

Unit - II

Section B.

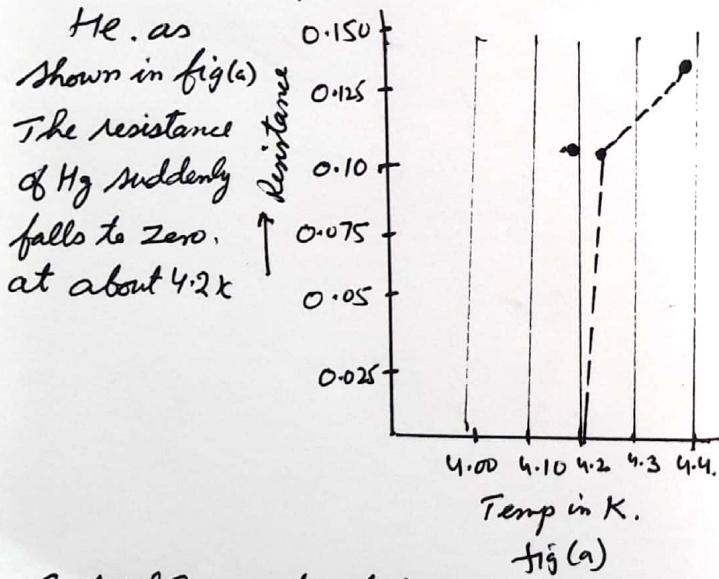
(#1 Unit-II
Section B)

Superconductivity

- Q.1 a) What is superconductivity
b) Give their main characteristic properties

Ans:- a) The phenomenon in which the electric resistivity of a material suddenly falls to 'zero' when the material is cooled to a sufficient low temperature is called as "superconductivity" and the material is called as a "superconductor".

It was discovered by Heike Kamer with his experiments with liquid He. as



Critical Temperature (T_c) of a material is defined as the temperature its resistance suddenly falls to zero. It is also called as Superconducting Transition temperature.

b) Characteristic Properties

- At critical temperature its conductivity falls to zero
- If the external magnetic field employed to cool below T_c is switched off, it

is found that the induced current in the material persists in it for a long duration and decays as per $I = I_0 e^{-\frac{R}{L}t}$ it is called as "persistent current".

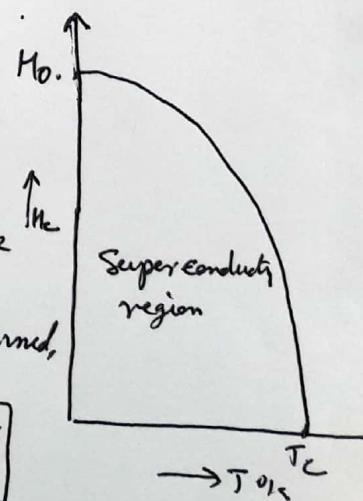
- When placed inside a magnetic field a superconductor material behaves as a perfect diamagnet.
- If the externally applied magnetic field is strong it may destroy superconductivity at "Critical field H_c ".
- Even if the amount of current through a superconducting material is larger than its critical value then also superconductivity is destroyed.
- Properties of superconductors show a change in properties when current through it is of very high frequency ($> 10 \text{ MHz}$).
- Introduction of impurities affects the superconducting properties.
- When placed under stress the temperature of superconductor rises ($= \frac{dT_c}{dP}$). This also affects the superconductivity of the material.

q) Important

The critical magnetic field (H_c) is defined as that magnetic field where half the normal resistance has returned. From graph.

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

At 0K $H_c = H_0$ & $T = T_c$, $H_c = 0$.

