

Unit - V

Superconductors and Nano-Materials.

Introduction :-

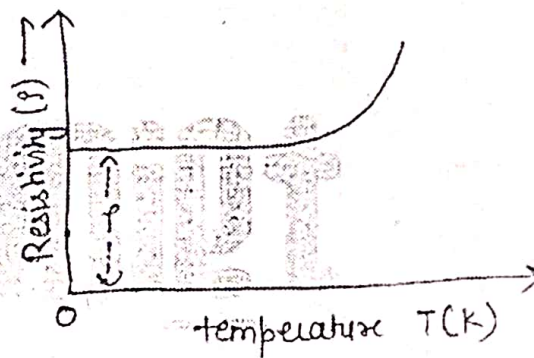
The phenomenon of superconductivity was discovered by Kammerlingh Onnes in 1911, when he was measuring the resistivity of mercury at low temperature. He observed that the electrical resistivity of pure mercury drops to zero at temperature about 4.2 K. The sudden drop in resistivity was not in accordance with the expectations. Kammerlingh Onnes recognized that this is a new phenomenon & mercury has passed into a new state. He called it as Superconductivity.

When the electrical resistance of a substance drops suddenly to zero, when it is cooled below a certain temperature, the phenomenon is known as Superconductivity.

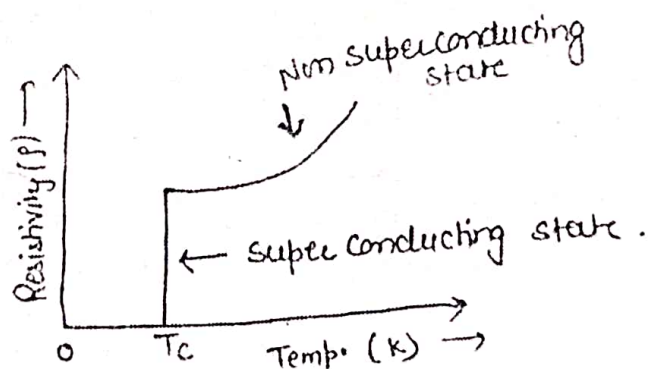
The substances showing this property is called as superconductors. Other substances showing superconductivity are silver, lead, gallium, iridium etc.

⇒ Temperature Dependence of Resistivity in Superconducting Materials

Metals are good conductors of electricity as they have plenty of free electrons. However they offer resistance to the flow of charges, i.e. current. Even at 0K, the metals offer some resistance called residual resistance. Variation of resistivity (ρ) of metal with temperature shown in below diagram.



→ The dependence of resistivity of superconductors shown in below



The resistance of superconductor in non-superconducting state decreases in temperature as in case of normal metal.

But at particular temperature T_c , the resistivity abruptly drops to zero. T_c is called as critical temperature.

⇒ The temperature at which a normal material turns into a superconductor is called as critical temperature. critical temperature is different for different material for Example —

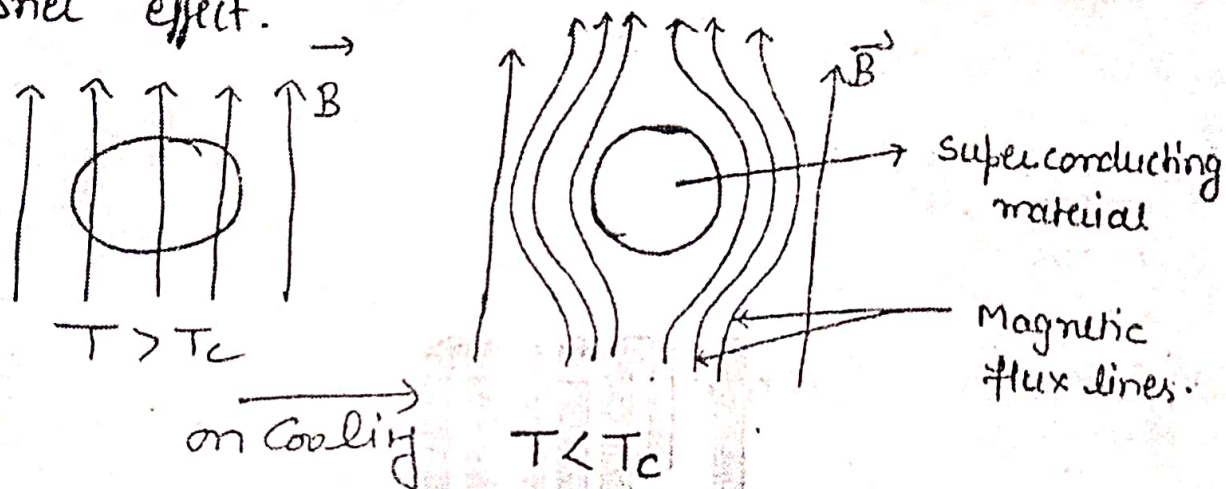
Element	T_c (K)	Compound	T_c (K)
Tungsten	0.01	Zr Al ₂	0.30
Cadmium	0.56	Au Be	2.60
Aluminium	1.19	Ni Bi	4.25
Mercury	4.15	Nb ₃ Al	17.5

⇒ Important Points

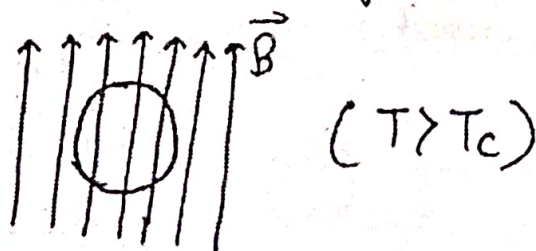
- 1) In an, ordinary metal, there exist a small resistivity even at lower temperature. The residual resistivity depends on impurities present in the metal. On other hand, transformation to superconducting state is independent to the impurity.
- 2) The critical temp. is characteristic of superconducting material.
- 3) If the temperature of superconducting material is increased, the material transforms into a normal material above the critical temperature T_c .

Meissner Effect (flux Exclusion)

Meissner in 1933 observed that if a superconductor is cooled in a Magnetic field, below critical temperature corresponding to that field, then the lines of Induction are Expelled from the material. This effect is called Meissner effect.



In normal state, magnetic lines of force pass through it. But when specimen is cooled below its transition temperature (shown in above fig.), magnetic lines of force are expelled out of the specimen.



Therefore, the Expulsion of magnetic lines of force from a superconducting material when it is cooled below the transition temperature in a magnetic field is called Meissner effect.

• Important Points

- (1) Meissner effect is reversible. When the temperature is increased below T_c , the flux suddenly penetrates through the specimen and the substance comes to its normal state.
- (2) A superconductor is a perfect diamagnetic. The reason is that the magnetic induction B in a superconductor is zero.

Therefore, for Superconductors

$$B = \mu_0 (H + M) = 0 \quad \text{or} \quad M = -H \quad \text{--- (1)}$$

The magnetic susceptibility χ is given by

$$\chi = \frac{M}{H} \quad \text{--- (2)}$$

M = Intensity of magnetization
 H = magnetising field Intensity.

from (1) & (2)

$$\chi = \frac{-H}{H} = -1 \quad \text{--- (3)}$$

This is the maximum value for the susceptibility of a diamagnetic material, means a superconductor is a perfect diamagnet.

