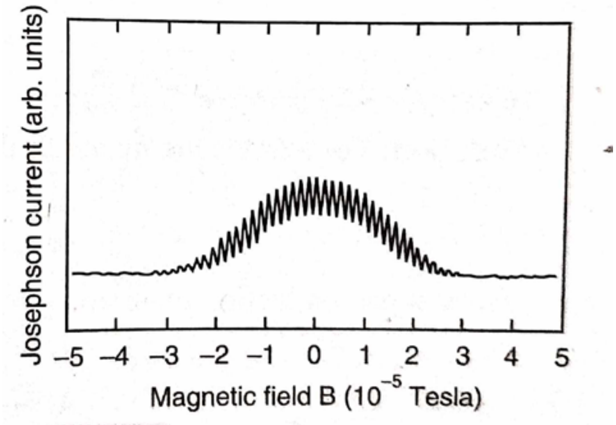
A two junction DC SQUID consists of two Josephosons arranged in parallel so that electron tunneling through the junctions demonstrate the quantum interference.

Working

As DC super current is applied to the SQUID which is the bias current, it enters the device through the arm C. It is divided along two paths a and b and again merge into one and leaves through the arm D. P and Q are the Josephson junctions and. I_1 and I_2 are the currents tunneling through the junction P and Q respectively.

When a magnetic field is applied perpendicular to the loop, the flux passes through the loop changes the quantum mechanical phase difference across each of the two junctions. Then the wave functions at the two Josephson junctions interferer with each other. Then the total current through two parallel Josephson junction is

$$I_T = 2(I_0 \sin\delta_0)\cos\frac{2\pi e\Phi}{hC}$$



The above relation indicates that a progressive increase or decrease of magnetic flux, causes the current to oscillate between a maximum and a minimum value. The period of the oscillation is one flux quantum $\Phi_0 = \frac{h}{2e}$ = 2.06 x 10^{-15} Weber

Uses of SQUID.

1. SQUIDS are used to study tiny magnetic signals from the brain and heart.
2. SQUID magneto meters are used to detect the paramagnetic response in the liver. This gives the information about the amount of iron held in the lever of the body accurately

NANOTECHNOLOGY

Nano is a prefix to mean 10^{-9}. It refers to a nanometer (nm).one nanometer is one billionth of a meter or one millionth of a millimeter or about eighty thousandth the width of a human hair.

Nanomaterial:

The word Nano materials literally means that it is the material having at least one of its dimensions in the range of a nanometer. Thus the material needs not to be so small that it cannot be seen. It can be a large surface area or a long wire whose thickness is in the scale of nanometer.

Nano materials can be natural or manmade. Nano materials are produced naturally by plants, algae and volcanic activity. Some proteins in our body which control things like flexing muscles and repairing cells are Nano sized.

Generally there are three types of Nano materials;

1. Materials that are Nano scale in one dimension (and are extended in other two dimensions) such as a thin film or surface coating.
2. Materials that are Nano scale in two dimensions (and are extended in one dimension) such as Nano wires, Nano tubes, etc.
3. Materials that are Nano scale in three dimensions such as precipitates, colloids and quantum dots. Etc.

Different properties of Nano materials:

The properties of Nano materials are different from bulk materials.

A number of physical phenomena are changes as the size of the system decreased. This includes statistical mechanical effects as well as quantum mechanical effects. For example due to reduction in size opaque substances become transparent (copper), inert materials become catalysts (platinum), stable material become combustible (aluminum) solid turns into liquid at room temperature (gold) and semiconductor become conductor (silicon)

Two principal factors are responsible for change in the properties due to reduction in the size. They are,

1) Increase in surface area to volume ratio:

Nano materials have relatively larger surface area when compared to same volume or mass of the material produced in a bulk form.

For example let us consider a sphere of radius ‘r’. Then,

Surface area of the sphere is = $4\pi r^2$

Volume of the sphere = $4/3\ \pi r^3$

Surface area to volume ratio = 3/r

When the radius is decrease its surface to volume ratio increases.

I.e. R = r/4

Then surface are = $4\pi r^2/16 = \pi r^2/4$

Volume = $4/3\ \pi r^3/64 = \pi r^3/48$

So surface area to its volume ratio = 12/r

Hence as the size of the particle decreases a greater portion of atoms are found at the surface compared to those inside. For example a particle of size 30nm has 5% of its atoms are found on the surface. If the size becomes 10nm 20% of its atoms are found on the surface and for the size 3nm, 50% of its atoms are found on the surface.

