CHAPTER – 1
INTRODUCTION
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1.1 History of Superconductivity

Superconductivity manifests itself mainly as an absence of resistivity when electrical resistivity of the specimen drops to zero when cooled to an adequately low temperature known as critical (transition) temperature, $T_C$. It was discovered in 1911 by H. Kamerlingh Onnes in Leiden, three years after he first liquefied Helium. He measured the resistivity of mercury and found the critical temperature $T_C = 4.2$K. The resistivity behavior as a function of temperature is shown in Fig.

![Graph showing resistivity of mercury](image)

Fig. 1.1: Below the transition temperature, the resistivity drops to zero.

The resistivity of mercury vanished completely below 4.2 K, the transition from normal conductivity to superconductivity occurring over a very narrow range of temperature of the order of 0.05 K.
If a superconductor has the shape of a ring and a current could be induced in it by electromagnetic induction, then allow the ring to cool under the effect of magnetic field from a temperature above the critical temperature to below $T_c$ and then to remove the field. It was observed that this current continues to persist with undiminished strength for days. In another experiment a lead ring was able to carry an induced of several hundred amperes for over a year without any change. Such currents are called ‘**Persistent current**’.

On applying a sufficiently strong magnetic field on a superconductor the superconductivity of the material is destroyed by the application of magnetic field and the material restores back to the normal conducting state. The critical value of the magnetic field for the destruction of superconductivity is denoted by $H_c$ and is a function of temperature.

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

where $H_0$, is the critical field at 0°K and has specific value for each material. It must be added that the original observation by K. Onnes on the destruction of superconductivity by passage of an electric current down a superconducting wire when the current exceeds a certain critical value.

**Meissner Effect**
The next major discovery, was made in Berlin around 1933, by Walther Meissner and Robert Ochsenfeld. They stated that a superconducting material expelled magnetic fields from their interiors. The effect is of fundamental important as it shows that how a bulk superconductor behaves in an external magnetic field. Because superconductors are perfect conductors of electricity, it is easy to see by Lenz’s law that any imposed magnetic field will cause itself to be expelled from a superconductor by inducing eddy currents. The discovery by Meissner and Ochsenfeld, was well recognized and later branded as the Meissner effect. Commonly we can say that all superconductors have two separate fundamental properties.

Fig. 1.2: Meissner Effect
Electrically, they are perfect conductors. Magnetically, they are perfect diamagnets.

In 1957, Bardeen, Cooper and Schrieffer proposed a theory (also well known as the BCS theory) that discussed the microscopic origins of superconductivity, and could quantitatively predict the properties of superconductors. Before the development of BCS theory, Ginzburg-Landau theory was suggested in 1950, which was a macroscopic theory. Mathematically the BCS theory is complex, but develops itself from an earlier discovery made by Cooper in 1956. The BCS theory states that two electrons experience a force of attraction due to an electron-phonon interaction. These pairs are known as *Cooper pairs*. Technically speaking it means an electron in the cation lattice will distort the lattice around it, creating an area of greater positive charge density around itself.

The next big discovery was made in 1986 by Johannes Georg Bednorz and Karl Alexander Müller at the IBM laboratories in Zurich by creating a brittle ceramic compound that showed superconductivity at the highest transition temperature at that time about 30 K.
Since then many High $T_C$ superconductors have been developed with the highest $T_C$ as of 2009, (at ambient pressure) is mercury barium calcium copper oxide (HgBa$_2$Ca$_2$Cu$_3$O$_x$), around 135 K and is held by a cuprate-perovskite material, which possibly reaches 164 K under high pressure.

**1.2 Types of Superconductors**

Depending upon their behavior in an external magnetic field, superconductors are divided into two types: Type – I and Type – II superconductors.

