TUNNELING STUDY OF SUPERCONDUCTIVITY IN MAGNESIUM DIBORIDE

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ABSTRACT OF DISSERTATION

Mohamed Hosiny Badr

The Graduate School
University of Kentucky
2003
TUNNELING STUDY OF SUPERCONDUCTIVITY
IN MAGNESIUM DIBORIDE

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor of Philosophy
in the College of Arts and Sciences at
University of Kentucky

By

Mohamed Hosiny Badr

Lexington, Kentucky

Director: Dr. Kwok-Wai Ng, Professor of Physics and Astronomy
Lexington, Kentucky
2003

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ABSTRACT OF DISSERTATION

TUNNELING STUDY OF SUPERCONDUCTIVITY IN MAGNESIUM DIBORIDE

Although the pairing mechanism in MgB₂ is thought to be phonon mediated, there are still many experimental results that lack appropriate explanation. For example, there is no consensus about the magnitude of the energy gap, its temperature dependence, and whether it has only one-gap or not. Many techniques have been used to investigate this, like Raman spectroscopy, far-infrared transmission, specific heat, high-resolution photoemission and tunneling. Most tunneling data on MgB₂ are obtained from mechanical junctions. Measurements of energy gap by these junctions have many disadvantages like the instability to temperature and field changes. On the other hand, sandwich-like planar junctions offer a stable and reliable measurement for temperature dependence of the energy gap, where any variation in the tunneling spectra can be interpreted as a direct result from the sample under study.

To the best of our knowledge, we report the first energy gap temperature- and magnetic field-dependence of MgB₂/Pb planar junctions. Study of the temperature-dependence shows that the small gap value (reported by many groups and explained as a result of surface degradation) is a real bulk property of MgB₂. Moreover, our data is in favor of the two-gap model rather than the one-gap, multi-gap, or single anisotropic gap models. The study of magnetic field effect on the junctions gave an estimation of the upper critical field of about 5.6 T. The dependence of energy gap on the field has been studied as well.

Our junctions show stability against temperature changes, but "collapsed" when the magnetic field (applied normal to the junction barrier) is higher than 3.2 T. The irreversible structural change switched the tunneling mechanism from quasiparticle tunneling into Josephson tunneling. Josephson I-V curves at different temperatures have been studied and the characteristic voltages are
calculated. The estimated MgB$_2$ energy gap from supercurrent tunneling in weak link junctions agrees very well with that from quasiparticle tunneling.

Reported properties on polycrystalline, single crystal and thin film MgB$_2$ samples are widely varied, depending on the details of preparation procedure. MgB$_2$ single crystals are synthesized mainly by heat treatment at high temperature and pressure. Single crystals prepared by this way have the disadvantages of Mg deficiency and shape irregularity. On the other hand, improving the coupling of grain boundaries in polycrystalline MgB$_2$ (has the lowest normal state resistivity in comparison to many other practical superconductors) will be of practical interest. Consequently, we have been motivated to look for a new heat treatment to prepare high quality polycrystalline and single crystal MgB$_2$ in the same process. The importance of our new method is its simplicity in preparing single crystals (neither high pressure cells nor very high sintering temperatures are required to prepare single crystals) and the quality of the obtained single crystal and polycrystalline MgB$_2$. This method gives high quality and dense polycrystalline MgB$_2$ with very low normal state resistivity ($\rho_n(40\, \text{K}) = 0.28\, \mu\Omega\text{cm}$). Single crystals have an average diagonal of 50 $\mu$m and 10 $\mu$m thickness with a unique shape that resembles the hexagonal crystal structure. Furthermore, preparing both forms in same process gives a great opportunity to study inconsistencies in their properties. On the other hand, magnesium diboride thin films have also been prepared by magnetron sputtering under new preparation conditions. The prepared thin films have a transition temperature of about 35.2 K and they are promising in fabricating tunnel junctions.

**KEYWORDS:** MgB$_2$ superconductor, tunneling junctions, single crystals, Josephson effect, magnetic field effect

Mohamed H. Badr

(Author's Name)
TUNNELING STUDY OF SUPERCONDUCTIVITY IN MAGNESIUM DIBORIDE

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پِنْئَ الْحَدَّ الرَّحْمَانِ الرَّحِيمِ

َرَبَّنَا فَقِيلُ هَبْ إِنَّكَ أَنتَ الصَّمِيعُ العَلِيمُ

Qur’an 2:127
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Chapter 1

Introduction

1.1 Superconductivity

1.1.1 Discovery

Superconductivity is characterized by two unique features, namely, *perfect conductivity* and *perfect diamagnetism*. The first was discovered by H. K. Onnes [1] in 1911 three years after his success in liquefying helium gas. He found that the electrical resistivity of mercury disappeared suddenly when cooled below $T \approx 4.2$ K and reported: "mercury at 4.2 K has entered a new state, which owing to its particular electrical properties can be called the state of superconductivity" (see figure 1.1). Such particular temperature at which a material transits from normal to superconducting state is called the critical transition temperature ($T_c$) and the phenomenon is known as *superconductivity*.

Surprisingly, the second feature of superconductivity was discovered 22 years later by W. Meissner and R. Ochsenfeld [2]. They found that an external magnetic field was completely excluded by the superconductor, i.e., a superconductor showed *perfect diamagnetism*. The phenomenon of field exclusion is now known as the *Meissner effect*. In addition, a magnetic field already penetrating a superconductor in the normal state (at $T > T_c$) will be expelled as the material transits to the superconducting state (at $T < T_c$). This phenomenon is known as *reverse Meissner effect*. Perfect diamagnetism can be observed in *type I*, bulk, and clean superconductors. Otherwise partial penetration and trapping of magnetic field may occur.

1.1.2 Types of Superconductors

Superconductors are classified as type I (soft) and type II (hard) superconductors according to their magnetization behavior. Type I superconductors were discovered first and mainly observed in pure metallic elements. Table (1.1)
Figure 1.1: Temperature-dependence of resistance for mercury. Resistance disappeared at $T = 4.2 \text{ K}$. Onnes stated that the material has entered a new state that he called “superconductivity” [1].

Table (1.2) lists some type I superconducting elements along with their $T_c$’s. On the other hand, compounds and alloys are in general type II superconductors. Table (1.2) lists some type II superconductive compounds and elements along with their $T_c$’s.

Type I superconductors show a complete Meissner effect up to certain critical field, $H_c$, at which complete penetration occurs as the superconductor becomes normal. Unlike Type I superconductors, type II superconductors are characterized by two critical fields, the lower critical field, $H_{c1}$, and the upper critical field $H_{c2}$. Up to $H_{c1}$, type II superconductors display perfect diamagnetism like the type I superconductors, then magnetic field starts penetrating the material partially. For fields $H \geq H_{c2}$ complete penetration takes place and the superconducting state disappears. Figure 1.2 shows the behavior of type I and type II superconductors. For type II superconductors, $H_c$ is known as the thermodynamic critical field, related to the stabilization of free energy of superconductor as:

$$
\Delta F = F_N(0) - F_S(0) = H_c^2 / 8\pi.
$$

(1.1)

By stabilization energy we mean the free energy difference between normal and superconducting state.
Table 1.1: Elements that show type I superconducting behavior along with their critical temperatures.