Thus nano particles have a much greater surface area per given volume compared to bulk particles. Therefore chemical reactivity increases. In this way some particles which are inert in bulk stage becomes more reactive at their nano stage. This also affects their strength of electrical properties.

2) Quantum confinement effect:

Nano particle are the intermediate particles between isolated atom and a crystal of solid. In an isolated atom the energy levels are desecrate where as in solid the energy levels split and form bands.

When a particle is in a potential well or in a potential box such that the dimensions of the well or box are of the order of de Broglie wave length of electron or mean free path of the electrons then the energy level of the electron changes. This effect is called quantum confinement. This can affect the optical, electrical and magnetic behavior of materials.

Electrical properties:

1) At Nano size ionization potential increases.
2) Electrical energy bands in metals become narrow.
3) Electrical conductivity in metal decreases.
4) In Nano ceramics and magnetic composites electrical conductivity increases.

Optical properties:

1) Depending upon the size of the particles different colors exhibit by Nano materials.
2) Gold Nano particles of size 100nm appear in orange color, while 50nm particle appears in green color.
3) By controlling the size of the material it can be made to emit or absorb specific wavelengths of light.
4) By controlling size of the particles the linear and nonlinear optical properties can be finally tailored.

Magnetic properties:

1) With decreasing in size coercivity and saturation magnetization value increases.
2) Coordination number decreases with decrease in size.
3) Magnetic moment increases with decrease in size.
4) Nano particles of nonmagnetic solids are found to be magnetic.
5) Nano particles of ferromagnetic substance like Fe, Ca, Ni.. act as super magnetic.

Mechanical properties:

1) In nano materials the inter face area within the material increases which increases the strength.
2) Elastic madulie decreases with decrease in size.
3) Hardness increases with decrease in size.
4) Toughness increases with decrease in size.
5) Ductility and super plasticity of ceramics increase with decrease in size.
6) Due to decrease in size temperature at which super plasticity occurs is lowered and strain rate for its occurrence is increased.

Production of Nano materials:

Mainly there are two methods to produce Nano materials.

(a) Top down process:

In this process Nano particles are formed due to crushing of solid in to fine nano powder.

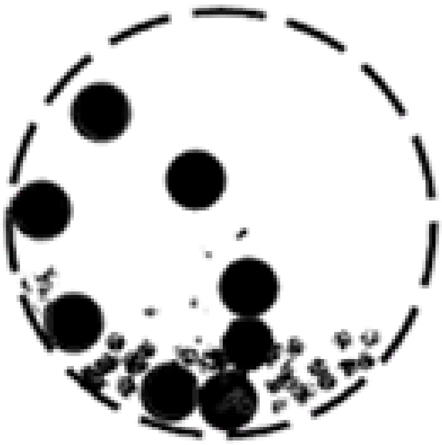
(b) Bottom up technique:

In this technique Nano particles are formed from crystal grown by “atom by atom” or “molecule by molecule”.

Following are the different methods to produce Nano particles.

<u>1) Ball milling:</u>

This process belongs to “top down” technique. This method is also known as mechanical crushing. In this method small balls are allowed to rotate around the inside of a drum and then fall on a solid with gravity force and crush the solid into Nano crystallites.



In this method a wide range of Nano materials can be prepared. E.g. iron with grain size 10 – 30nm can be formed. This method is preferred method for preparing metal oxides.

Advantage

The main advantage of this top down approach is high production rates of Nano powders.