- (3) Maxwell's equations is given by

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad \text{--- (4)}$$

According to Ohm's law

$$V = IR \quad \text{and} \quad E = V/d$$

$$E = \frac{IR}{d} = \frac{(JA)R}{d} = J \left(\frac{AR}{d} \right)$$

$$E = Jf \quad \text{where} \quad f = \left(\frac{AR}{d} \right) \quad \text{---(5)}$$

J = Current density

for finite J and zero f , E should be zero.

from (4) eq $\frac{\partial B}{\partial t} = 0$ or $B = \text{constant}$

This shows that magnetic flux should not change when specimen is cooled. This condition shows contradiction to Meissner effect. Therefore superconductor should be judged by both the conditions independently.
So for superconductor—

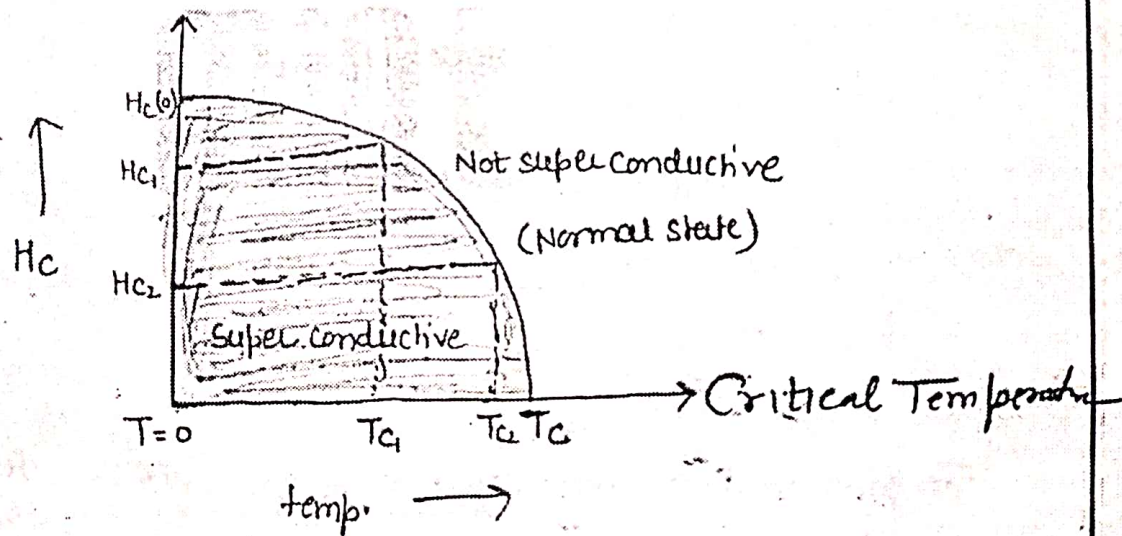
- (i) has zero resistance below critical temperature.
- (ii) shows Meissner effect below critical temperature.

(4) let us explain the difference between a perfect conductor and superconductor. We know that the susceptibility of noble metals do not change when their temperatures are lowered. Even the susceptibility does not change when the metals become perfect conductor. On the other hand, in case of superconductor the susceptibility change. for example, in normal state lead has susceptibility -0.18×10^{-6} while its value in superconducting state is -1.0 .

⇒ Effect of Magnetic field (Temperature dependence of critical field)

Superconducting material restores its normal resistance when a strong magnetic field is applied.

The minimum value of applied magnetic field when the superconductor loses its superconductivity is called the critical magnetic field. If the applied magnetic field exceeds the critical value $H_c(0)$, the superconducting state is destroyed. The variation of critical magnetic field with temperature shown in below



Normal conducting state of the material is restored if magnetic field is greater than the critical value or the temperature of the specimen is raised above critical temperature T_c .

The curve in the diagram is nearly parabolic and can be represented by the following relation. -

$$H_c(T) = H_c(0) \left[1 - \frac{T^2}{T_c^2} \right]$$

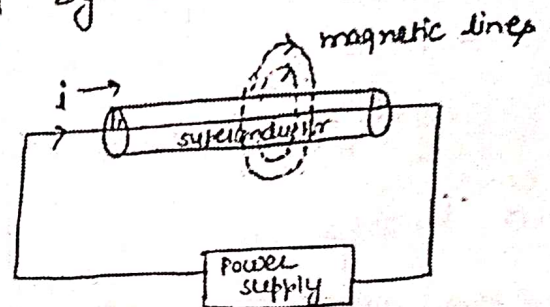
where $H_c(T)$ is the maximum critical field strength at temperature T , $H_c(0)$ is the maximum critical field strength at absolute zero (characteristic of a material) and T_c is the critical temperature.

In general the higher is the value of T_c , the higher is the value of $H_c(0)$.

Critical current

The maximum current that can be passed in a superconductor without destroying its superconductivity is called critical current. It is denoted by I_c .

Consider a superconducting wire of radius (r) and carrying a current I



Applying Ampere's law

$$\oint H \cdot dl = I$$

$$H (2\pi r) = I$$

at $H = H_c$, let $I = I_c$ then

$$\boxed{I_c = 2\pi r H_c} \quad \text{--- (1)}$$

If I become I_c , superconductivity will be destroyed

$\Rightarrow$ If external transverse magnetic field H is applied then total magnetic strength should be less than the critical magnetic field. Therefore -

$$H_c = H_t + 2H$$

$$H_t = H_c - 2H$$

$$\frac{I_c}{2\pi r} = H_c - 2H$$

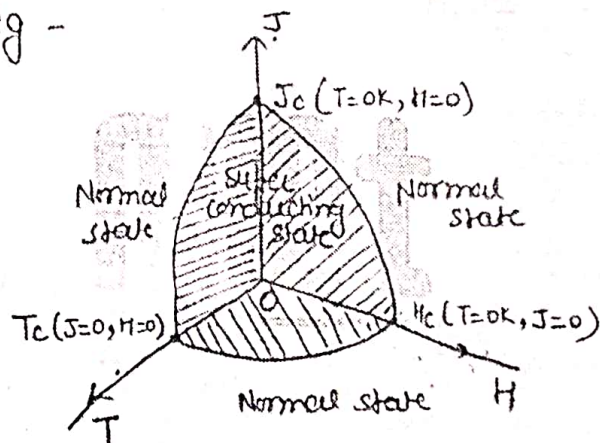
$$\boxed{I_c = 2\pi r (H_c - 2H)} \quad \text{--- (2)}$$

This is called Pilsbeck rule.

from eq (2) we conclude that critical current I_c decrease with applied field H . It becomes zero for $H = H_c/2$. If applied field is zero then

$$I_c = \frac{2}{\sqrt{3}} H_c \quad \text{--- (3)}$$

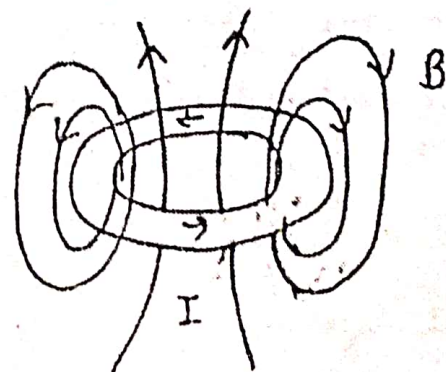
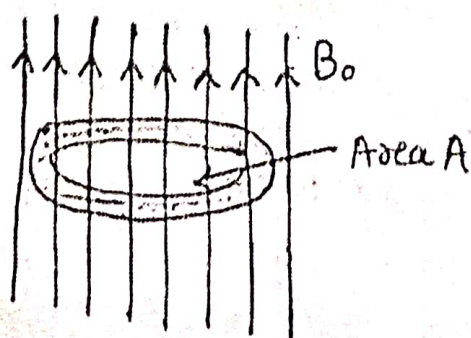
Means, Superconducting state not only depend on temperature and magnetic field but also depends on current or current density. There exists a critical surface in T , H and J for a particular superconductor as shown in fig -



Therefore within the boundary of phase diagram, the material is a superconductor & beyond it, the material exist in a normal state.