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>$T_c$(K)</th>
<th>Superconductor</th>
<th>$T_c$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>15.0</td>
<td>Zinc</td>
<td>0.85</td>
</tr>
<tr>
<td>Lead</td>
<td>7.20</td>
<td>Osmium</td>
<td>0.66</td>
</tr>
<tr>
<td>Lanthanum</td>
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<td>Tantalum</td>
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<td>Cadmium</td>
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<tr>
<td>Mercury</td>
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<td>Ruthenium</td>
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<td>Tin</td>
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<td>Titanium</td>
<td>0.40</td>
</tr>
<tr>
<td>Indium</td>
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<td>Rhenium</td>
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<td>Iridium</td>
<td>0.11</td>
</tr>
<tr>
<td>Protactinium</td>
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<td>Lutetium</td>
<td>0.10</td>
</tr>
<tr>
<td>Thorium</td>
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<td>Beryllium</td>
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<td>Rhodium</td>
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For type II superconductors, $H_c$ can be determined by the point at which the area under magnetization curve equals to that of type I. The material is in the vortex (mixed or Schubnikov) state when the field is between $H_{c1}$ and $H_{c2}$, figure 1.2. In this state both normal and superconducting phases co-exist and the magnetic field penetrates the material in form of vortices with cores in the normal state. Figure 1.3 shows a Scanning Tunneling Microscopy (STM) picture of magnetic flux penetrating a type II superconductor ($\text{NbSe}_2$ at $T=0.3$ K and 1 Tesla) in the vortex state [3]. The flux penetrates in tube-like forms, each carrying a quantized amount of flux $\phi_o = \frac{hc}{2e}$. The resulting pattern of penetrated flux forms a lattice which is known as Abrikosov flux lattice. Conductance measurements show that electronic states are bound to each vortex core where bright spots represent high density of electron states, corresponding to the normal phase. On the other hand, darker areas represent superconducting regions with no states at Fermi level. The degree of darkness is due to the spatial variation of the energy gap.
Table 1.2: Elements and compounds that show type II superconducting behavior along with their critical transition temperatures.

<table>
<thead>
<tr>
<th>Superconductor</th>
<th>$T_c$ (K)</th>
<th>Superconductor</th>
<th>$T_c$ (K)</th>
</tr>
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<tbody>
<tr>
<td>Hg$<em>{0.8}$Tl$</em>{0.2}$Ba$_2$Ca$_2$Cu$<em>3$O$</em>{8.33}$</td>
<td>138</td>
<td>La$_2$Ba$_2$CaCu$<em>5$O$</em>{7+\delta}$</td>
<td>79</td>
</tr>
<tr>
<td>HgBa$<em>2$Ca$</em>{1-x}$Sr$_x$Cu$<em>2$O$</em>{6+\delta}$</td>
<td>123</td>
<td>La$<em>{1.85}$Sr$</em>{0.15}$CuO$_4$</td>
<td>40</td>
</tr>
<tr>
<td>HgBa$<em>2$CuO$</em>{4+\delta}$</td>
<td>94</td>
<td>La$<em>{1.85}$Ba$</em>{1.15}$CuO$_4$</td>
<td>30</td>
</tr>
<tr>
<td>Tl$_{2}$Ba$_2$Ca$_3$Cu$<em>4$O$</em>{12}$</td>
<td>120</td>
<td>MgB$_2$</td>
<td>39</td>
</tr>
<tr>
<td>Tl$<em>{0.5}$Pb$</em>{0.5}$Sr$_2$Ca$_2$Cu$_3$O$_9$</td>
<td>112</td>
<td>Nb$_3$Ge</td>
<td>23.2</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>110</td>
<td>Tc</td>
<td>7.8</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CaCu$_2$O$_8$</td>
<td>91</td>
<td>V</td>
<td>5.4</td>
</tr>
<tr>
<td>GdBa$_2$Cu$_3$O$_7$</td>
<td>94</td>
<td>RuSr$_2$GdCu$_2$O$_8$</td>
<td>58</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{7+\delta}$</td>
<td>93</td>
<td>UGe$_2$</td>
<td>1</td>
</tr>
<tr>
<td>YbBa$<em>{1.6}$Sr$</em>{0.4}$Cu$_4$O$_8$</td>
<td>78</td>
<td>AuIn$_3$</td>
<td>0.00005</td>
</tr>
</tbody>
</table>

1.1.3 High Temperature Superconductors (HTS)

Since the discovery of superconductivity in mercury in 1911, the search for new superconductors with higher $T_c$ was not very productive and ended up with the discovery of superconductivity in Nb$_3$Ge [4] in 1973 with $T_c = 23.2$ K. A breakthrough took place in 1986 when Bednorz and Muller [5] discovered the first member in High Temperature Superconductors (HTS) cuprates family in La$_{1-x}$Ba$_x$CuO$_4$ with $T_c \approx 30$ K. Within a few years, new members were discovered with $T_c$ as high as 138 K. High $T_c$ superconductors can be classified into the following families: La$_2$CuO$_4$ (also known as La214) [5], YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO or Y-123) [6], Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_8$ (BSCCO or Bi-2223) [7], and Tl$_2$Ba$_2$Cu$_3$O$_{8+\delta}$ (TBCCO) [8]. Table (1.2) shows $T_c$s for different family members. One main feature that characterizes HTS is their crystal structures which belong to the family of perovskites (named after the mineralogist C. von Perovski). Perovskites have the general formula ABO$_3$, with A and B as anions and O as the cation. The structure reveals the presence of Cu-O planes that thought to play an important role in the mechanism of superconductivity in high temperature superconductors and in the high anisotropic properties characterizing them.
Figure 1.2: Magnetization behavior of type I and type II superconductors. Type I is characterized by one critical field $H_c$ (top right) while Type II has lower and upper critical fields $H_{c1}$ and $H_{c2}$, respectively. Between the two critical fields, type II superconductor is in a vortex state.

Figure 1.3: Abrikosov flux lattice for NbSe$_2$ superconductor at $T = 0.3$ K and an applied field of 1.0 T. Magnetic field (between the two critical fields $H_{c1}$ and $H_{c2}$) penetrates a superconductor (bright spots) in a regular manner forming the flux lattice. The degree of brightness reflects different degrees of DOS in normal and superconducting regions [3].
1.1.4 Theories prior to BCS theory

**London theory:** We should note that Meissner effect reflects the fact that diamagnetism is a main feature in superconductivity which can not be explained by considering superconductivity as a normal state with zero resistance. In other words, Ohm’s law failed to describe the two hallmarks of superconductivity, namely, absence of resistance and presence of perfect diamagnetism.