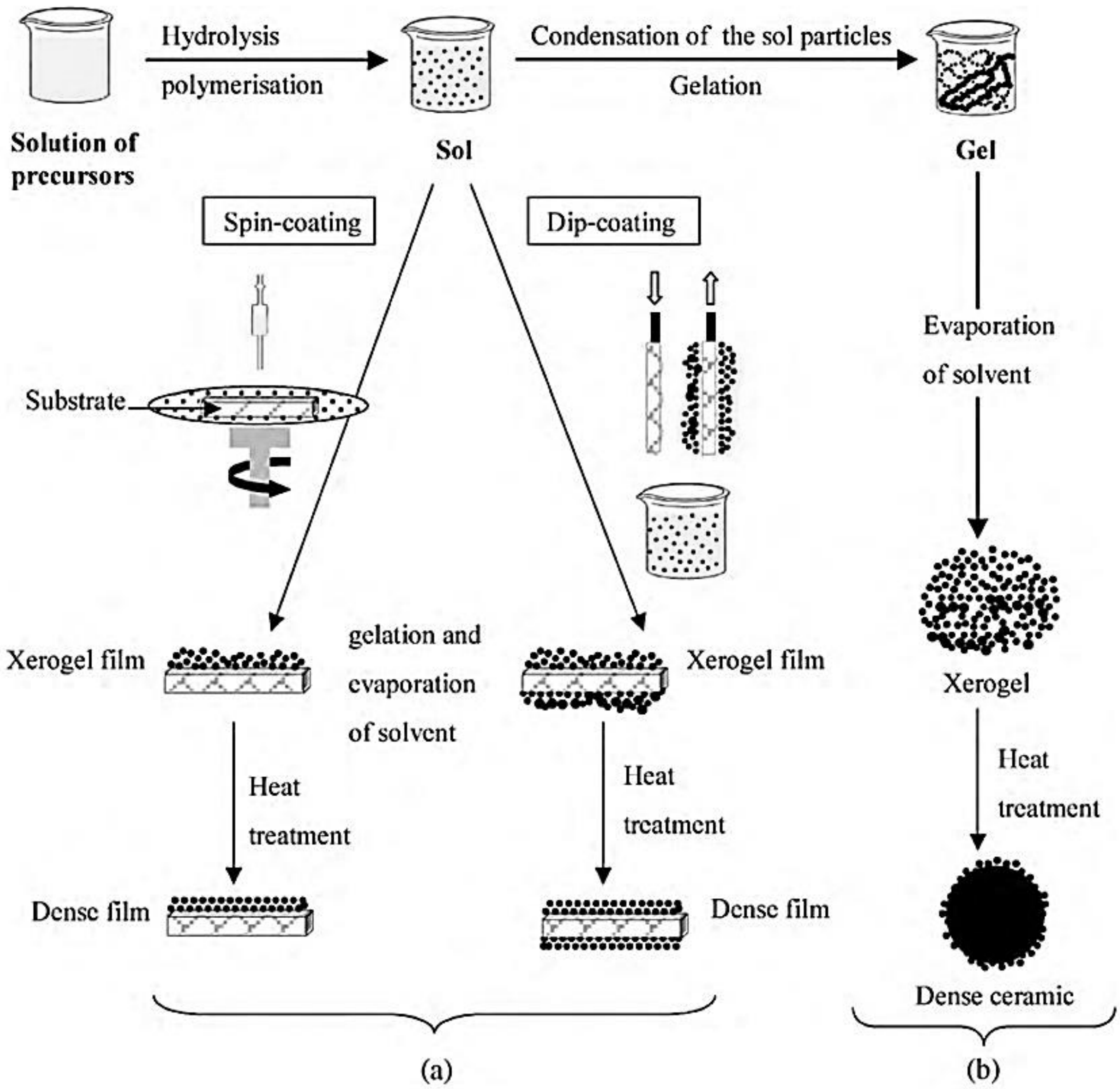
Disadvantage

1. Though the process is simple, but all the particles are not broken down to the required particle size.
2. During the process contamination by the milling tools and atmosphere can be a problem.

2) Sol – Gel method:

This process belongs to "bottom up" technique This is a chemical process to produce Nano materials. In this process a homogeneous solution of a material is prepared and then it is sprayed on a suitable substrate so that sol (homogeneous solution) is deposited on the substrate. This can be done by dipping or spinning. The deposited sol is allowed free for some time to form gel (gelation). Then the Nano particles are fabricated from the gel by further processing of heat treatment.

Examples of some Nano materials prepared by this method, tetra ethyl ortho silicate, tri methyl borate, aluminum sec-butoxide etc.



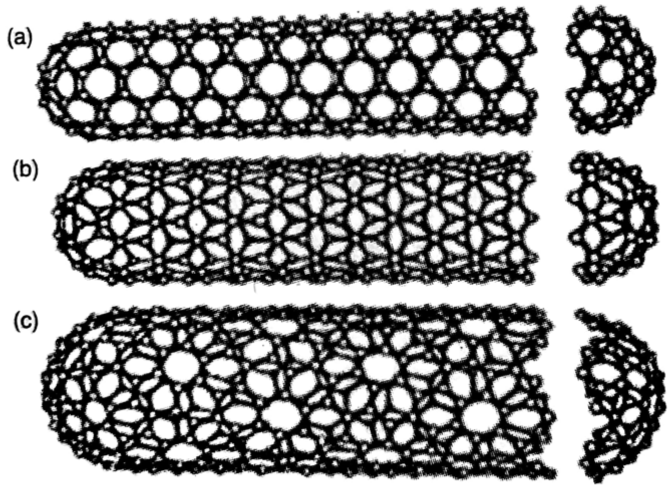
Carbon Nano Tubes (CNT):

Till 1991 there were three forms of carbon. They were diamond, graphite and amorphous carbon. After the discovery of carbon nano tube, this name was added in the family of carbon.