Persistent current in superconductor

- Persistent current refers to a perpetual electric current, not requiring an external power source. Such a current is impossible in normal electrical devices since all commonly-used conductors have a non-zero resistance and this resistance would rapidly dissipate any such current as heat.
- Persistent current will continue indefinitely as long as the medium is superconducting. The magnetic field inside the open area of the cylinder will also persist.
- Persistent current is one which flows in superconductors without any loss in its value for long time. Since in superconductors as the resistance is zero, the amount of current flowing remain same.
- Persistent current carry in superconductor have to carry very high current, normally in the range of few thousand Amperes, compared to less than 1000 Amperes in conventional termination leads.



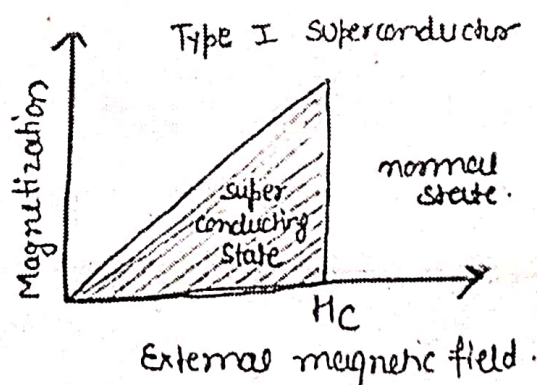
Type-I and type-II Superconductors

Based on magnetic behaviour, the superconductors are classified into following two categories:

- (1) Type-I superconductors or soft superconductors.
- (2) Type-II superconductors or hard superconductors.

⇒ Type-I superconductors

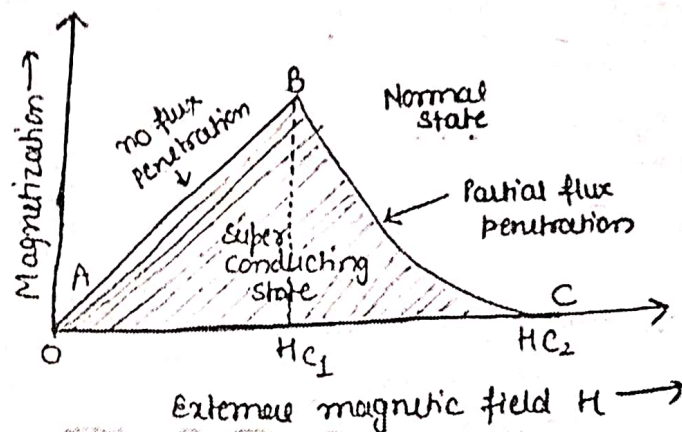
The dependence of magnetization of a superconductor of type-I as a function of external field H . Upto the critical field strength (H_c), the magnetization of superconductor grows in proportion to the external field. As soon as the applied field H exceeds H_c , the magnetization abruptly drops to zero, as shown in fig.



It loses its diamagnetic property completely, when H exceeds H_c . In this state, the magnetic flux penetrates throughout the superconductor. So type-I superconductor is one in which the transition from superconducting state to normal state in presence of magnetic field occurs sharply at the critical value H_c .

The critical field value H_c for type-I superconductors is found to be very low. Aluminium, lead and Indium are example of type-I superconductors.

⇒ Type-II superconductors



The magnetization of type-II superconductor shown in above fig. The type-II superconductor is characterized by two critical magnetic field H_{c1} and H_{c2} . The description of curve is as follows:

- (i) for the field strength below H_{c1} , the superconductor expels the magnetic field from its body completely and behaves as a perfect diamagnet. H_{c1} is called the lower critical field. The curve is represented by AB.
- (ii) As the magnetic field increases from H_{c1} , the magnetic field lines begin to penetrate the material. The penetration increases until H_{c2} is reached. H_{c2} is called the upper critical field. At H_{c2} , the magnetization vanished completely, i.e. the external field has completely

penetrated into superconductor and destroyed the superconductivity.

In region from H_{c1} to H_{c2} , the specimen assumes a complicated mixed structure of normal & superconducting states. The superconductor is said to be in a mixed state which is commonly known as vortex state.

ii) After H_{c2} , the material turns to normal state.

ϕ_0 , type-II superconductor is one which is characterized by two critical field H_{c1} and H_{c2} and transition to normal state take place gradually as magnetic field is increased from H_{c1} to H_{c2} .

Difference between type-I and type-II superconductors

Type-I superconductors

- 1) Type-I superconductors exhibit complete Meissner effect.
- 2) Above critical field H_c , the superconductor becomes normal conductor.
- 3) Type-I superconductors are known as soft superconductors.
- 4) The critical field H_c is relatively low. They can generate field about 100 to 1000 gauss.
- 5) Type-I superconductors are materials such as Al, Zn, Ga etc.

Type-II superconductors

- 1) Type-II superconductors show complete Meissner effect below H_{c1} and allow the flux to penetrate the superconductor between H_{c1} and H_{c2} . Between H_{c1} and H_{c2} , the material shows a region of mixed state.
- 2) Between H_{c1} and H_{c2} , the superconductor exists in a mixed state called as vortex state and above H_{c2} , it comes in normal state.
- 3) Type-II superconductors are known as hard superconductors.
- 4) The value of H_{c2} is very large. They are able to produce very high magnetic field. They can carry larger current when the magnetic field is b/w H_{c1} & H_{c2} .
- 5) Type-II are alloys like lead-indium alloy etc.

High Temperature Superconductors

The high temperature superconductors are also called as high T_c material. By 1988, the long standing 30K ceiling of T_c in intermetallic compound has been elevated to 125K in bulk superconducting oxides. All high temperature superconductors are different type of oxides of copper. high temperature superconductors showed promise in pre-commercial applications, as in thin film devices & wires being fabricated. few examples are -

$\text{Ba Pb}_{0.75} \text{Bi}_{0.25} \text{O}_3$	$T_c = 12 \text{ K}$	[BPBO]
$\text{La}_{1.65} \text{Ba}_{0.15} \text{Cu O}_4$	$T_c = 36 \text{ K}$	[LBLO]
$\text{Y Ba}_2 \text{Cu}_3 \text{O}_7$	$T_c = 90 \text{ K}$	[YBCO]
$\text{Tl}_2 \text{Ba}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_{10}$	$T_c = 120 \text{ K}$	[TBLCO]

Important observations

- (1) All high temperature superconductors bear a particular type of crystal structure called the Perovskite structure.
- (2) The addition of extra copper oxygen layer into the structure unit of superconducting copper oxide complexes pushes the critical temperature to high values.
- (3) The addition of any atom into copper oxide layer either bring down or destroy the effect of superconductivity.
- (4) The important observation is that the formation of supercurrents in high T_c superconductors is direction dependent. The supercurrents are strong in copper-oxygen planes and weak in direction perpendicular to the planes.

Properties and Application of Superconductors

⇒ Properties :-

- 1) It is a low temperature phenomenon.
- 2) The transition temperature is different for different substances.
- 3) Materials having high normal resistivity exhibit superconductivity.
- 4) Materials for which $Z\rho = 10^6$ (where Z is atomic number & ρ is resistivity) show superconductivity.
- 5) For chemically pure and structurally perfect specimen, the superconductivity is very sharp.
- 6) Ferro magnetic and Antiferromagnetic materials are not superconductors.
- 7) Below the transition temperature the magnetic flux lines are rejected out of the superconductors.
- 8) Superconducting elements, in general, lie in the inner columns of periodic table.
- 9) Below the transition temperature the specific heat curve is discontinuous.
- 10) Those metallic elements having their valence electrons lie between 2 to 8 exhibit superconductivity.