According to Ohm’s law \( \vec{J}_n = \sigma_n \vec{E} \), the electric field should be zero for finite current density and infinite conductivity. Since by Maxwell equation \( d\vec{B}/dt \) is proportional to \( \text{curl}\vec{E} \), then \( \vec{E} = 0 \) requires \( d\vec{B}/dt = 0 \), i.e., magnetic field should be constant inside a superconductor. This is in contradiction with the phenomenon of field exclusion, i.e. \( B_a = 0 \) once \( T < T_c \). To describe these two phenomena simultaneously, F. and H. London [9] modified Ohm’s law by the following two equations, based on a two-fluid concept with densities \( n_s \) and \( n_n \):

\[
\frac{\partial}{\partial t} \vec{J}_s = \frac{n_s e^2}{m} \vec{E} \quad (\vec{J}_s = -en_s \vec{v}_s) \quad (1.2)
\]

\[
\vec{J}_n = \sigma_n \vec{E} \quad (\vec{J}_n = -en_n \vec{v}_n)
\]

\[
\text{curl} \vec{J}_s = \frac{n_s e^2}{mc} \vec{B} \quad (1.3)
\]

Equation (1.2) reflects the perfect conductivity of a superconductor where superelectrons are being accelerated in electric field rather than following \( \vec{J}_n = \sigma_n \vec{E} \) for a normal conductor. Although equation (1.2) can be derived for perfect conductor (electron gas with infinite mean free path), the non-locality of electric field will always keep the effective conductivity finite. Using Maxwell equation \( \nabla \times \vec{B} = \frac{4\pi}{c} \vec{J} \) and ignoring the normal component \( \vec{J}_n \), equation (1.3) takes the form \( \nabla^2 \vec{B} = \vec{B}/\lambda_L^2 \) and this leads to the exponential decay of magnetic field (applied parallel to the surface) inside a superconductor with a *London penetration depth* \( \lambda_L(0) = \sqrt{mc^2/4\pi n_s e^2} \), at \( T \to 0 \). Therefore, magnetic field
vanishes inside the bulk of a superconductor as required by perfect diamagnetism.

London combined these two equations into a single one by the use of vector potential $\vec{A}$ and canonical momentum, defined as $\vec{P} = m\vec{v} + (e/c)\vec{A}$. With the condition $<\vec{P}> = 0$ that gives the rigidity to the superconducting state; the average local velocity in the presence of magnetic field will be $<\vec{v}> = -(e/mc)\vec{A}$.

Since $\vec{J}_s = -en\vec{v}_e$, we get the compact London equation:

$$\vec{J}_s = -\left(n_se^3/mc\right)\vec{A}.$$  \hspace{1cm} (1.4)

The time derivative of equation (1.4) gives the first London equation (1.2) and its curl leads to equation (1.3).

To find the temperature-dependence of the penetration depth, $\lambda_L(T)$, London used a result from Gorter-Casimir Theory [10]. This theory, established in 1934, based on the two-fluid model with assumed electron free energy

$$F(x,T) = \sqrt{x}f_n(T) + (1-x)f_c(T)$$

where $x$ is the fraction of normal electrons and $(1-x)$ is that of condensed electrons. Since the free energy for normal electrons is $f_n(T) = -\frac{1}{2}\gamma T^2$ and assuming $f_c(T) = -\beta$, then $F(x,T)$ can be minimized with respect to $x$ with a minimum at $x = (T/T_c)^4$. From this we have $n_s(T) = 1 - x = 1 - (T/T_c)^4$, and

$$\lambda_L(T) = \sqrt{mc^2/4\pi e^2} \left\{1 - (T/T_c)^4\right\}^{-1/2} = \lambda_0 \left\{1 - (T/T_c)^4\right\}^{-1/2}$$ \hspace{1cm} (1.5)

It is clear that this result reflects Meissner effect for $T < T_c$ and it is in fair agreement with experimental results. Furthermore, London predicted that the magnetic flux penetrating a superconductor should be quantized in units (called fluxiod) of $\Phi_n = n(hc/e)$, where $n$ is an integer. Later, Deaver and Fairbank [11] pointed out that the flux should be quantized in half the value suggested by London, i.e., $\Phi_n = n(hc/2e)$. This final form indicates that the effective charge for a carrier in a superconductor is $2e$ rather than $e$ as we will see later.
**Pippard theory:** As we have pointed out before, London theory relates current densities at a point to field strengths at the same point. In other words, London equations are local and can not account for changes resulting from inhomogeneities due to impurities. Such impurities will strongly affect the penetration depth. The non-local generalization of London theory was done by A. B. Pippard [12] in 1953 by assuming the supercurrent at a point to be related to an average of the vector potential over a region $\xi_0$ around this point. $\xi_0$ is known as *Pippard coherence length*. In other words, a significant change in the superconducting density will not take place over any arbitrary short distance but within a distance in order of $\xi_0$. Pippard assumed that at $T_c$ only electrons with energies around $kT_c$ from the Fermi surface are expected to be effective. Consequently, he used the uncertainty principle to estimate the coherence length of a pure metal as:

$$\xi_0 = a \frac{\hbar v_F}{kT_c}$$

(1.6)

where $a$ is a constant and $v_F$ is the Fermi velocity.

The purity of a superconductor can be described by the ratio $l/\xi_0$ where $l$ is the mean free path of electrons in the normal state. Therefore, a superconductor is in the *clean limit* if $l/\xi_0 > 1$ and in *dirty limit* if $l/\xi_0 << 1$. Since the coherence length depends on the mean free path, Pippard defined an effective coherence length $\xi(l)$ as

$$1/\xi(l) = 1/\xi_0 + 1/l.$$  

(1.7)

Now, a superconductor (at $T = 0$) is in the clean limit if $\xi(l) = \xi_0$ (where $l >> \xi_0$) and in dirty limit if $\xi(l) = l$ (where $l << \xi_0$). For dirty superconductors, London equation for the current density equation (1.4) should be multiplied by a factor $\xi/\xi_0$ to take the effect of impurities into consideration, where as, in the clean limit the penetration depth will be simply the one suggested by London. London theory becomes a special case for clean superconductors under Pippard theory.
Ginzburg-Landau (GL) theory: This is another example of extension in London theory to describe spatial variations in the condensed electron density, $n_e$, whether the variation is a result of sample inhomogeneity or magnetic field. The theory employed a quantum mechanical approach based on the construction of an effective wave function $\psi(\mathbf{r})$ such that $|\psi(\mathbf{r})|^2 = n_s(\mathbf{r})$ is the superconducting electron density at position $\mathbf{r}$. $\psi(\mathbf{r})$ is treated as an order parameter which can be determined at each point in space and it is a measure of the strength of the superconducting state at location $\mathbf{r}$. This assumption puts a restriction on GL theory to be valid only at temperatures near the transition temperature ($T \approx T_c$) or near the critical field ($H \approx H_c$) when the order parameter is small and varies slowly in space. One important impact of this theory is in the treatment of type II superconductors when both superconducting and normal phases co-exist. In addition, it predicted the temperature-dependence of coherence length to be in the form $\xi(T) = \hbar/\sqrt{2m^*\alpha(T)}^{1/2}$. Near $T_c$, $\xi(T)$ diverges as $(T_c-T)^{-1/2}$ where $\alpha(T)$ vanishes as $(T_c-T)$. For pure superconductors, far below $T_c$, $\xi(T)$ will become Pippard coherence length, $\xi_o$.

A similar temperature-dependence of penetration depth $\lambda(T)$ was derived, leading to a nearly temperature-independent parameter $\kappa = \lambda(T)/\xi(T)$, known as
the \textit{GL-parameter}. Accordingly, $\kappa < \frac{1}{\sqrt{2}}$ defines a type I superconductor and otherwise for type II. Figure 1.4 shows the variation of magnetic field and order parameter at the interface between superconducting and normal phases for both types of superconductors [13].