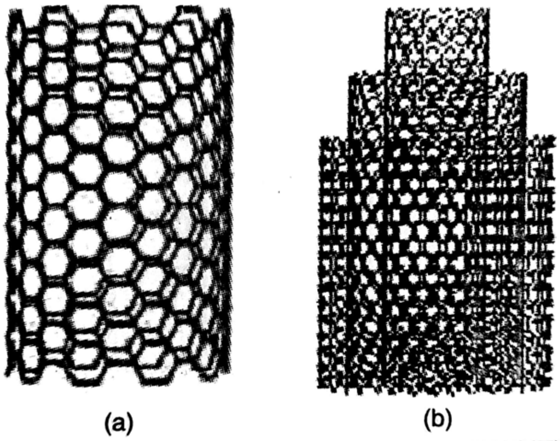
In 1991 Sumio Ijima discovered nano tubes which are related to graphite. These are the extended tubes of rolled graphite sheets. The bonding of a nano tube is SP^2 which is stronger than SP^3 bonds found in diamond.

Carbon nano tubes are fabricated by different methods like plasma – arching, laser evaporation, chemical vapor deposition etc. the diameter of the tubes is about 1 – 20nm and length is in micro meter to mille meter range.

There are two types of carbon nano tubes. They are single walled and multi walled nano tubes. Depending up on the different ways of rolling graphite sheets CNTs are zigzag, armchair and chiral type.



Models of different single wall nanotubes: (a) armchair, (b) zigzag and (c) chiral structure



(a) A single-walled carbon nanotube (SWNT), (b) Multi-walled carbon nanotubes (MWNT)

Properties of CNTs:

1. They are strong about 20 times stronger than high strength steel hence do not break easily.
2. Nano tube is stiff, almost 10 times stiffer than steel wire of same thickness because Young's modulus of nano tube is more.
3. When nano tubes are bent, they can be straightened back without any damage. This property is known as resilient.
4. Due to less crystal defects, thermal conductivity is very high.
5. Metallic carbon nano tubes have 1000 times more electrical conductivity than copper.
6. Due to application of d c magnetic field their resistance changes. This effect is known as magneto resistance. So nano tubes shoe magneto resistance.
7. Depending upon the diameter and how nano tubes are rolled, they may be metallic or semiconducting nano tubes.
8. Most single walled nano tubes have diameter of 1nm with a tube length many thousands times longer than diameter.
9. The structure of SWNT is like a wrapping a one atom thick layer of graphite called graphene in to a seamless cylinder.
10. The way graphene sheets wrapped is represented by a pair of indices (n, m) called the chiral vectors,

    If m = 0, the nano tubes are called zigzag.

    If m = n, the nano tubes are called armchair.

If $m \neq n$, the Nano tubes are called chiral.

Uses:

1. Due to large surface area they are highly absorbent. Therefore they are used for air, gas, and water filtration.
2. SWCNTs are used for production of FET logic gates.
3. Nano tubes are used in field emission display (FED).

Applications of Nano materials:

Since Nano materials are having small size, large specific surface area, high strength and stiffness they are used in a wide Varity of functions.

1. **Better insulation Materials**
   Some Nano materials like Aerogels prepared by sol-gel technique are used for better insulations. They are extremely light weight and can with stand 100 times their weight. This Aerogel is also used as materials for smart windows which becomes dark when the sun is too bright and they allow more light when the intensity of sunlight is less.
2. **Elimination of pollutants**
   Nano materials can be used as catalysts to react with harmful and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment. This can avoid environmental pollution from burning petrol and coal.
3. **High energy density batteries**
   Nano crystalline materials prepared by sol-gel technique are useful for separator plates in batteries because of their foam like structure, which can hold considerably more energy. By using nanomaterial in batteries frequent recharging is not required and hence once charged last much longer time.
4. **Nano machines and Nano devices**
   Nano size machines are used in biological system. These machines are very much handy and suitable for biological systems. Now a day researchers are developing Nano-gears fabricated from Fullerene.