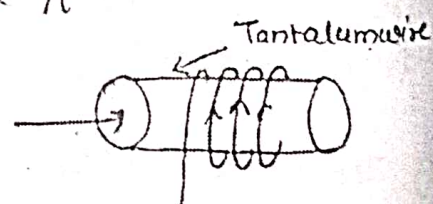
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Application of Superconductors

① Power transmission $\Rightarrow$ Electrical power transmission through any conductor is always accompanied by energy loss I^2R , where I is current & R is the resistance of the conductor. If superconductors are used, the losses will be eliminated & power transmission can be done at a lower voltage level.

②) Superconducting Magnets $\rightarrow$ An electromagnet made by using coils of superconducting wires or cables is called superconducting magnet. The main advantage is that once the current is set-up, the coil requires no source of emf to drive the current.

③) Electrical applications. Cryotom :- Cryotom consist of a wire of superconducting material A (Tantalum with $T_c = 4.4\text{K}$) around which another wire of superconducting material B (Niobium with $T_c = 9.3\text{K}$) is wound in the form of solenoid. The wire A is called as gate.



The cryotom is based on the principle of disappearance of superconductivity above H_c . At a temperature below 4.4K both A and B are in superconducting state. If a current is made to flow through Niobium wire B,

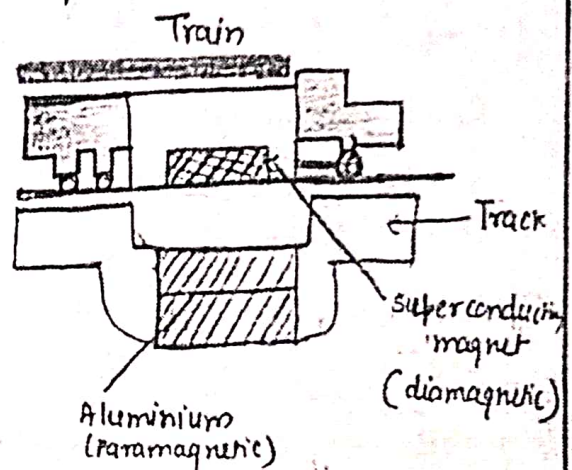
then it will produce a magnetic field around Tantalum wire A. If this current is enough to produce magnetic field greater than H_c , then Tantalum will become a normal conductor. Thus A is switched to its normal state & offer high resistance to the flow of current through Tantalum. Now current through A is stopped.

By removing the current through Niobium, the magnetic field around tantalum could be brought below H_c . Now A switches back to superconducting state. The current will again flow through A. Therefore, tantalum act as a gate & Niobium as control and the system act as a fast acting switch.

4) Maglev Vehicles $\Rightarrow$ In a superconductor, the magnetization is in the direction opposite to that of external magnetic field. This is known as diamagnetism. When a superconductor magnet is brought near a permanent magnet, there is a strong repulsive force between them. This force causes the lighter one to float over the other. This is known as Magnetic levitation.

The Maglev vehicle (say a train) consisting of superconducting magnets built into its base. say the vehicle runs over an aluminium track in which a current is flowing. The train is set afloat by magnetic levitation as shown in fig. This is due to enormous repulsion b/w two highly

powerful magnetic fields, one produced by the superconducting magnet inside the train & other due to electric currents in the aluminium track. As in the fig, the train floats without touching the track as a repulsion between superconducting magnets & the magnetic field induced in the track.



5) Very strong magnetic fields:-

Very strong magnetic field (of order of 50 Tesla by consuming only 10kV) can be generated with cold made superconducting materials. High magnetic field are required in many areas of research and diagnostic equipments in medicine.

6) SQUIDS (superconducting quantum interference devices):-

SQUIDS are fundamentally superconducting ring that act as storage devices of magnetic flux. They are used to detect very minute changes in magnetic field of human brain or body.

7) For progress of computer technology → At present, due to heat generated through I^2R losses, there is a limit to which the components can be crowded on a chip of given size. The use of superconductors will make it possible to cram more circuit in given area.

Characteristics of Superconductors in Superconducting States

1) characteristics which do not change in Superconducting transition $\Rightarrow$

i) There is no change in crystal structure as revealed by X-Ray diffraction studies. This suggests that superconductivity is more connected with the conduction electrons than with atoms themselves.

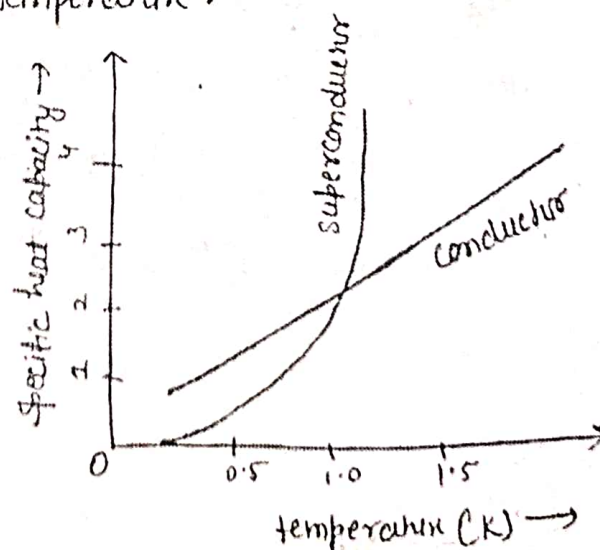
ii) The photoelectric properties are unchanged i.e. no change in absorption of fast or slow electrons.

iii) The thermal expansion and elastic properties do not change in transition.

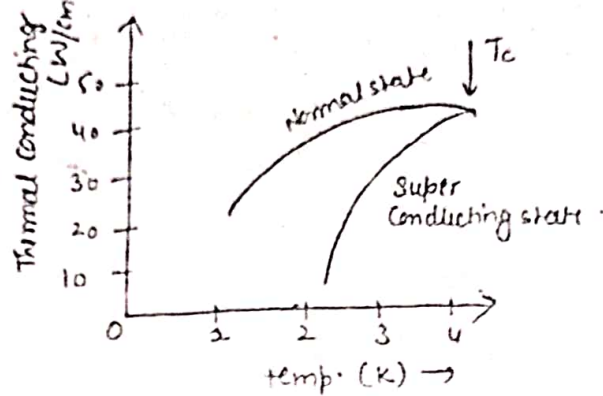
iv) In absence of magnetic field, there is no change of latent heat & no change of volume in transition.

2) characteristic which change in Superconducting transition.

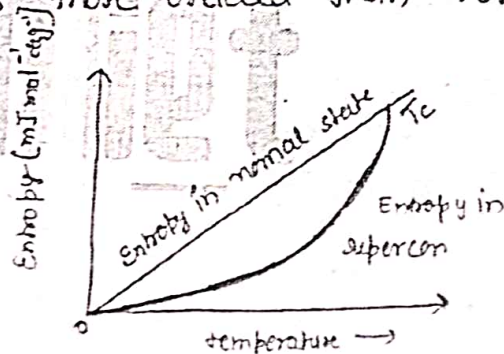
(i) specific heat $\rightarrow$ It does not vary as the absolute temperature in superconducting state but it is found to vary exponentially with temperature.



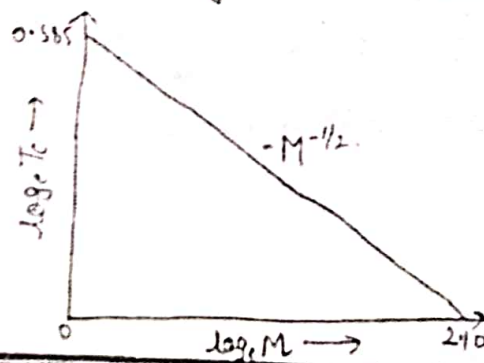
ii) Thermal conductivity → Thermal conductivity of superconductor undergoes a continuous change b/w two phases.



iii) Entropy → Entropy is a measure of the disorder in a system. The entropy of a superconductor decreases rapidly on cooling below the transition temperature. This means superconducting state is more ordered than normal state.