**TYPE – I SUPERCONDUCTORS**

Type – I superconductors exhibit zero resistivity at low temperatures and posses the nature of repelling magnetic fields from the interior of the superconductor
(Meissner effect). The perceiving characteristics of these metals are zero electrical resistivity, zero internal magnetic field below a critical temperature, and a critical magnetic field above which superconductivity ceases. These superconductors are modeled by the BCS theory. The best known conductors (eg. copper etc) at room temperature do not become superconducting at any temperature.

![Fig 1.4: Types of Superconductors](image)

Type I superconductors have been of limited practical usefulness because the critical magnetic fields are so small that the superconducting state disappears suddenly at small temperature. Type I superconductors are sometimes called
"soft" superconductors while the Type II are "hard", maintaining the superconducting state to higher temperatures and magnetic fields.

**TYPE – II SUPERCONDUCTORS**

A type-II superconductor is characterized by the formation of magnetic vortices in an applied magnetic field. Besides being mechanically harder than Type I superconductors, they exhibit much higher critical magnetic fields. Type II superconductors such as niobium-titanium (NbTi) are used in the construction of high field superconducting magnets.

Type-II superconductors usually exist in a mixed state of normal and superconducting regions. This is sometimes called a vortex state, because vortices of superconducting currents surround filaments or cores of normal material. Type II superconductors show two critical magnetic field values, one at the onset of a mixed superconducting and normal state, \( B_{c1} \), and one where superconductivity ceases, \( B_{c2} \).

Fig. 1.5 Type-II Superconductor magnetic field in not excluded completely
In Type II superconductors the magnetic field is not excluded completely, but is constrained in filaments within the material. These filaments are in the normal state, surrounded by supercurrents in what is called a vortex state.

### 1.3 Properties of Superconductors

**Zero electrical resistance**

The sudden disappearance of resistivity ($<10^{-5} \, \Omega$) when a metal is cooled was first observed for Mercury by Kammerlingh Onnes in 1911. Although the resistance is never an absolute zero it reduces to ten/millionth times to that of a good conductor. Even today with the best possible technological advancement it is impossible to measure whether a superconductor has a practical zero resistance. Therefore the term zero resistance is attributed to resistance of the order of $10^{-5} \, \Omega$ or less.

Because a superconductor has zero DC resistance hence a large current must flow through it, but on the contrary a superconductor has a critical value of current above which it loses its superconductivity. The critical current generally is of the order of 100Å in a 1mm wire.

**Critical Temperature**

The temperature below which a metal turn into a superconducting material is called critical temperature. In other words it’s the temperature at which the
superconductivity of a material is destroyed, the energy gap vanishes and the conductor reverts to its original state. The BCS calculations give

$$k_B T_c = 1.14 \hbar \omega_D \exp\left( -\frac{1}{U_0 D(E_F)} \right)$$

where $D(E_F)$ denotes density of electronic levels, $U_0$ the interaction parameter.

**Energy Gap**

The thermal properties of superconductors suggest that there are gaps in the distribution of energy levels available to the electrons. Therefore a finite amount of energy, denoted by delta ($\Delta$), should be provided to an electron to excite it. This energy is greatest at absolute zero denoted by $\Delta_0$ and at transition temperature it approaches to zero, which corresponds to its value in the normal state.

![Fig. 1.6 Energy Gap (2$\Delta$) centered at Fermi level $E_F$ in the superconducting state.](image)
The Cooper pairs are broken when the superconductor is heated. Each time a pair is broken; energy greater or equal to the energy gap ($\Delta$) must be supplied to each of the two electrons.

![Graph of reduced energy gap versus reduced temperature](image)

Fig. 1.7 Graph of reduced energy gap versus reduced temperature

Theory and experiments suggest that energy equal to twice the energy gap ($2\Delta$) must be supplied to the superconductor. The value of $2\Delta_0$ is of the order of $k_B T_c$, where $k_B$ is Boltzmann’s constant ($1.38 \times 10^{-23}$ joule per kelvin). This behavior can be verified from fig 1.7

**Heat Capacity**

The heat capacity of a superconductor in its normal state may be written as

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\[ C_V = \gamma T + \alpha T^3 \]

The first term denoting electronic contribution and second term denoting Debye term.