1.1.5 The BCS theory

\textbf{Basic ideas and isotope effect:} The BCS theory was introduced in 1957 by J. Bardeen, L. N. Cooper, J. R. Schrieffer [14] as the first microscopic theory describing the superconducting properties in weakly coupled superconductors. The theory was based on the idea that an electron passing by adjacent ions can polarize the lattice as a result of screening the repulsion forces between them. Due to lattice polarization, a region of increased positive charge density will be formed. This region will propagate as a wave carrying momentum (supplied by the electron) through the lattice. If an electron sees this positively charged region, it will experience an attractive Coulomb force and can absorb momentum (phonon) from the lattice. The net situation is that the two electrons are related by such phonon-exchange. Under certain conditions (will be mentioned later) such phonon-exchange between these two electrons can overcome the usual Coulomb repulsion force leading to a weakly bound electron pair, called a \textit{Cooper pair}.

Historically, the two main ideas of BCS theory, namely, electron-phonon interaction and electron pairing, were introduced a few years prior to the theory by Frohlich in 1950. Frohlich [15] suggested that an attractive interaction between electrons could take place through phonon exchange. Within the same year, Frohlich’s idea has been confirmed by the discovery of the isotope effect in Hg [16,17] with

$$\alpha = -\frac{M}{T_c} \frac{\Delta T_c}{\Delta M}$$

(1.8)

where $\alpha$ is the isotope coefficient and $\Delta T_c$ is the change in critical temperature due to a mass difference $\Delta M$ between isotopes. For many conventional super-
conductors $\alpha = 1/2$ while others like Zr and Ru have $\alpha = 0$. Absence of isotope effect in such elements has been attributed to their complicated electron band structure. On the other hand, Schafroth [18] suggested that “an ideal gas of charged bosons exhibits all the essential features of a superconductor” and also suggested that bosons in a superconductor are two-electron states.

While BCS theory is the first complete microscopic theory describing superconductors with weak electron-phonon coupling and is in great agreement with experiment, a deviation was observed for some metal superconductors and alloys. McMillan [19] used experimental results for such metals and alloys and fitted them with empirical equations as a correction and generalization of the BCS results. He introduced a coupling constant $\lambda$ such that superconductors could be classified as strong-coupled if $\lambda > 1$ and weak-coupled if $\lambda < 1$. In addition to correcting the $T_c^{BCS}$ formula to account for strong coupling, McMillan also showed (empirically) that the coupling constant $\lambda$ (in transition metals with bcc structure) depends mainly on the phonon frequency, while being insensitive to variations in the band structure density of states. This remarkable result is in contrast to the general statement of $\lambda$ being governed by the density of states.

**Origin of attractive potential and Cooper pairs**: An important insight to BCS theory came from Cooper [20] who showed that the ground state of a normal (nonmagnetic) metal is unstable at $T = 0$ K, i.e. the system preferred to be in the superconducting state. Cooper assumed two electrons will form a pair if they have equal and opposite momentum and spin. The screened interaction potential between two electrons $V_s(q, \omega)$ is the sum of two terms, a repulsive positive Coulomb term which is frequency independent at low temperatures, and a screened phonon interaction term. The second term depends on frequency as $\left(\omega^2 - \omega_q^2\right)^{-1}$, where $\omega$ is the electrons frequency and $\omega_q$ is the phonon frequency. Figure 1.5 shows the variation of the interaction potential with frequency where the repulsive (positive) potential is due to Coulomb repulsion forces. As can be seen, for certain frequencies a negative potential can exist and electrons can
bind and form a pair. Cooper made the simplified assumption (for $\omega \leq \omega_q$)

$$V_s(q, \omega) = \begin{cases} -V & \text{for } |\xi_q| \leq \hbar \omega_D \\ 0 & \text{for } |\xi_q| \geq \hbar \omega_D \end{cases}$$

(1.9)

where $\omega_D$ is the Debye frequency and $\xi_q$ is the electron energy relative to Fermi surface. Using this simplified potential along with Born approximations, Cooper calculated the effective scattering potential. He showed that the instability in the ground state of a normal metal is a result of interaction of electrons on the opposite sides of the Fermi surface. Such mutual scattering will maximize the scattering potential responsible for pair formation and so the whole metal undergoes a phase transition. In other words, electrons with $k > k_F$ can have a lower energy with respect to Fermi surface after pairing. Although the kinetic energy of these electrons are higher than when in normal state, a bound state is formed due to the fact that the attractive potential overwhelms that increase when pairs are formed. Cooper also suggested $T_c$ to depend on $\omega_D$ as

$$k_B T_c = 1.14 \hbar \omega_D e^{V(0)/V}$$

(1.10)

As expected, the critical temperature is proportional to Debye energy in accordance with the isotope effect.

Figure 1.5: Variation of the interaction potential between electrons with frequency. The repulsive (positive) potential is due to Coulomb repulsion forces.
1.1.5.1 BCS formalism and predictions

BCS theory [14] based on pairing of two electrons with \((k, \uparrow)\) and \((-k, \downarrow)\) to form Cooper pairs. The choice of spin singlet, \(S = 0\), reflects the fact that there is no magnetic properties associated with such pairs. As we mentioned above, there will be a phase transition to superconducting state due to involvement of all electrons above \(k_F\) in the process. To construct a single wave function describing all the pairs in a compact form, the method of second quantization is used. It requires the definition of creation and annihilation operators. An electron with momentum \(k\) and spin \(\uparrow\) can be created in the state \((k, \uparrow)\) by the operator \(C_{\sigma \uparrow}^*\), while \(C_{\sigma \uparrow}\) annihilates (empties) this state. The suggested pairing Hamiltonian has a reduced form that accounts only for electrons paired as \((k_\uparrow, -k_\downarrow)\) and has the form

\[
H = \sum_{k, \sigma} \xi_k C_{k \sigma}^* C_{k \sigma} + \sum_{k l} V_{k l} C_{k \uparrow}^* C_{-k \downarrow} C_{-l \downarrow} C_{l \uparrow}
\]

where the interaction potential \(V_{k l}\) will take the simple form proposed by Cooper (equation 1.9). The BCS ground state wave function was constructed using a mean-field approach to account for the large number of electrons involved in the condensation process where the probability of a state to be occupied depends mainly on that of other states. In brief,

\[
|\psi_G\rangle = \prod_{k \sim k, \ldots, k_u} \left( u_k + v_k C_{k \uparrow}^* C_{-k \downarrow} \right) |\psi_0\rangle
\]

\(u_k\) and \(v_k\) are the weight amplitudes for \((k_\uparrow, -k_\downarrow)\) pair state occupancy. As seen, the probability for this state to be occupied is \(|v_k|^2\), while \(|\mu_k|^2 = 1 - |v_k|^2\) is the probability for the state to be empty. \(|\psi_0\rangle\) is the vacuum state where no pairs exist. By variational principal, BCS theory showed both parameters to depend on \(\xi_k\) and \(\Delta\) as

\[
v_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right)
\]
Figure 1.6: The dependence of $v_k^2$ on $\xi_k$ behaves like Fermi function at $T = T_c$ for normal metals. The figure also reflects the BCS result $\Delta = 1.76kT_c$.

$$u_k^2 = \frac{1}{2} \left( 1 + \frac{\xi_k}{E_k} \right) = 1 - v_k^2$$

where $E_k$ is defined by equation (1.13) assuming an isotropic energy gap, i.e. $\Delta$ is $k$-independent. The dependence of $v_k^2$ on $\xi_k$ is shown in figure 1.6. It behaves like Fermi function at $T = T_c$ for a normal metal. The figure also reflects the BCS result $\Delta = 1.76kT_c$.