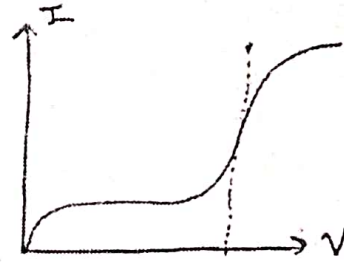
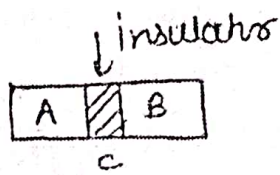


iv) Isotope effect → It has been observed that critical temperature of semiconductors varies with the isotopic mass. More precisely transition temperature is found to vary as the square root of atomic mass [$T_c \propto M^{-1/2}$]



v) Tunneling Phenomenon

Tunneling phenomenon between two metals separated by a thin insulating layer. If the film is very thin, then there is high probability of electron moving from one metal to another metal.



D.C current flow across the junction (called as Josephson Junction) in absence of any electric or magnetic field, called Josephson effect.

Numericals

- 1) The transition temperature for Pb is 7.2 K. However at 5 K it loses the superconducting property if subjected to a magnetic field of 3.3×10^4 A/m. Find the value of $H_c(0)$ which will allow the metal to retain its superconductivity at 0 K.

Sol. →

$$H_c(T) = H_c(0) \left[1 - \frac{T^2}{T_c^2} \right]$$

$$H_c(0) = \frac{H_c(T)}{\left[1 - \frac{T^2}{T_c^2} \right]}$$

$$H_c(0) = \frac{3.3 \times 10^4}{\left[1 - \frac{(5)^2}{(7.2)^2} \right]} = \frac{3.3 \times 10^4}{\left[1 - \frac{25}{51.84} \right]}$$

$$H_c(0) = 6.37 \times 10^4 \text{ A/m}$$

- 2) The transition temperature for lead is 7.26 K. The maximum critical field for the material is 8×10^5 A/m. lead has to be used as a superconductor subjected to magnetic field of 4×10^4 A/m. what precaution will have to be taken?

Sol. →

$$T = T_c \left[1 - \frac{H_c(T)}{H_c(0)} \right]^{1/2}$$

$$= 7.26 \left[1 - \frac{4 \times 10^4}{8 \times 10^5} \right]^{1/2}$$

$$= 7.08 \text{ K}$$

The temp. of metal should be held below 7.08 K.

3) At what temperature is $H_c(T) = 0.1 H_c(0)$ for lead (Pb) having $T_c = 7.2 \text{ K}$.

Sol.

$$H_c(T) = H_c(0) \left[1 - \frac{T^2}{T_c^2} \right]$$

$$0.1 H_c(0) = H_c(0) \left[1 - \frac{T^2}{(7.2)^2} \right]$$

$$0.1 = 1 - \frac{T^2}{(7.2)^2}$$

$$T^2 = (7.2)^2 [1 - 0.1]$$

$$T^2 = (7.2)^2 \times 0.9$$

$$\boxed{T = 6.83 \text{ K}}$$

4) A superconducting material has a critical temperature of 3.7 K in zero magnetic field of 0.306 Tesla at 0 K . Find the critical field at 2 K .

Sol.

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right]$$

$$H_c(T) = 0.306 \left[1 - \left(\frac{2}{3.7} \right)^2 \right]$$

$$H_c(T) = 0.306 [1 - 0.2900^2]$$

$$H_c(T) = 0.217 \text{ Tesla}$$

- 5) The critical field for niobium is 1×10^4 A/m at 8 K & 2×10^5 A/m at 0 K. Calculate the transition temperature of the element.

Sol.

$$T_c = \frac{T}{\left[1 - \frac{H_c(T)}{H_c(0)}\right]^{1/2}} = \frac{8}{\left[1 - \frac{1 \times 10^4}{2 \times 10^5}\right]^{1/2}}$$

$$= \frac{8}{\left[1 - \frac{1}{20}\right]^{1/2}} = \frac{8}{(19/20)^{1/2}} = 7.08 \text{ K.}$$

- 6) The magnetic field intensity in the material is zero at 3.69 K and $(3 \times 10^5 / 4\pi)$ at 0 K. Calculate the temperature of the semiconductor if the field intensity is measured as $(2 \times 10^5 / 4\pi)$.

Sol.

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

$$B_c(T) = B_c(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

$$\frac{2 \times 10^5}{4\pi} = \frac{3 \times 10^5}{4\pi} \left[1 - \left(\frac{T}{3.69}\right)^2\right]$$

$$\frac{2}{3} = \left[1 - \left(\frac{T}{3.69}\right)^2\right]$$

$$\left(\frac{T}{3.69}\right)^2 = 1 - \frac{2}{3} = \frac{1}{3}$$

$$T = 2.13 \text{ K}$$

7) for a specimen of superconductor, the critical field are 1.4×10^5 and 4.2×10^5 A/m resp. for temperature 1.4 K and 13 K resp. Calculate the transition temperature and critical field at 0 K & 4.2 K.

Sol.

$$(H_c)_1 = H_0 \left[1 - \left(\frac{14}{T_c} \right)^2 \right] = 1.40 \times 10^5 \quad \text{--- (1)}$$

$$(H_c)_2 = H_0 \left[1 - \left(\frac{13}{T_c} \right)^2 \right] = 4.2 \times 10^5 \quad \text{--- (2)}$$

dividing eq (2) by eq (1) we get

$$\frac{(H_c)_2}{(H_c)_1} = \frac{T_c^2 - (13)^2}{T_c^2 - (14)^2} = \frac{4.2}{1.4} \quad \text{--- (3)}$$

$$T_c = 14.5 \text{ K}$$

Put T_c in eq (1)

$$H_0 \left[1 - \left(\frac{14}{14.5} \right)^2 \right] = 1.40 \times 10^5$$

$$H_0 = \frac{1.40 \times 10^5}{\left[1 - \left(\frac{14}{14.5} \right)^2 \right]} = 20.67 \times 10^5 \text{ A/m}$$

Now

$$(H_c)_{4.2} = H_0 \left[\frac{1 - (4.2)^2}{(14.5)^2} \right]$$

$$= (20.67 \times 10^5) \times (0.916)$$

$$= 18.9 \times 10^5 \text{ A/m}$$

- 8) Calculate the critical current which can flow through a long thin superconducting wire of diameter 10^{-3} m. Given $H_c = 7.9 \times 10^3$ amp/m.

Sol.

$$\begin{aligned} I_c &= 2\pi r H_c \\ &= 2 \times 3.14 \times \left(\frac{10^{-3}}{2}\right) \times (7.9 \times 10^3) \\ I_c &= 24.81 \text{ amp.} \end{aligned}$$

- 9) Determine the critical current & critical current density for a superconducting ring of diameter 10^{-3} m at temperature of 4.2 K. Given the critical temperature for the sample is 7.18 K & critical magnetic field is 6.5×10^4 A/m.

Sol.

