

# SUPERCONDUCTIVITY

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When certain metals are cooled, their electrical resistance decreases in the usual way, but on reaching a temperature a few degrees above absolute zero, they suddenly lose all trace of electrical resistance. They are then said to have passed into the superconducting state. Superconductivity was first discovered by Heike Kamerlingh Onnes. A characteristic property of a superconductor is that its electrical resistance is zero below a well defined temperature called the critical or transition temperature,  $T_c$ . So, the conductivity in this range of temperature is infinite.

Niobium is the metallic element with the highest transition temperature (9.3 K), but some alloys and metallic compounds remain superconducting up to even higher temperature. During the phase transition between superconductor and normal conductor, the following properties don't change:

- Lattice
- Electric Reflectivity
- Rate of absorption of slow/fast electrons.
- Elastic properties

## MECHANISM OF SUPERCONDUCTORS

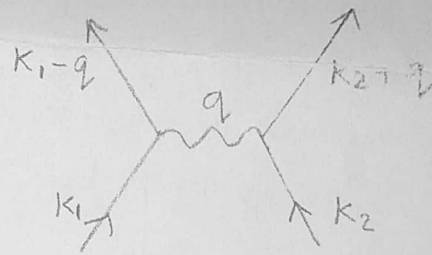
Bardeen, Cooper and Schrieffer showed that superconductivity occurs when a special state of affairs exists between the conduction electrons.

Two electrons in free state will be mutually repelled by the Coulomb force between, but, in the solid state, the force between the 2 electrons will be modified by the interaction of the electrons with the crystal lattice. In certain substances, the lattice interaction is so great that simple repulsive force becomes modified

into an attractive force binding certain electrons together into what are called Cooper pairs. Cooper pairs are thus formed by electron-phonon interactions.

Let an electron of wave vector  $k_1$  emits a virtual phonon  $q$ , which is absorbed by an electron  $k_2$ .  $k_1$  is thus scattered as  $k_1 - q$  and  $k_2$  as  $k_2 + q$ . The process being a virtual one, energy need not be conserved. In fact, the nature of the resulting electron-electron interactions depend on the relative magnitudes of the electronic energy and phonon energy. If this phonon energy exceeds electronic energy, the interaction is attractive.

The fundamental postulate of BCS theory is that the superconductivity occurs when such an attractive interaction between 2 electrons by means of a phonon exchange dominate the usual repulsive interaction.



The energy difference between the free state of the electron and the paired state appears as the energy gap at the Fermi surface. The normal electron states are above the energy and the superconducting electron states are below the energy gap at the Fermi surface. Energy gap is a function of temperature. At  $T = T_c$ , pairing is dissolved and energy gap reduces to zero. Across the energy gap, there are many excited states for the superconducting Cooper pairs. Thus BCS theory predicts many electron ground states as well as excited states for the superconductor in the range 0 to  $T_c$ .

## EFFECTS OF MAGNETIC FIELD

The superconducting state of a metal exists only in a particular range of temperature and field strengths. The condition for the superconducting state to exist in the metal is that some combination of temperature and field strengths should be less than a critical value. Superconductivity will disappear if the temperature and field strengths should be increased. The curves are nearly parabolic and can be reasonably be represented by the relation.

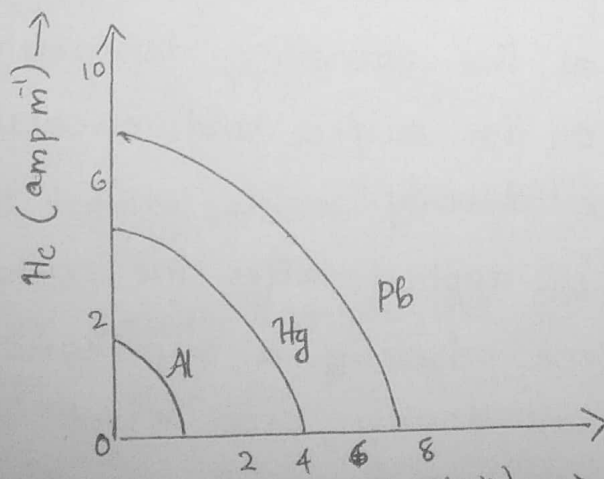
$$H_c = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

where,  $H_c \rightarrow$  Maximum critical field strengths at the temperature  $T$

$H_0 \rightarrow$  Maximum critical field strengths at absolute zero.

$T_c \rightarrow$  Critical temperature

Thus the above equation defines a curve which divides the normal region of the field temperature diagrams of the metal from the superconducting region. The critical field curves for a number of pure metals are shown below:



## ISOTOPE EFFECT

Experimental study of superconducting materials show that the transition temperature varies with the average isotopic mass,  $M$  of their constituents

$$T_c \propto M^{-1/2}$$

For eg:- In mercury,  $T_c$  was found to vary from 4.185K to 4.146K with the variation of the average isotopic mass from 199.5 to 203.4 atomic mass units.