Back to equation (1.11), after solving the Hamiltonian with approximations that leads to some limitations (e.g. weak coupling and gap is real and isotropic), the theory gave the excitation energy of a superconductor $E$, as

$$E = \left( \xi^2 + \Delta^2 \right)^{1/2} \quad (1.13)$$

$E$ is known also as the quasiparticle excitation energy. It is clear that the minimum excitation energy (corresponds to electrons at Fermi energy, $\xi = 0$) is $\Delta$. To excite a superconductor, pairs should be broken and so double this excitation energy is required to excite a pair and therefore the energy gap of a superconductor is $E_g = 2\Delta$. The energy gap value can be evaluated by solving the integral

$$1 = \frac{N(0)}{2} \int_{-\beta \Delta}^{\beta \Delta} \frac{d\xi}{E} \tanh \left( \frac{\beta E}{2} \right) \quad (1.14)$$

where $E$ is defined by equation (1.13). In the limiting case of $T = 0$; $\tanh \left( \frac{\beta E}{2} \right) = 1$ and
Figure 1.7: Temperature-dependence of the normalized energy gap versus normalized critical temperature for tin. Solid line is BCS fitting and dots are ultrasonic attenuation data [21].

\[
E_g(0) = 2\Delta(0) = 4k\omega_{D}e^{-1/N(0)w} \tag{1.15}
\]

Solving equation (1.14) for \( T \neq 0 \) gives the same result suggested by Cooper (equation 1.10). From equations (1.15) and (1.10), we get

\[
\frac{E_g}{kT_c} = \frac{2\Delta(0)}{kT_c} = 3.51 \tag{1.16}
\]

for \( T = 0 \), while

\[
\frac{\Delta(T)}{\Delta(0)} \approx 1.74\left(1 - \frac{T}{T_c}\right)^{1/2}
\]

gives the temperature-dependence of \( \Delta \) near \( T_c \). Figure 1.7 shows temperature-dependence of the normalized energy gap versus normalized critical temperature for tin. The solid line is BCS fitting and dots are energy gap data obtained from ultrasonic attenuation [21].

**Ground state energy:** As we mentioned before, the superconducting state is a state of higher kinetic energy compared to the normal state, even though the net energy is lower due to the negative potential energy. The internal energy difference between the two states defines the condensation energy of a superconductor, and depends on the energy gap as

\[
F_s(0) - F_N(0) = -\frac{1}{2} N(0)\Delta^2(0) \tag{1.17}
\]
Using equation (1.1); the thermodynamic critical field is proportional to the energy gap as

\[ \frac{1}{2} N(0) \Delta^2(0) = H_c^2(0) / 8\pi. \]  

(1.18)

**Critical field:** A third example of BCS success is the suggested dependence of critical magnetic field on temperature. The BCS temperature-dependence of critical field shows a small deviation of just 4% as compared to that predicted by Gorter and Casimir. A similar small deviation between the two theories has been observed in the temperature-dependence of electronic specific heat.

**Coherence length and penetration depth:** BCS theory predicted the temperature-dependence of coherence length and penetration depth (at \( T \approx T_c \)) to have the forms:

\[ \xi(T) = 0.74 \xi_0 \left( \frac{T_c}{T_c - T} \right)^{1/2} \]  

(1.19)

\[ \lambda(T) = 0.71 \lambda_0 \left( \frac{T_c}{T_c - T} \right)^{1/2} \]  

(1.20)

in the clean limit, and

\[ \xi(T) = 0.85 \sqrt{\xi_0 / I} \left( \frac{T_c}{T_c - T} \right)^{1/2} \]  

(1.21)

\[ \lambda(T) = 0.62 \lambda_0 \sqrt{\xi_0 / I} \left( \frac{T_c}{T_c - T} \right)^{1/2} \]  

(1.22)

in the dirty limit.

**Density Of States (DOS):** Another successful prediction of BCS theory is the behavior of density of states of superconducting excitations. Quasiparticles are created by pair annihilation, e.g., creating an electron-like excitation is equivalent to annihilating a pair and creating a hole-like excitation. These created quasiparticles are in one-to-one correspondence with that of normal metal. Therefore, the DOS of a superconductor \( (N_s(E)) \) can be obtained by setting \( N_s(E) \, dE = N_n(\xi) \, d\xi \), where \( \xi(k) = \left( \frac{\hbar^2 k^2}{2m} \right) - E_F \) is the independent-particle
kinetic energy relative to Fermi energy. As long as we are interested in energies a few meV from Fermi energy, we can consider \( N_n(\xi) \) a constant, i.e., \( N_n(\xi) = N(0) \). Then, by using equation (1.13), we get

\[
\frac{N_s(E)}{N(0)} = \rho(E) = \frac{d}{dE} \left[ \frac{E}{(E^2 - \Delta^2)^{1/2}} \right] \begin{cases} , & E > \Delta \\ 0, & E < \Delta \end{cases}
\]

This means that there will be no states for excitation energies less than the gap value. We should keep in mind that \( \rho(E) \) is normalized by the normal DOS. The behavior of DOS versus \( E \) is shown in figure 1.8 along with the dependence of elementary excitations in the normal \( (E_{kn}) \) and superconducting states \( (E_{ks}) \) on \( \xi_k \).

As we will see later, the DOS is a measurable quantity that can be determined directly by tunneling measurements.

### 1.1.6 Beyond BCS theory

In the previous section we have briefly discussed the BCS theory. In this section we will focus on the efforts that have been done to generalize the BCS theory to account for strong coupling. A theory for strong coupling has been developed after the BCS theory by J. P. Carbotte [22]. The kernels used to formalize the
energy gap equation includes the electron-phonon (or more generally electron-boson) spectral density $\alpha^2 F(\omega)$ that describes the interaction of electron pairs through exchange of bosons and the Coulomb pseudo-potential $\mu^*$ ($\mu^* = 0$ for pure electron-phonon interaction). Both of these two kernels can be obtained from I-V tunneling measurements by extending the voltage from the gap edge to values correspond to the end of phonon spectrum. The gap equation is given as

$$\Delta(i \omega_n) Z(i \omega_n) = \pi T \sum_m \left[ \lambda(i \omega_m - i \omega_n) - \mu^*(\omega_c) \theta(\omega_c - |\omega_m|) \frac{\Delta(i \omega_n)}{\sqrt{\omega_m^2 + \Delta^2(i \omega_m)}} \right]$$  \hspace{1cm} (1.24)

where the renormalization factor $Z(i\omega)$ is defined as

$$Z(i \omega_n) = 1 + \frac{\pi T}{\omega_n} \sum_m \lambda(i \omega_m - i \omega_n) \frac{\omega_m}{\sqrt{\omega_m^2 + \Delta^2(i \omega_m)}}$$  \hspace{1cm} (1.25)

$i\omega_n$ is the Matsubara frequency, defined as $i\omega_n = i\pi(2n - 1)$ where $n$ is an integer. Coulomb pseudo-potential is defined in terms of the cut-off frequency $\omega_c$. $\lambda$ is an electron-boson parameter defined in terms of the spectral density $\alpha^2 F(\omega)$ as

$$\lambda(i \omega_m - i \omega_n) = 2 \int_0^{\pi} \frac{\Omega \alpha^2 F(\Omega) d\Omega}{\Omega^2 + (\omega_n - \omega_m)^2}$$  \hspace{1cm} (1.26)