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \quad \text{--- (1)}$$

$$T_c = 7.18 \text{ K}, \quad H_c(0) = 6.5 \times 10^4 \text{ A/m}$$

$$\underline{T_c = 4.2 \text{ K}}$$

put in (1)

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

$$\Rightarrow \boxed{H_c(T) = 4.276 \times 10^4 \text{ A/m}}$$

$\Rightarrow$ critical current

$$\begin{aligned} I_c &= 2\pi r H_c \\ &= 2 \times 3.14 \times \left(\frac{10^{-3}}{2}\right) \times 4.276 \times 10^4 \end{aligned}$$

$$\boxed{I_c = 134.3 \text{ amp}}$$

$\Rightarrow$ current density

$$J_c = \frac{I_c}{A_c} = \frac{134.3}{\pi r^2} = \frac{134.3}{3.14 \times \left(\frac{10^{-3}}{2}\right)^2} = 1.71 \times 10^8 \text{ A/m}^2$$

Nanomaterials

Introduction

The word "nano" has a Greek origin meaning dwarf. A nanometer is used to measure things that are very small such as atoms and molecules.

The materials whose size lies between range 1nm - 100nm are called nanomaterials.

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

⇒ Nanoscience is the study of phenomena & manipulation of materials at atomic, molecular and macromolecular scales.

⇒ In nanoscience, the properties differ significantly from those at a larger scale.

The reason of the above mentioned is as follows;

- ① Nanomaterials have a relatively larger surface to volume ratio than their bulk counterpart. This makes them more chemically reactive and affect their strength or electrical properties.
- ② Quantum effects starts dominating in atomic ranges affecting various behaviour of materials.

For ex:- (i) Opaque substances can become transparent i.e. copper

(ii) Inert materials can become catalyst e.g. platinum

(iii) Stable materials can turn combustible e.g. aluminium

(iv) Insulators can become conductors e.g. silicon

(v) Solids can turn into liquids at room temperature e.g. gold

⇒ Nanotechnology is the technology of design, synthesis, characterization and application of materials on nanoscale.

Quantum Well

If one dimension is reduced to the nanorange while other dimensions remain large, then the structure formed is known as quantum well.

A quantum well is a nanometer thin layer which can confine particles in the dimension perpendicular to the layer surface, whereas the ~~movement~~ movement in other dimension is not restricted.

- ⇒ Quantum wells are used widely in diode lasers, including red lasers for DVDs & laser printers, infra red lasers and also to make HEMTs (high electron mobility transistors) which are used in low-noise electronics.
- ⇒ They can be made to a high degree of precision by modern epitaxial crystal growth techniques.

Quantum Wire

If two dimensions are reduced to nanorange while the third remains the same, then the structure so formed is called quantum wire.

- A quantum wire is a cable or a wire, often similar in function to copper wire, but made with usually carbon Nano-tubes
- Quantum wires are usually conductors, but may be made as insulators or semiconductors.
- Nano-wires have two quantum-confined directions but one unconfined direction available for electrical conduction.

Quantum Dots

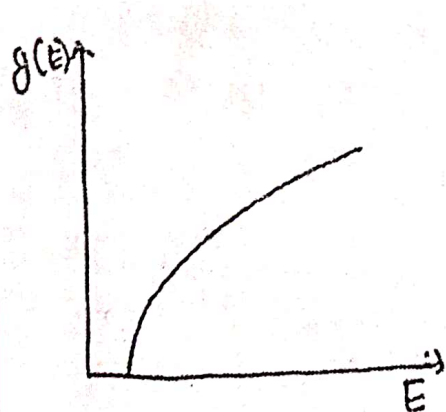
When all the three dimensions of the material are reduced to nano range, then it is called as quantum dot.

- Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules.
- These are semiconductor particles a few nanometers in size having optical and electrical properties.
- e.g. Larger QDs (5-6nm) emits longer wavelength while smaller QDs (2-3nm) emits shorter wavelength.

examples of Quantum dots are:- Cadmium selenide (CdSe),
cadmium telluride (CdTe)
Zinc selenide (ZnSe)
Indium Phosphide (InP)

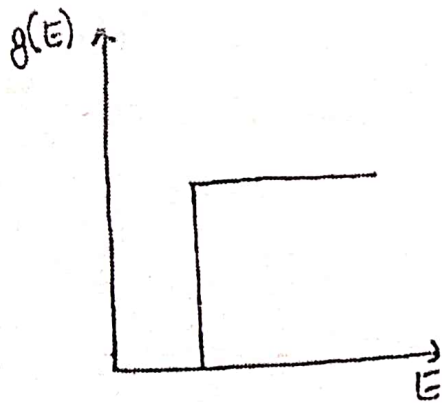
- These are zero-dimensional nanostructures.

Density of states: It is defined as number of states per unit energy per unit volume that electrons are allowed to occupy. $g(E)$ → density of states



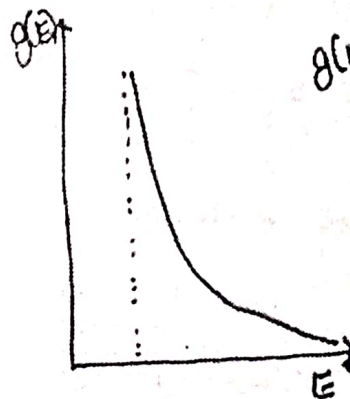
Bulk (3-D)

$$g(E) \propto E^{1/2}$$



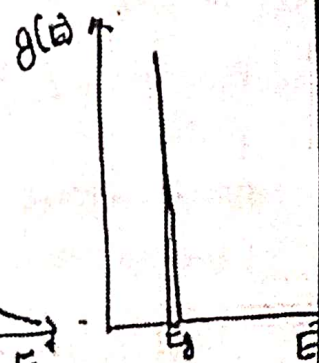
Quantum Well (2-D)

$$g(E) \propto E^0 = \text{constant}$$



Quantum wire (1-D)

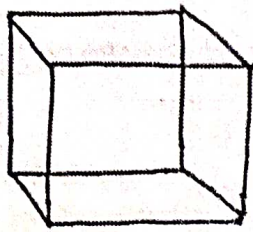
$$g(E) \propto E^{-1/2}$$



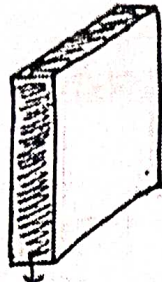
Quantum Dot (0-D)

$$g(E) \propto \delta(E - E_g)$$

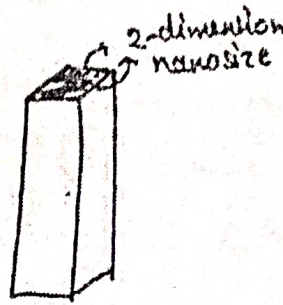
Size comparison



Bulk



nm size
Quantum
Well



Quantum
Wire



All 3-dimension of
nano order.

Quantum
Dot

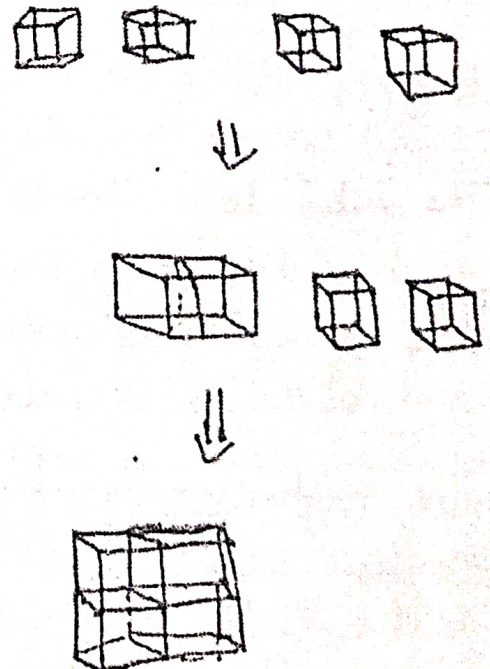
Synthesis of Nanomaterials (Fabrication)

The following two main techniques are used for the preparation of nanomaterials;

→ Bottom-up Technique:

This is a technique in which materials and devices are build up atom by atom i.e., a technique to collect, consolidate and fashion individual atoms and molecule into the structure.