Fig. 1.8 Temperature variation of heat capacity

![Graph showing temperature variation of heat capacity](image)

Fig. 1.8 presents a comparative view of temperature versus heat capacity of vanadium in its superconducting and normal state.

### 1.4 BCS Theory

In classical physics the resistance of a metal is mainly due to collision of free electrons and the crystal lattice vibrations called phonons. A small resistance is

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2 Introduction to Solid State Physics (Seventh edition) Charles Kittel
produced by the scattering of electrons due to impurities and defect in the metal. The answer to the question what happens in a superconductor was discussed by the microscopic theory of superconductivity named BCS theory given in 1957 by its inventors Bardeen, Cooper and Schrieffer. It emphasizes that the interaction of an electron with lattice vibrations need to be examined more closely. There is a mutual attraction between the electron and the ion core because of Coulomb interaction.

A cooper pair takes the character of a boson and condenses in the ground state. This coupling of these electrons take place over a range of 100 nanometers and have a binding energy of the order of milli-electron volts.

The key to BCS theory was given in terms of Cooper pair. A Cooper pair is a pair of electron which conventionally should have a force of repulsion between them, but experience an attractive force due to phonon interaction. This condensation
of Cooper pair takes place when the difference in energies of the two electrons is of the order of $\hbar \omega_D$, where $\omega_D$ is the Debye frequency.

The sequence of events that materialize a Cooper pair condensation is as follows. Firstly a electron deforms a lattice in vicinity, creating a phonon that moves through the crystal. This phonon is absorbed by the second electron which is moving in the direction opposite to the direction of the first electron and is attracted by the deformed lattice.

According to BCS theory transition temperature is given by the following expression:

$$T_c = 1.14 \hbar \omega_D \exp[-1/N(0)\sqrt{V}]$$
where, $\omega_D$ is phonon frequency, $N(0)$ is density of states, $V$ is cooper pair interaction.

### 1.5 High Temperature Superconductors

Ever since the discovery of superconductors scientists have been searching for materials that can show superconductivity at room temperature. In 1986, a discovery revolutionized the field of superconductivity. J Georg Bednornz and K A Müller of IBM Research Laboratory in Zurich discovered an oxide of lanthanum-barium-copper which exhibited superconductivity at about 30K. For this research Bednorz and Müller received Nobel Prize in 1987. The discovery of high-temperature superconductivity in ceramic cuprate oxides led to unprecedented effort to explore new superconducting materials with higher transition temperatures. The value of $T_C$ in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was found to increase upto 57K under pressure. This discovery in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ increased the interest in scientist for finding still higher temperature superconductors.

These efforts came true for the team of Chu and co-workers who reported a notable high superconductivity transition temperature of 92K by replacing Lanthanum by Yttrium. The highest transition temperature of 133K is observed
for HgBa$_2$Ca$_2$Cu$_3$O$_8$ at ambient pressure which increases up to 164K under hydrostatic pressure of 45 GPa.

![Fig. 1.11 Y-Ba-Cu-O structure](image)

Many of the properties of these conventional high $T_C$ superconductors are identical to those of conventional low $T_C$ superconductors. However, there are certain properties which do not match with those of conventional ones. For example, small isotope effect, small coherence length, and unconventional temperature dependencies of the normal state response function. Also, pressure is found to increase the transition temperature in high $T_C$ superconductors.

The coherence length between cooper pairs in these superconductors can be as small as one or two atomic spacing. For such short distances, the coulomb repulsion force will generally dominate, causing electron to repel rather than
attract. Therefore high-$T_C$ superconductivity cannot be explained on the basis of BCS theory. Cooper pairs in these superconductors may be explained on the basis of antiferromagnetism in the copper oxide layers. Researches are still continuing for the exact mechanism responsible for superconductivity in these materials.