Using equations (1.24) and (1.25), we can get the BCS equations. Allen and Dynes [23] showed that for

$$\lambda(i \omega_m - i \omega_n) = \begin{cases} \lambda & \text{for both } |\omega_n|, |\omega_m| < \omega_c \\ 0 & \text{otherwise} \end{cases},$$

Equation (1.25) can then be reduced to

$$Z(i \omega_n) = 1 + \lambda$$  \hspace{1cm} (1.27)

where $\lambda$ is defined by equation (1.26) for $m = n$. Substituting from equation (1.27) into (1.24);

$$\Delta(i \omega_n) = \begin{cases} \Delta(T), & |\omega_n| < \omega_c \\ 0 & |\omega_n| > \omega_c \end{cases}$$

where

$$\Delta(T) = \frac{\lambda - \mu^*}{1 + \lambda} \pi T \sum_{|\omega_m| < \omega_c} \frac{\Delta(T)}{\sqrt{\omega_m^2 + \Delta^2(T)}}$$  \hspace{1cm} (1.28)
Equation (1.28) has the same BCS form [14] with

\[ N(0) \psi' = \frac{\lambda - \mu^*}{1 + \lambda}. \]  \hspace{1cm} (1.29)

The role played by the pairing potential \( N(0)V \) in BCS theory is now in the form \( \left( \frac{\lambda - \mu^*}{1 + \lambda} \right) \). At temperatures near \( T_c \), equation (1.28) gives

\[ k_B T_c = 1.13 h \omega_\lambda \exp \left( -\frac{1 + \lambda}{\lambda - \mu^*} \right) \]  \hspace{1cm} (1.30)

which is the same BCS result given in equation (1.10). Equation (1.30) has been modified later by Allen and Dynes [23] to

\[ k_B T_c = \frac{h \omega_\lambda}{1.2} \exp \left( -\frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right) \]

where \( \omega_\lambda = e^{\frac{\pi}{2\lambda}} \int_0^\infty \ln(\omega) \frac{\alpha^2 F'(\omega)}{\omega} d\omega \)

For \( T = 0 \), equation (1.28) gives

\[ 1 = \frac{\lambda - \mu^*}{1 + \lambda} \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{\sqrt{\omega^2 + \Delta^2(0)}} \approx \frac{\lambda - \mu^*}{1 + \lambda} \ln \left( \frac{2\hbar \omega_\lambda}{\Delta(0)} \right) \]  \hspace{1cm} (1.31)

Using equation (1.30); equation (1.31) is reduced to \( \frac{2\Delta(0)}{k_B T_c} = 3.54 \) which is the well known BCS universal relation (equation 1.16).

1.2 Electron tunneling

The phenomenon of electron tunneling can be illustrated by a one-dimensional model as follows. An electron moving in z-direction with momentum \( p_z \) under a potential \( U(z) \) is described classically as

\[ \frac{p_z^2}{2m} = E - U(z) \]

where \( E \) and \( m \) are the electron's energy and mass, respectively. The particle will have zero probability to penetrate the potential barrier \( U(z) \) when \( U(z) > E \).
Quantum mechanically, the electron is described by a wave function $\psi(z)$ that satisfies Schrödinger's equation

$$ \frac{d^2}{dz^2} \psi(z) = -\frac{2m}{\hbar^2} (E - U(z)) \psi(z). $$

Let us consider $U(z) = U$, then Schrödinger equation has a solution

$$ \psi(z) = \psi(0) e^{\pm ikz} $$

where the wave vector $k = \sqrt{2m (E - U)/\hbar^2}$ and $E > U$. On the other hand, when $E < U$ the solution (in $+z$ direction) takes the form

$$ \psi(z) = \psi(0) e^{-Kz}, $$

where $K = \sqrt{2m (U - E)/\hbar^2}$, which describes the decaying electron wave function in the classically forbidden region with a non-zero probability $|\psi(z)|^2 = |\psi(0)|^2 e^{-2Kz}$. Therefore, if forbidden region (barrier) is narrow, there will be a probability for electrons to tunnel from one side to the other.

### 1.2.1 Quasiparticle tunneling

In 1960, Giaever [24] used tunneling technique to prove the existence of energy gap and its temperature-dependence to have a BCS behavior. In his pioneering work, Giaever measured the current-voltage relation between a normal metal (N) and a metal superconductor (S) separated by an oxide layer (I). Such a device is known as NIS junction. Giaever constructed such sandwich-like junction with Al as N, Al$_2$O$_3$ as I and Pb as S by using thermal evaporation. At temperatures and magnetic fields less than $T_c$ and $H_c$ of lead, he found no current to flow until the potential difference ($V$) between N and S satisfies $|V| \geq \Delta/e$ as showed in figure 1.9, left. As can be seen, the conductance curve (figure 1.9, right) is in good agreement with the DOS predicted by BCS theory (figure 1.8a). More precise tunneling data was obtained by Gaiever [25] two years later. Figure 1.10 shows the normalized dynamical conductance $(dI/dV)_{NS} / (dI/dV)_{NN}$ versus the applied energy ($eV$) of Mg/MgO/Pb junction. Measurements took place at $T = 0.33$ K with Pb as the superconductor ($T_c = 7.2$ K) and Mg as the normal electrode. The conductance, up to the energy gap, is in excellent agreement
Figure 1.9: (Left) I-V curves for Al/Al$_2$O$_3$/Pb at (1) $T=4.2$ K and $T=1.6$K for $H=2.7$ KOe, (2) $H=0.8$KOe, (3) $T=1.6$K and $H=0.8$KOe, (4) $T=4.2$K and $H=0$ KOe and (5) $T=1.6$K and $H=0.8$KOe. Pb is superconductor for last two curves. (Right) Conductance versus bias voltage for curve (5) normalized by curve (1) [24].

within DOS as predicted by BCS theory. The bumps at higher energies can be attributed to phonons and can only be explained in terms of strong electron-phonon coupling in Pb.

Within the same year (1960), Giaever [26] studied tunneling in SIS junctions with aluminum as S, aluminum oxide as I, and lead, indium, or aluminum as the other S. The oxide layer had an estimated thickness of 15-20 Å. Junctions Al/Al$_2$O$_3$/Al and Al/Al$_2$O$_3$/In were measured at $T = 1.1$ K. All metals (Al, In and Pb) of these junctions are superconducting at this temperature. The measured energy gaps were

$$\frac{2\Delta_{pb}(0)}{kT_c} \approx 4.33, \quad \frac{2\Delta_{in}(0)}{kT_c} \approx 3.63$$

and

$$\frac{2\Delta_{al}(0)}{kT_c} \approx 3.15.$$

The severe deviation of lead from the expected BCS value (equation 1.16) reflects the fact that the electron-phonon interaction in lead is strong rather than weak and so a modification to the BCS theory was required to account for such coupling.
1.2.2 Semiconductor model

The theoretical treatment of tunneling [13,27] came by introducing a tunneling Hamiltonian

\[ H = H_R + H_L + H_T \]

where \( H_R \) and \( H_L \) are the Hamiltonians on the right and left sides of the junction, respectively. Tunneling takes place through the Hamiltonian \( H_T \) defined as

\[ H_T = \sum_{\sigma kp} (T_{kp} C_k^\sigma C_p + \text{herm. conj.}) \]

\( T_{kp} \) is the tunneling matrix element able to transfer a particle with wave vector \( K \) in one side of the junction to the other side with wave vector \( P \). The first term represents the transfer of an electron from metal \( P \) to metal \( K \), whereas the second Hermitian conjugate term transfers it from \( K \) to \( P \). The tunneling probability is proportional to \( |T_{kp}|^2 \) and so is the tunneling current through the insulating layer. The formalism based on the assumption that \( H_R \) and \( H_L \) are independent and therefore they can be represented with independent set of operators, \( C \)'s. Furthermore, the transfer rate is independent of energy of the particles. This is true as long as the particle energy is small, a few meV around...
Fermi energy. In this case the tunneling rate can be assumed constant with a value $T$.