This is carried out by a sequence of chemical reactions controlled by series of catalysts.

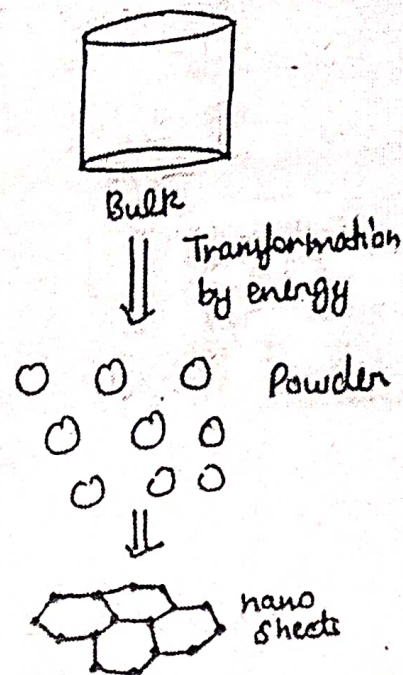


→ Top-down Technique:

This is a technique in which materials and devices are synthesized or constructed by removing existing material from larger entities.

Therefore in this technique a large scale object or pattern is gradually reduced in dimension to nanoscale pattern.

This can be accomplished by a technique called lithography.



Chemical Vapour Deposition (CVD)

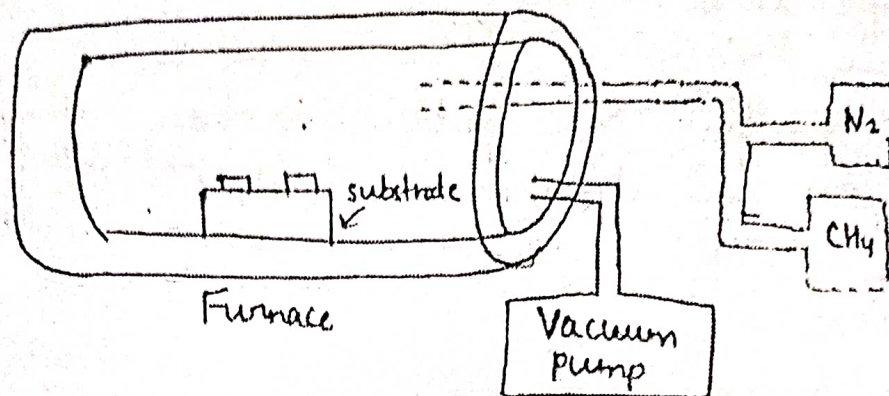
In this method a substrate is prepared with a layer of metal catalyst particle such as nickel, cobalt or iron.

The substrate is heated to approximately 700°C in a chamber. To initiate the growth of nanotubes, two gases are blown into the chamber (precursors) which are methane (carbon containing gas) and other is a process gas ammonia, nitrogen or hydrogen.

The high temperature breaks the bonds between the carbon atoms and hydrogen atoms in the methane molecules. This results in carbon atoms with no hydrogen atoms attached. These carbon atoms attach to the catalyst particles where they bond to other carbon atoms.

This results in the formation of nanotube.

Nanotubes formed can be SWNT (Single walled nanotubes)
or MWNT (Multi walled nanotubes)



CVD Process

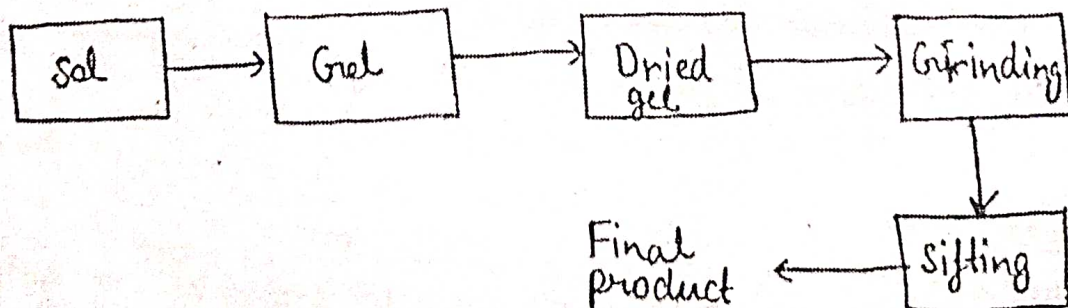
Sol-gel Method

It is bottom up approach and chemical based method to synthesize nanomaterials.

This method is used to synthesize metal oxide nanoparticles.

⇒ A sol is a colloidal (the dispersed phase in which size of particles is so small that gravitational forces do not exist.)

⇒ A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles left behind begin to join together in a continuous network. This is accomplished by sedimentation or centrifugation.



- ⇒ The remaining liquid is removed using the drying process accomplished by thermal treatment and remaining left as dried gel. This further enhanced the mechanical stability.
- ⇒ The dried gel is grinded to get the material into powdered form.
- ⇒ The powder then is sifted (process of removing lumps) to get the final product.
- ⇒ This final product can be deposited on a substrate to get a thin film or we can cast it into desired shapes.

Advantages of sol-gel method

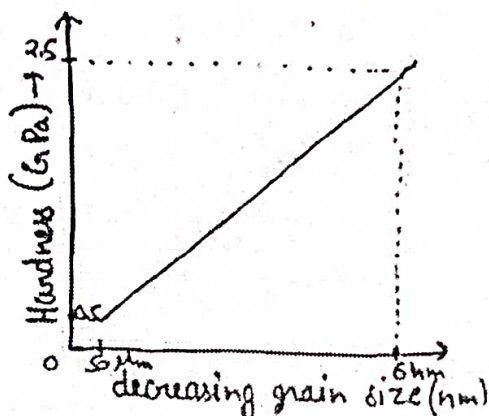
- It is a cheap and low-temperature technique.
- It gives us fine control of product's chemical composition.
- Rate of reaction can be easily controlled.
- Even small quantities of dopants can be uniformly dispersed in the final product.

Advantages of CVD method

- It is used to produce high purity, high performance solid materials.
- By-products are removed by carrier gas flow through the reaction chamber.
- Substrate is exposed to one or more volatile precursors which react or decompose on substrate surface to produce desired compound.
- This is widely applied to produce coatings, powders, fibers and monolithic components.

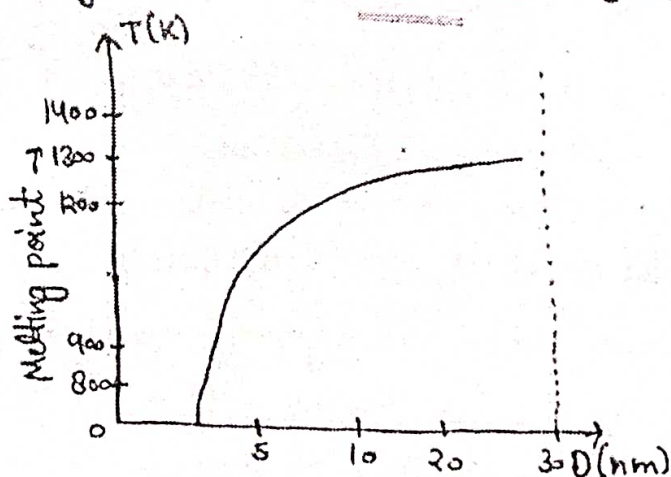
Properties of Nanoparticles

- ① Mechanical Properties: Very small nanoparticles have almost all their atoms on the surface which give them more freedom to go larger from their equilibrium positions. Nanophase metals with their exceptionally small grain size are found to be exceptionally strong.