In general form,

$$T_c \propto M^{-\alpha}$$

where,  $\alpha$  is called the isotope effect coefficient.

The Debye temperature,  $\theta_D$  is proportional to  $M^{-1/2}$ , therefore the transition temperature of superconducting materials is closely related to the corresponding Debye temperature.

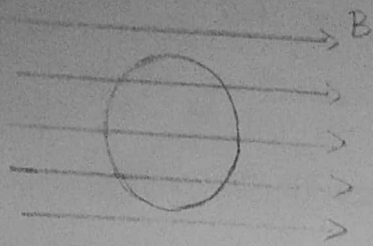
$$\text{ie. } T_c \propto \theta_D$$

$$\text{or } \frac{T_c}{\theta_D} = \text{constant.}$$

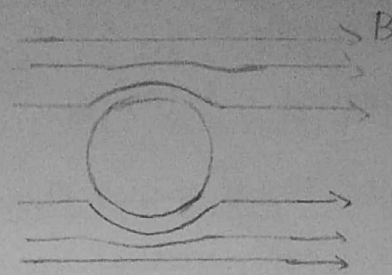
This implies that the lattice vibrations play an important role in superconductivity.

## MEISSNER EFFECT

When a superconductor is cooled in a weak magnetic field, at the transition temperature, persistent currents arise on the surface and circulate so as to cancel the flux density inside, in just the way as a magnetic field is applied after the metal has been cooled. This effect, whereby a superconductor never has a flux density even when is applied magnetic field is called Meissner Effect.



$$T > T_c$$



$$T < T_c$$

Magnetic induction inside the specimen is given by

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

$H \rightarrow$  External Applied field

$M \rightarrow$  Magnetisation produced inside the specimen

According to Meissner effect, the magnetic induction  $B = 0$  inside the bulk superconductor.

$$\therefore \mu_0(H + M) = 0$$

$$\text{or } M = -H$$

Such a material is perfectly diamagnetic whose magnetic susceptibility is given by,

$$\chi = \frac{M}{H} = -1$$

\* If resistivity,  $\rho$  tends to zero while the current  $J$  is held finite, then from Ohm's law,  $E = J\rho$ ,  $E$  must be zero.

From Maxwell's equation,

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

We obtain,  $\frac{\partial B}{\partial t} = 0 \Rightarrow B = \text{constant}$

ie. the flux passing through the specimen cannot change on cooling through the transition. The Meissner effect contradicts this result and suggests that perfect

diamagnetism is an essential property of defining superconducting state. Therefore, we have two independent properties defining the superconducting state.

- $E=0$   $\longrightarrow$  from zero resistivity
- $B=0$   $\longrightarrow$  from Meissner effect.

### ENERGY GAP

It has been found that the electronic heat capacity ( $C_{es}$ ) in the superconducting state varies with temperature in an exponential manner.

$$\text{ie. } C_{es}(T) = Ae^{-\Delta/kT}$$

where,  $A$  is a constant,  $\Delta$  is related to energy gap and  $k$  is the Boltzmann's constant. The above equation suggests that it requires a finite energy to excite an individual electron in a superconductor. In other words the exponential form is an indication of the existence of an energy gap in the superconducting electron levels.

The electrons present in the excited states behave as normal electrons and create resistance whereas those present below it behave as superconducting electrons. The energy gap varies with temperature. It is maximum at zero kelvin and decreases continuously to zero as the temperature is increased to  $T_c$ . Owing to the presence of energy gap, the superconductors respond to high frequency EM radiations of a particular frequency. Thus energy gap is a characteristic feature of all superconductors which determines their thermal properties as well as their response to high frequency EM fields.

$$E_g = 2\Delta = 2bkT_c$$

$2b$  is a constant and varies from element to element.

# TYPES OF SUPER CONDUCTORS

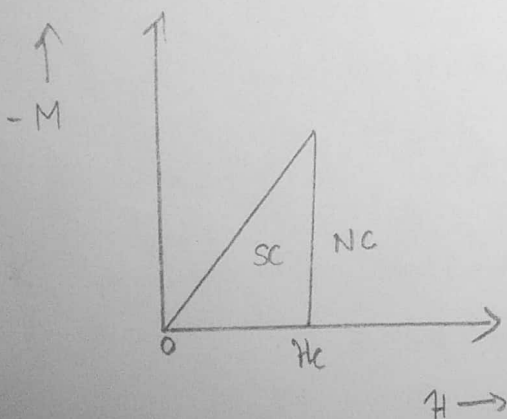
Superconductors are of 2 types in accordance with their diamagnetic response. Superconductors exhibiting a complete Meissner effect are called type I superconductors. They are also known as soft superconductors. In this case diamagnetism abruptly disappears at the critical magnetic field value  $H_c$  and the transition from superconducting to normal state is sharp.