When $T$ is considered a constant, a semiconductor model can be employed to account for tunneling current. In that model a superconductor is represented by its DOS (as given by equation 1.13) and its mirror reflection separated by twice the energy gap (see figure 1.11). The lower half ($E < 0$) reflects the fact that DOS should be equal to that of normal metal as the gap vanishes. We should keep in mind that this model is a simple one, for instance, it does not show the superconducting ground state that may play a role in the tunneling process.

After some mathematical details, the tunneling current from metal 1 to metal 2 due to bias energy $eV$ can be calculated as

$$I_{1\rightarrow 2} = A |T|^2 \int_{-\infty}^{\infty} N_1(E) f(E) N_2(E + eV) \left[1 - f(E + eV)\right] dE$$

where $A$ is a proportionality constant, $f$ is the Fermi distribution function

$$f(E) = \left( e^{E/k_BT} + 1 \right)^{-1},$$

$N_1 f$ is the number of quasiparticles in 1 that can tunnel to side 2, and $N_2 (1-f)$ is the number of empty states available in side 2. A reverse current will flow from 2 to 1 with

$$I_{2\rightarrow 1} = A |T|^2 \int_{-\infty}^{\infty} N_1(E) \left[1 - f(E)\right] N_2(E + eV) f(E + eV) dE.$$ 

Therefore, the net current will be

$$I = A |T|^2 \int_{-\infty}^{\infty} N_1(E) N_2(E + eV) \left[ f(E) - f(E + eV)\right] dE. \quad (1.32)$$

Now we can study different tunneling cases:

(a) N/I/N

For tunneling from one metal to another, DOS can be considered as a constant and the effect of $V$ (as shown explicitly on the right side of equation 1.24) is to shift the chemical potential of one metal with respect to the other by $eV$. In that case, equation (1.32) reduces to
Figure 1.11: Semiconductor model for (a) N/I/S and (b) S/I/S sandwich junctions. For both cases, the I-V curve and normalized conductance are given. Dashed lines show I-V and conductance curves at T > 0 K, while solid lines at T = 0 K.

Substituting Fermi function into this equation, the integral gives \( eV \). Then,

\[
I_{nn} = G_{nn} V
\]

where \( G_{nn} = eA |T|^2 N_1(0) N_2(0) \) is the normal conductance. In case of tunneling between to metals, the conductance will be a straight line and independent of energy.

(b) N/I/S

This situation is shown in figure 1.11a along with the expected I-V and conductance versus \( V \) behaviors. In this case, the density of states of the superconductor is energy-dependent (equation 1.23) and equation (1.32) becomes
\[ I_{ns} = \frac{G_{mn}}{e} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_{2}(0)} \left[ f(E) - f(E + eV) \right] dE \]

where \( \frac{N_{2s}(E)}{N_{2}(0)} \) is the normalized DOS of the superconductor. To put this equation in more meaningful form, we consider the conductance:

\[ G_{ns} = \frac{dI_{ns}}{dV} = G_{mn} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_{2}(0)} \left[ -\hat{\partial}f(E + eV) \right] dE. \]

As \( T \to 0 \), this equation approaches

\[ G_{ns} \big|_{T=0} = \frac{dI_{ns}}{dV} \big|_{T=0} = G_{mn} \frac{N_{2s}(e|V|)}{N_{2}(0)} \]

i.e., the differential conductance is a direct measure of DOS.

Figure 1.11a indicates that at \( T = 0 \) there is no tunneling current will tunnel until \( e|V| \geq \Delta \). In other words, the energy \( eV \) should be enough to create excitations in the superconductor to have tunneling current. The modulus of \( V \) ensures that both electron or hole tunneling are equal. At \( T > 0 \) (figure 1.11a, dashed lines), tunneling will take place at lower applied voltage as temperature will contribute to generating of excitations. The differential conductance (as function of energy) at low temperatures is a very good measure of DOS.

(c) S/I/S

With both sides are superconductors, (1.24) takes the form

\[ I_{ss} = \frac{G_{nn}}{e} \int_{-\infty}^{\infty} \frac{N_{1s}(E)}{N_{1}(0)} \frac{N_{2s}(E + eV)}{N_{2}(0)} \left[ f(E) - f(E + eV) \right] dE \]

\[ \frac{N_{2s}(E + eV)}{N_{2s}(E)} \left[ f(E) - f(E + eV) \right] dE \]

Figure 1.11b shows a qualitative behavior of tunneling current as a function of \( eV \). As we can see, no current will tunnel until the applied potential energy supplies energy enough to create a hole on one side and a particle on the other, i.e. until \( eV = \Delta_1 + \Delta_2 \). At \( T > 0 \), the dashed lines show the current to tunnel at lower energies due to the thermally excited quasi-particles. For \( T > 0 \), a tunneling current peaked at \( eV = |\Delta_1 - \Delta_2| \) can be observed in voltage-source
measurements where such voltage will allow the thermally excited quasi-particles
peaked at DOS of one superconductor to tunnel into the available states peaked
at DOS of the other.

1.2.3 Josephson tunneling

In the previous section we have focused on single quasi-particle tunneling while
another kind of tunneling will be discussed here. Josephson [28] showed that,
under certain circumstances superconducting pairs can tunnel from one
superconductor to another separated by an insulating layer. There are two
different kinds of effect, namely, dc Josephson effect and ac Josephson effect.
In dc effect, current tunnels through the junction in the absence of electric field.
In ac effect, if a dc voltage is applied across the junction an oscillating current
with radio frequency will be generated.

Both phenomena can be understood by solving the time-dependent
Schrödinger equation for the junction. We can assume the order parameters on
the two sides to be $\psi_1$ and $\psi_2$ governed by time-dependent equation in the form

$$i\hbar \frac{\partial \psi_1}{\partial t} = H \psi_2 \quad \text{and} \quad i\hbar \frac{\partial \psi_2}{\partial t} = H \psi_1$$  \hspace{1cm} (1.33)

$H$ is the coupling of the wave function across the insulator, $\frac{H}{\hbar}$ has units of rate
and so $H = 0$ for thick barrier. Assuming

$$\psi_1 = \sqrt{n_1} e^{i\varphi_1} \quad \text{and} \quad \psi_2 = \sqrt{n_2} e^{i\varphi_2}$$  \hspace{1cm} (1.34)

and substituting in equation (1.33) one can get the superconductor current $J$
passing through the junction to be

$$J = J_0 \sin \delta = J_0 \sin (\varphi_1 - \varphi_2)$$  \hspace{1cm} (1.35)

where $\delta$ is the phase difference between the two sides and $J_0$ is the maximum
current at zero voltage as shown in figure 1.12.