The variation of hardness with diameter of copper nanocrystal is shown.

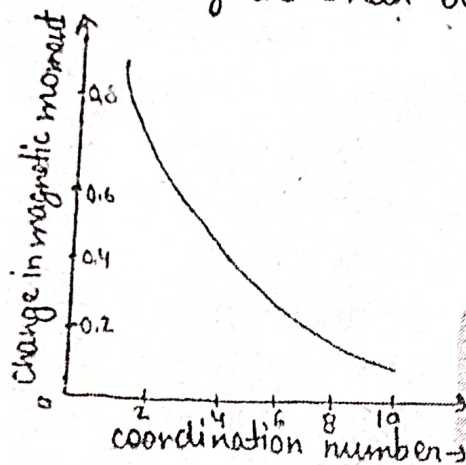
- The melting point of the cluster depends on the number of atoms in the crystal. It increases with increase in number of atoms & attains the value of bulk material when cluster contains >1000 atoms.



Melting point of gold as a function of grain size.

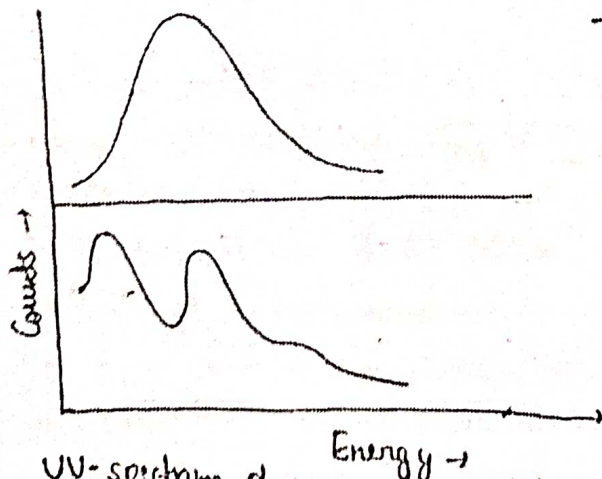
② Optical Properties: The absorption of photons occurs because electrons from lower energy state to higher energy states. It is observed that clusters of different sizes have different energy level separations. So, their absorption is different for different clusters hence the different colours.

③ Magnetic Properties: The nanoparticles of magnetic solid exhibits a new class of magnetic properties. The smaller particles are more magnetic than bulk material.



Metal	Bulk	Cluster
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, Ni	Ferromagnetic	Super paramagnetic
Gd, Tb	Ferromagnetic	Super paramagnetic
Rh	Paramagnetic	Ferromagnetic

④ Electronic Properties: The electronic structure of nanoparticles can be studied by UV-photoelectron spectroscopy. When UV photon strikes an electron in the valance band of atom, the e^- is ejected from the atom. The emitted e^- s are counted by spectroscope.



The graph indicating that the energy levels of nanoparticles are discrete.

UV-spectrum of copper nanoparticles having 40-20 atoms.

Lecture No:

Applications of Nano-Materials

- ① Electronics: Electronics is currently the workhorse technology for computing and communications. The electronics devices with typical dimensions of nanometers in either of the three directions, display many unique properties. Single electron transistor (SET), spin valves and magnetic tunnel junctions (MTJ) are conceptually new devices based on the nanotechnology.
- ② Optics: Nanoscience has entered in the field of light emission by the use of light emitting diode (LED). The phenomena of luminescence is also of substantial interest in a number of applications eg. luminescent bar code structures. Photovoltaics, is one of the most immediately attractive applications of nanostructures.
- ③ Diagnostics: Nanotechnology is helpful in medical diagnostics by providing faster, cheaper & portable diagnostic equipments.
- ④ Novel drugs: It aids in delivery of just the right amount of medicine to the exact spots of the body that need it.
- ⑤ Energy: It provide new methods to effectively utilize our current energy resources. Mono and poly-crystalline silicon are widely used in solar cells.
- ⑥ Sensors: Sense based on nanotechnology are more sensitive & hence more effective.
- ⑦ Superior, light weight materials: The strength & light weight of nanomaterials make them widely used in tear resistant clothes, sport materials, bullet proof cloathings, carbon fibre, etc.

Q: A copper ball of radius 2cm is converted into copper nano-powder in which the copper clusters are spherical in shape and having diameter of 56 nm. Calculate the surface to volume ratio in two cases.

Sol Copper ball

$$\text{Volume of sphere (V)} = \frac{4}{3}\pi r^3$$

$$\text{Surface area (A)} = 4\pi r^2$$

$$\text{Surface to Volume ratio; } \frac{A}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3}$$

$$\boxed{\frac{A}{V} = \frac{3}{r}}$$

(i) Copper ball:

$$r = 2\text{ cm} = 2 \times 10^{-2}\text{ m}$$

$$\frac{A}{V} = \frac{3}{r} = \frac{3}{2 \times 10^{-2}}$$

$$\boxed{\frac{A}{V} = 150\text{ m}^{-1}}$$

(ii) Copper nano-crystal

$$r = 56\text{ nm} = 56 \times 10^{-9}\text{ m}$$

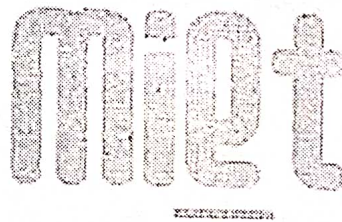
$$\frac{A}{V} = \frac{3}{r} = \frac{3}{56 \times 10^{-9}}$$

$$\frac{A}{V} = \frac{3 \times 10^9}{56}$$

$$\boxed{\frac{A}{V} = 5.36 \times 10^7\text{ m}^{-1}}$$

It is clear from above two cases that nano-size particles have very high surface to volume ratio.

5 Year's
University Paper Questions
(AKTU Question Bank)



Meerut Institute of Engineering and Technology, Meerut

Topic-Wise Important Questions for AKTU End Semester Examinations

Subject Code: BAS101		Subject Name : Engg. Physics		Taught in : I Year / All Branches		
Unit No.	Topics	Q. No.	Question (Statement) - As Appeared in AKTU	Year	Marks	Remarks
Unit-5	Temperature dependence of resistivity in superconducting materials	41	What is superconductivity? Discuss the temperature dependence of resistivity in superconducting materials.			
		42	The penetration depth of Hg at 3.5 K is about 750 Å. Find the penetration depth at 0K. Given T_c for Hg = 4.153 K			
		43	Explain the transition temperature and critical magnetic field. A superconducting material has a critical temperature of 3.7 K in zero magnetic field of 0.306 tesla at 0K. Find the critical field at 2 K.	2008-09, 2013-14, 2014-15 & 2015-16	7	
	Describe type I and type II superconductors	44	Describe type I and type II superconductors. Why are type-I superconductors poor current carrying conductors.	2012-13, 2013-14, 2014-15 & 2016-17	7	
	Meissner effect	45	Discuss Meissner effect. Show that the perfect diamagnetism and zero resistivity are two independent and essential properties of the superconductor.	2013-14, 2014-15 & 2017-18	7	
	Applications of superconductors	46	Discuss the different applications of superconductors and explain qualitative account of high temperature superconductivity.	2016-17	7	
	Nanomaterials.	47	What are nanomaterials.			
	Basic concept of quantum well, quantum	48	What do you mean by quantum well, quantum wire and quantum dots.			
	Fabrication of nano material	49	Describe the Top-down(CVD) and Bottom -Up (Sol Gel approach for the fabrication of Nanomaterials.			
	Properties and Applications of nanomaterials	50	Describe the properties and various applications of nanomaterials.			