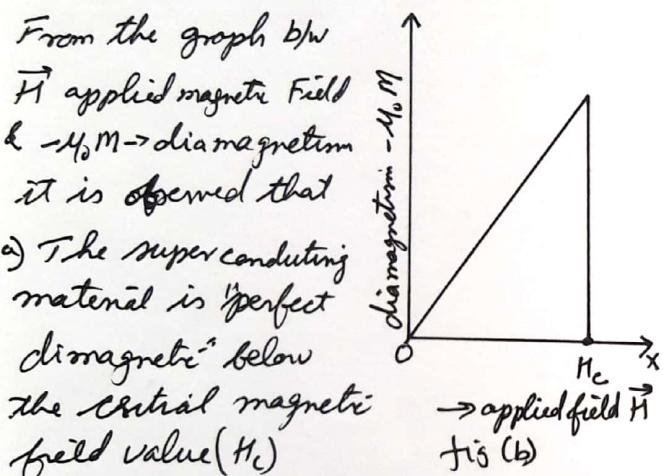


Q.2 Explain and distinguish b/w Type-I & Type-II super-conductors

Ans. Depending upon the magnetic behaviour in an external magnetic field. These are have two types

1. Type-I or soft superconductors

These are perfectly diamagnetic & exhibit Meissner effect completely

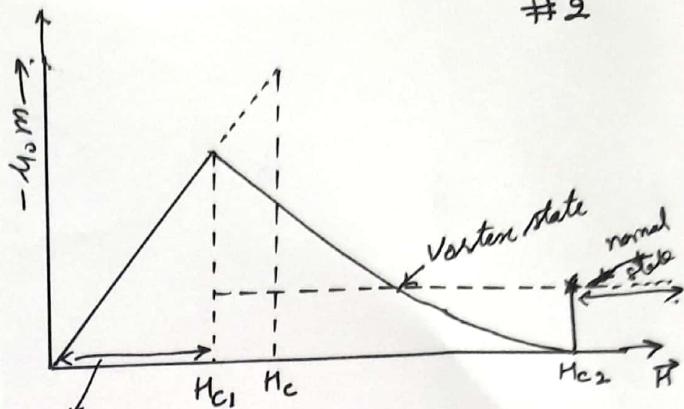


- b) The material loses its superconducting property suddenly at H_c and diamagnetism suddenly dies out i.e. the magnetic field lines enter the specimen.
- c) Above H_c it behaves as a normal conductor

d) As the value of H_c is too small, hence do not have much importance in applications.

e) Then are generally pure samples of ~~the~~ the materials.

2. Type-II In this case the graph b/w \vec{H} and $-M_0 M$ is more elaborate. (fig c)



- The magnetic flux lines start entering the material at H_c , at a value less than H_c .
- The material is said to be in Vortex state b/w H_c & H_{c2}
- In the vortex state $B \neq 0$ and Meissner effect is incomplete.
- Value of H_{c2} may be 100 times that of H_c .
- In Vortex state the material has properties of both superconductor & ordinary material.
- Beyond H_{c2} it is a normal state.

These materials are generally alloys of transition metals with high value of electrical resistance in normal state.

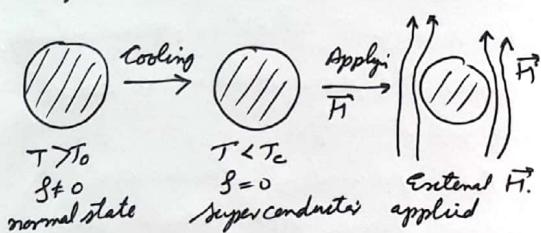
These materials are useful in technical applications.

Ans A close examination of specimen shows small ~~regions~~ regions in normal state called as vortices surrounded by large regions of superconducting ~~state~~ regions.

Q.3 What is Meissner effect

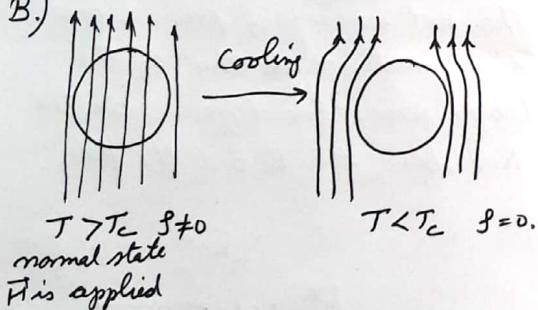
Ans:- The effect was observed by Meissner and Ochsenfeld in 1933. The observations were made in two ~~dis~~ distinct ways

A)



In the first case a specimen is made superconducting by cooling it at $T < T_c$. Then applying the external magnetic field. wherein it exhibits the property of diamagnetism i.e. no flux lines entre the specimen

B)



In this second case the specimen in normal state is placed in a magnetic field and as such the flux lines pass through it. But as the temperature of specimen is brought down at $T < T_c$ it becomes a superconductor and flux lines are pushed out of the specimen and it starts behaving as a perfect diamagnetic material.