Eg:- Al, Zn, Hg, Sn

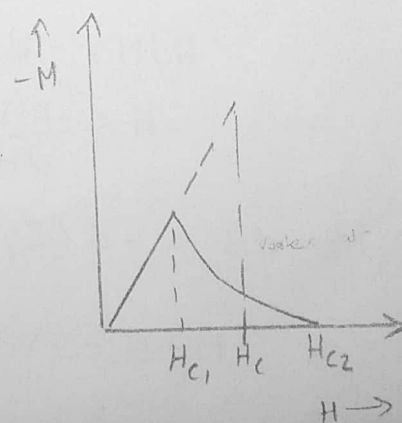
In type II superconductors, the magnetic flux starts penetrating the specimen at a field  $H_{c1}$ , the lower critical field which is lower than  $H_c$ . Above the upper critical field,  $H_{c2}$ , the specimen is a normal conductor. The specimen is in a mixed state between  $H_{c1}$  and  $H_{c2}$ . They are also known as hard superconductors.

Eg:- Ta, V, Nb.

It is found that whether the superconductor is type I or type II depends on whether the superconductor-normal interface energy is positive or negative. A material can change from type I to type II on the substitution of some impurities.



TYPE I



TYPE II

# THERMODYNAMICS OF SUPERCONDUCTING

## TRANSITIONS

Experimental observations show that the transition between the normal and superconducting state is thermodynamically reversible, just like the transition between liquid and vapour phases of a substance. The Meissner effect also suggests the same. Thus we may apply thermodynamics to this phase change and thereby obtain expressions for the difference in entropy and specific heat between normal and superconducting states near absolute zero. The Gibbs free energy per unit volume in the magnetic field is given by

$$G = U - TS - HM \quad \text{--- (1)}$$

where,  $M \rightarrow$  Magnetisation

$S \rightarrow$  Entropy

Also from second law of thermodynamics, the internal energy is given by

$$dU = Tds + HdM \quad \text{--- (2)}$$

where,  $HdM$  is the work done on superconductor per unit volume. Also we have,

$$dU = Tds - PdV \quad \text{--- (3)}$$

Comparing (2) and (3),

$$HdM = -PdV$$

$$H = \frac{-PdV}{dM}$$

$$\text{or } dH = -d\left(\frac{PV}{M}\right)$$

$$\Rightarrow MdH = -VdP$$



Now differentiating (1),

$$\begin{aligned}dG &= dU - Tds - sdT + PdV + VdP \\ &= dU - Tds - sdT - HdM - MdH \\ &= Tds + HdM - Tds - sdT - HdM - MdH\end{aligned}$$

$$dG = -sdT - MdH \quad \text{--- (4)}$$

At constant temperature,  $dT=0$

$$\Rightarrow dG = -MdH$$

On integrating this for the superconducting state,

$$\begin{aligned}\int_0^H dG &= - \int_0^H MdH \\ \text{or } G_S(H) - G_S(0) &= - \int_0^H MdH \quad \text{--- (5)}\end{aligned}$$

If the sample is in normal state, it is a paramagnet and therefore  $M \rightarrow 0$  or  $\chi \rightarrow 0$ , so that

$$\text{? (5)} \Rightarrow G_N(H) - G_N(0) = 0$$

$$\text{or } G_N(H) = G_N(0)$$

This implies that in the normal state the Gibbs function remains invariant under the application of the magnetic field.

Now, for the superconducting state,

$$B = H + 4\pi M = 0$$

$$\Rightarrow M = \frac{-H}{4\pi}$$

$$\begin{aligned}\therefore dG &= -sdT - MdH \\ &= -sdT + \frac{H}{4\pi} dH\end{aligned}$$

$$dT=0 \Rightarrow (dG)_S = \frac{H}{4\pi} dH$$

Integrating from 0 to  $H_c$ ,

$$G_S = \frac{1}{4\pi} \frac{H_c^2}{2} = \frac{H_c^2}{8\pi}$$

$$G_S = \frac{H_c^2}{2}$$

$$\therefore G_S(T, H_c) = G_S(T, 0) + \frac{H_c^2}{8\pi}$$

At the critical value  $H_c$ , the energies are equal in the normal and superconducting states:

$$\therefore G_N(T, H_c) = G_S(T, 0) + \frac{H_c^2}{2}$$