1.6 Oxypnictide Superconductors

Until 2008 high $T_C$ superconductors were generally known as cuprate superconductor because of Cu-O layers in them. But in 2008 Yoichi Kamihara reported superconductivity in a new type of material LaO$_{1-x}$F$_x$As having $T_C = 26$K. Higher transition temperature were obtained when Lanthanum was replaced with R (rare earth elements); R= La, Ce, Nd, Sm, Pr. The highest transition temperature obtained for iron-pnictides has been 55K for the compound SmFeAsO$_{1-x}$\(^3\).

The discovery of superconductivity in iron pnictides is generating enormous interest, because these materials are the first non-copper compounds with $T_c > 50$ K. These superconductors are obtained by doping their non superconducting parent compounds. The ground state of these non-superconductors is assumed to be either a non-magnetic metal or an antiferromagnetic semi metal.

Initial calculations suggest that superconductivity originates from the $d$ orbitals of Fe-ions, suggesting non-phonon pairing mechanism. Secondly, the semi metal exhibits strong antiferromagnetic fluctuations and a possible Spin Density Wave (SDW) instability. And lastly, superconductivity may emerge from disconnected pieces of Fermi Surface (FS), exhibiting multi-band model.

Calculations on band structure of oxypnictides show that FS is formed by nearly filled valence band (hole band) around $\Gamma$ and nearly empty conduction band (electron band) around $M$, suggesting a two band model.

All these hole-like pockets and electron-like pockets arise from the five $d$-orbitals of Fe atom.

Fig. 1.12 Schematic plot of the bare band dispersions of the valence (hole) and conduction (electron) bands for the undoped parent compound.\textsuperscript{4}

\textsuperscript{4} Q Han \textit{et al.} EPL 82, 37007 (2008)
The crystal structure of oxypnictides has REO layers separating FeAs layers as shown in figure 1.13. The REO layers act as spacers between Fe$_2$As$_2$ layers and are also charge reservoirs, similar to HTSC where the first layer is superconducting, the second is insulating layer, and the third layer is a hole-donating layer. The superconducting layer is the Fe$_2$As$_2$ layer. Thus, conduction carriers are two-dimensionally confined in the Fe$_2$As$_2$ layer, causing strong interactions among the electrons.

![Fig. 1.13 Tetragonal Structure of Oxypnictide](image)

HTSC and iron based superconductors share some close similarities:

1) Both have layered structure.
2) Both exhibit antiferromagnetic layers.
3) Phase diagram is similar.
4) Both are type – II superconductors.
The iron pnictides are multi-band systems in contrast to cuprates which are single-band systems. In both classes superconductivity emerges with carrier doping in the antiferromagnetic parent compounds, however the parent compound of cuprates is a Mott insulator and that of iron pnictides is a bad metal or semiconductor.

A comparison of superconducting properties for high $T_C$ superconductors and iron based superconductors is given below.

<table>
<thead>
<tr>
<th>Type</th>
<th>Penetration Depth $\lambda$ (nm)</th>
<th>Coherence Length $\xi$ (nm)</th>
<th>Critical Field $H$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High $T_C$ superconductors</td>
<td>100 – 250</td>
<td>1 – 2</td>
<td>400</td>
</tr>
<tr>
<td>Iron-based superconductors</td>
<td>180 – 250</td>
<td>1 – 5</td>
<td>50</td>
</tr>
</tbody>
</table>

The microscopic theory for oxypnictides is not very clear but it is believed that the antiferromagnetic layers could play a crucial role in the electron coupling mechanism.
OBJECTIVES

1. To obtain an expression for magnetization and Neel Temperature for iron-pnictides.

2. To study the role of interlayer magnetic interaction on the magnetism of oxypnictides.

3. To obtain an expression for $T_c$ using two band model for oxypnictides.

4. To study dependence of $T_C$ on various parameters.