Mathematically

$$B = \mu_0 H + M$$

Applied field magnetisation produced inside Specimen.

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At superconducting stage

$$B = 0 \Rightarrow \vec{M} = -\vec{H}$$

Now $\chi = \frac{\vec{M}}{\vec{H}} = -1$ (magnetic susceptibility) = perfect diamagnet.

Let in normal state the current density be j and $\sigma \rightarrow$ resistivity. From Ohm's law in microscopic form.

$$\vec{E} = \sigma \vec{j}$$

At temp $T < T_c$. Superconducting stage $j = 0$ if j is finite (residual current)

$$\Rightarrow E = 0$$

Applying Maxwell's eqn.

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

$$\text{as } E = 0 \Rightarrow \frac{\partial B}{\partial t} = 0. B = \text{constant.}$$

i.e. it should not change on. Cooling but as observed in second case. it is not so.

Thus from

a) Zero resistivity $\vec{E} = 0$

b) from Meissner effect $\vec{B} = 0$

coexist in a superconductor

Do. Thermodynamic Properties of superconductors from book.

- 1) Specific heat
- 2) Entropy
- 3) Thermal conductivity

AND

Also do uses of semiconductors.

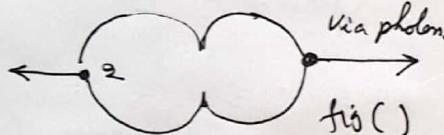
BCS Bardeen, Cooper, Schrieffer
Theory of superconductivity

As per the BCS theory the basic interaction b/w pair of e^- 's via the interchange of virtual photons is responsible for the superconductivity in the material as explained in the following steps

- When an e^- approaches a +ve ion core it undergoes attractive coulomb interaction thereby

Setting the ion core in motion which in turn distorts the lattice.

2)



- When a second e^- approaches it interacts with distorted lattice s.t the energy of 2nd e^- is lowered.

- This above applies that the e^- 's interact via lattice distortion or "photon field" which lowers the energy of the e^- 's. It is also called as electron-lattice-electron interaction.

- Thus it appears that e^- 's 1 & 2 are bound via the generation of phonon.

- The two bound e^- 's must have opposite spins or opposite linear momentum s.t net momenta of the pair is zero. fig()

- Due to phonon exchange the interaction energy is -ve, or attractive force.

7) Now at lower temperature $\xrightarrow{\#4}$ this attractive force b/w pair of electrons exceeds the coulomb repulsion.

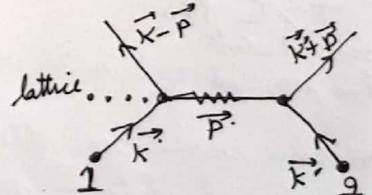
8) This leads to the formation of loosely bound state b/w electrons called as "COOPER PAIR" having an energy $\approx 10^3$ eV in superconductors. Thus the pair behaves as a single entity.

9) The paired e^- 's forms as BOSON. hence net spin is zero. Called as "Cooper pairs"

- When such pairs are produced the property of superconductivity is manifested. The pairing being completed at $T=0K$ and completely broken at $T \geq T_c$. During conduction these pairs do not interact with lattice s.t resistance zero

11) Binding energy

The net energy of pair of free e^- is greater than that of the Cooper pair. The difference b/w the two being the BE of the pair.



let e^- 1 interacts having wave vector K interacts with lattice to produce virtual phonon of momentum P . This is absorbed by e^- 2 having wave vector K' . Thus after interaction

$$K - P \rightarrow \text{momentum of 1st } e^-$$

$$K' + P \rightarrow \dots \text{ " 2nd } e^-$$

This involves the exchange of "Virtual phonon" it is so called because it is a very short time interaction hence energy is not conserved.

Defects in crystals.

The defects in natural crystals arise due to the conditions under which they are crystallized.

Defects are also called as imperfections

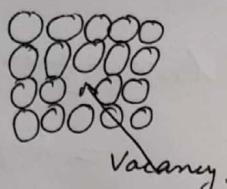
Crystalline defects can be classified on basis of their geometry as

- 1) Point Defects
- 2) Line defects
- 3) Surface Defects
- 4) Volume defects

Point defects

a). Vacancies:-

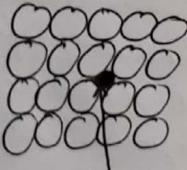
It In this case atom is missing from the crystal giving rise to a vacancy.



b). Interstitial Defects

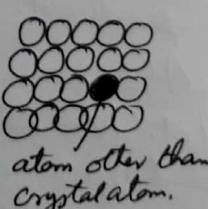
It refers to a condition when an external atom is found in interstitial voids of a regular crystal.

Such an atom is smaller in size than the atoms of the crystal.
eg in FCC ion crystal $r = 0.225 \text{ nm}$ is occupied by C-atom $r = 0.077 \text{ nm}$



c). Substitutional defect

It happens when one of the atoms of crystal gets replaced by a foreign atom.

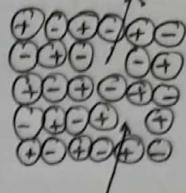


This defect is deliberately introduced in case of Extrinsic Semiconductors where a trivalent atom is introduced in intrinsic (pure) semiconductors to form n-type.

or a pentavalent atom is introduced to form p-type semiconductors.

d) Schottky Defect

Whenever an equal number of cation & anion are missing in a crystal lattice. It is called as Schottky defect.



+ve ion

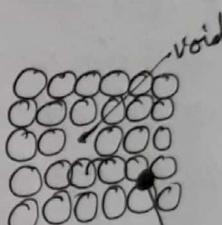
-ve ion

The crystal is electrically neutral. These defects are abnormally prevalent in Alkali halides, NaCl, CsCl etc.

e) Frankel Defect

In this type of defect the crystal again remains electrically neutral as an ion leaves its actual

position in crystal and occupies an interstitial position. This defect is a combination of a "Vacancy" - ("Interstitial" defect). These are present in Ag halides.



Difference b/w Schottky and Frankel defects

Schottky Defect

i) It resembles a vacancy defect.

ii) These are formed when atoms or ions move towards the surface of the crystal. Thereby leaving voids in actual crystal lattice.

iii) The crystals having this defect are less dense

iv) Mostly found in alkali halides

Frankel Defect

i) Related to both "vacancy" & "interstitial" defects

ii) An atom/ion leaves its regular position & occupies an interstitial position.

iv) Density of crystal remains same.

v) Mostly found in silver halides.

eg AgBr.

- Q Determine Equilibrium number of
 a) Frankel defect &
 b) Schottky defect.

Ans:

(a) The disorder / defect increases with temperature as energy is required to ~~displace~~ a atom/ion from its regular position ~~to the surface of the crystal~~.

At equilibrium

Let $N \rightarrow$ total ions in a crystal & having $n' \rightarrow$ no. of interstitial atoms or $n' \rightarrow$ no. of vacancies.

No. of ways the $\frac{n'}{n}$ defect can occur:

$$W = \frac{N!}{(N-n_f)! n_f!} \cdot \frac{n'}{(n'-n_f)! n_f!} \quad (1)$$

Increase in entropy

$$S = k \ln W = k \ln \left[\frac{N!}{(N-n_f)!} \cdot \frac{n'}{(n'-n_f)! n_f!} \right] \quad (2)$$

If E_i is energy required to displace an atom from its regular position to interstitial position. Then for n' no. of Frankel defects, Energy required will be

$$U = n' E_i$$

and change in Helmholtz Energy.

$$F = U - TS = n_f E_i - k \ln \left[\frac{N!}{(N-n_f)!} \cdot \frac{n'}{(n'-n_f)! n_f!} \right] \quad (3)$$

Applying Sterlings Relation (Expansion)

$$(\ln x! = x \ln x - x) \text{ (solving bracket)}$$

$$\ln \left[\frac{N!}{(N-n_f)! n_f!} \right] + \ln \left[\frac{n'!}{(n'-n_f)! n_f!} \right]$$

$$F = n_f E_i = N \ln N + n' \ln n' - (N-n_f) \ln (N-n_f) - (n'-n_f) \ln (n'-n_f) - 2 n_f \ln n_f$$

$$\text{At } \Xi m \left(\frac{\partial F}{\partial n} \right)_T = 0.$$

$$E_i - k T \left[\ln (N-n_f) + \ln (n'-n_f) - 2 \ln n_f \right] = 0.$$

$$E_i = k T \ln \left[\frac{(N-n_f)(n'-n_f)}{n_f^2} \right] \quad \#6$$

$$\Rightarrow \frac{E_i}{k T} = \ln \left[\frac{(N-n_f)(n'-n_f)}{n_f^2} \right]$$

applying approx.

$$n_f \ll N \& n_f \ll n'$$

$$\Rightarrow (N-n_f) \approx N \& (n'-n_f) \approx n'$$

$$\frac{E_i}{k T} = \ln \left[\frac{N n'}{n_f^2} \right]$$

$$\ln (N n') - 2 \ln n_f = \frac{E_i}{k T}$$

determination of n_f by transposing

$$\ln n_f = \frac{1}{2} \ln (N n') - \frac{E_i}{2 k T} = \ln (N n')^{\frac{1}{2}} + \ln e^{-\frac{E_i}{2 k T}}$$

$$\ln n_f = \ln (N n')^{\frac{1}{2}} e^{-\frac{E_i}{2 k T}}$$

$$\text{or } n_f = (N n')^{\frac{1}{2}} e^{-\frac{E_i}{2 k T}}$$

Thus the defect rises/increased with increase of temperature exponentially.

(b) Density / number of Schottky defect at Ξm

As energy is required to pull an atom/ion from its regular lattice position to surface of crystal hence greater the temperature greater will be the number of defects produced.

At Ξm

Let. $N \rightarrow$ total ions of a crystal.

& $n_s \rightarrow$ no. of scattkey defects.

(i.e. n_s no. of cation/danion defects)

No. of ways the defects can be produced

$$W = \left[\frac{N!}{(N-n_s)! n_s!} \right]^2 \quad (i)$$

factor of '2' as it is produced in pairs.

Due to defects produced the increase in entropy is given by

$$S = \ln W = k \ln \left[\frac{N!}{(N-n_s)! n_s!} \right] \quad \text{(ii)}$$

Also total energy required to produce n_s no of defect if E_i is energy required to produce a pair of vacancies

$$U = n_s E_i$$

& Helmholtz energy

$$F = U - TS.$$

$$= n E_i - kT \ln \left[\frac{N!}{(N-n_s)! n_s!} \right]$$

$$= n E_i - kT \left[\ln N! - \ln (N-n_s)! - \ln n_s! \right]$$

Using Stirling formula.

$$\ln x! = n \ln x - x.$$

$$F = n E_i - 2kT \left[N \ln N - N - (N-n_s) \ln (N-n_s) - (N-n_s) + n_s \ln n_s - n_s \right]$$

$$= n E_i - 2kT \left[N \ln N - (N-n_s) \ln (N-n_s) - n_s \ln n_s \right]$$

$\Delta F \equiv 0$

$$\left(\frac{\partial F}{\partial n_s} \right) = 0.$$

$$\Rightarrow E_i - 2kT \left[0 + \ln(N-n_s) + 1 - \ln n_s - 1 \right] = 0.$$

$$E_i = 2kT \ln \left[\frac{N-n_s}{n_s} \right]$$

determination of n_s by transposing

$$\ln \left[\frac{N-n_s}{n_s} \right] = \frac{E_i}{2kT}$$

taking antilog.

$$\frac{N-n_s}{n_s} = e^{\frac{E_i}{2kT}}$$

as $n_s \ll N \Rightarrow N-n_s \approx N$

$$\frac{N}{n_s} = e^{\frac{E_i}{2kT}}$$

$$\text{or } n_s = N \exp \left(-E_i / 2kT \right)$$

NOTE

Students should note that in both cases the only difference is that in W . Rest of the steps are the same

Usefulness of the two defects

Both the defects play a vital role in the use / application of the crystals such as

- i) They alter the optical property
- ii) They alter the magnetic property
- iii) ~~Today~~ These defects reduces / obstructs the mobility of ions.
- iv) These defects can act as acceptors and donor points.
- v) They alter the mechanical properties.