For the ac effect, a potential difference $V$ across the junction will raise the
energy in one superconductor by $eV$ and lower the other by $-eV$ generating a gap
Figure 1.12: dc Josephson effect. If a current $I$ is applied between two superconductors separated by a weak link, a dc current (at $V = 0$) flows up to a critical value $J_0$.

$2eV$ (= $e^* V$) against electron pairs to tunnel. Therefore equation (1.33) will be replaced by

$$i \hbar \frac{\partial \psi_1}{\partial t} = H \psi_2 - eV \psi_1 \quad \text{and} \quad i \hbar \frac{\partial \psi_2}{\partial t} = H \psi_1 + eV \psi_2$$

(1.36)

Following same argument as for dc effect and substituting equation (1.34) into (1.36), one can get the relative phase of the probability amplitudes to have the form

$$\delta(t) = \delta(0) - \frac{2eVt}{\hbar}$$

and therefore

$$J = J_0 \sin \delta(t) = J_0 \sin \left( \delta(0) - \frac{2eVt}{\hbar} \right)$$

Current will oscillate with frequency $\omega = 2eV/\hbar$ and therefore a photon with the same frequency will be emitted or absorbed when a pair crosses the insulating barrier.
Chapter 2
Superconductivity in Magnesium diboride

2.1 Discovery

On January 10th 2001 in the Symposium on Transition Metal Oxides held in Sendai (Japan), Jun Akimitsu and co-workers (Aoyama-Gakuin University, Tokyo) announced the discovery of superconductivity in MgB₂ with T_c = 39 K. This discovery was published two months later [29]. Figure 2.1 (left) shows susceptibility measurements for samples made from pressed MgB₂ powder for both Field-Cooled (FC) and Zero Field-Cooled (ZFC) modes at an applied magnetic field of 10 Oe. The observed broad transition and high FC signal are typical for powder-like samples. Both susceptibility and resistance measurements (figure 2.1, right) show an onset of transition at about 39 K.

Powder x-ray diffraction pattern has been fully indexed assuming a hexagonal unit cell with lattice constants a = 3.086 Å and c = 3.524 Å (figure 2.2, left). Unlike HTS, MgB₂ has a simple crystal structure (figure 2.2, right) in which boron atoms are graphite-like layered with Mg atoms at the centers of the hexagonal cells formed by boron structure.

2.2 MgB₂: An interesting superconductor

MgB₂ has been known and commonly available since 1953 without any particular interest. Surprisingly, it has the highest T_c for non-copper based superconductors and the highest T_c among intermetallic superconductors known so far (see table 1.2). The previous highest transition temperature record for a metallic superconductor has been held by Nb₃Ge with T_c = 23.2 K. Since its discovery, a great attention has been given to MgB₂ for both the interesting physics it has raised and the possible technological applications it has promised.
Figure 2.1: (Left) Magnetic susceptibility of MgB$_2$ vs. temperature for both ZFC and FC modes measured at 10 Oe. (Right) Temperature dependence of the resistivity at zero magnetic field [29].

Figure 2.2: (Left) X-ray diffraction pattern of MgB$_2$ at room temperature [29]. (Right) Crystal structure of MgB$_2$. Boron atoms are graphite-like layered with Mg atoms at the centers of the hexagonal cells formed by boron structure.
Superconductors put in practice so far are Nb47wt%Ti, Nb3Sn, YBCO, and Bi-2223 with Tc’s of 9, 18, 92 and 108K, respectively [30]. Magnesium diboride (Tc = 39 K) can be a potential candidate in power applications for many reasons, like low-cost production of the basic materials and the ease of metalworking and fabrication. Moreover, unlike Bi-2223, grain boundaries in MgB2 have a minimal effect on supereurrent and they can actually enhance current density by pinning the magnetic flux inside it. In comparison to superconductors that are being used, MgB2 has the lowest normal state resistivity (ρo(40 K) < 1 μΩcm). Thus, MgB2 magnet wires are expected to handle quenching more efficiently than Nb47wt%Ti (ρo (10 K) = 60 μΩcm) and Nb3Sn (ρo (20 K) = 5 μΩcm).

2.3 Mechanism of superconductivity in MgB2

The first insight on the mechanism of superconductivity in MgB2 came from the study of isotope effect [31,32]. Bud’ko et al. [31] studied the effect of 10B and 11B on the superconducting properties of MgB2. Their study of temperature dependent magnetization for ZFC mode for both Mg10B2 and Mg11B2 showed that Mg11B2 has Tc = 39.2 K with ΔTc = 0.4 K, while Mg10B2 has Tc = 40.2 K and ΔTc = 0.5 K. Therefore, replacing 11B by 10B shifts Tc by 1.0 K. This corresponds to a boron isotope exponent αB ≈ 0.26. Such isotope effect reflects the fact that superconductivity in MgB2 is driven by a phonon-mediated BCS mechanism. Neutron scattering studies [33,34] also show that MgB2 is different from the cuprates and its Cooper pairs are phonon mediated. Although the pairing mechanism in MgB2 is thought to be phonon mediated, there are still many experimental results that lack appropriate explanation like the energy gap value. Many of these unanswered problems may lead to unexpected and interesting physics.
2.4 Energy gap measurements

Although the crystal structure of MgB$_2$ (with just three atoms per unit cell) is much simpler than HTS, it also has a layer structure (like cuprates) and hence many of its superconducting properties may show anisotropic effect. For instance, the anisotropy ratio $\gamma = \xi_{ab}/\xi_c$ has a reported value that varies from 1.1 to 9.0 [35-42]. There are evidences that the energy gap can be either anisotropic s-wave or possessing two different gap values along the two directions [43-48]. In general, there is no consensus about the magnitude of the energy gap and its temperature dependence. Many techniques have been used to investigate this, like Raman spectroscopy [49-51], far-infrared transmission [52-54], specific heat [55-57], high-resolution photoemission [58] and tunneling [43-45,46,47,48,59-66]. Most tunneling data on MgB$_2$, as in the case of many other newly discovered superconductors, are obtained from mechanical junctions like scanning tunneling microscope [45,59,60,67-69], point contact [46,62,65,70-80], and planar tunnel junctions [81-85]. The reported values of MgB$_2$ energy gap and its temperature dependence from tunneling measurements are inconsistent as well. There are many models that have been suggested to explain this as the one-gap, two-gaps, many-gaps, and gap anisotropy scenarios.

2.5 Motivations and goals of the work

Since there is no consensus about the magnitude of the energy gap and its temperature dependence, it is critical to determine whether the small gap value reported by many groups is a real bulk property or a result of surface degradation. One direct method to investigate this is by measuring the temperature dependence of the energy gap. Since the structure of a mechanical junction will change as temperature is varied or when an external field is applied, such tunneling techniques are not stable enough to study temperature dependence of the energy gap. The situation is worse if the sample is not homogeneous and the gap value varies with the probe position. The only reliable measurement for temperature dependence of the energy gap is from sandwich-
like planar junctions. In this case any variation in tunneling spectra will be related to sample properties and not due to structural change in the junction.

Furthermore, measurements of the energy gap from pair tunneling rather than quasiparticle tunneling will serve as another confirmation of the gap value. This also gives the opportunity to investigate the critical current and its temperature dependence, which can be of interest in practical applications. This is achieved by the study of Josephson effect in junctions with weak link.

On the other hand, reported properties of polycrystalline, thin film and single crystal MgB₂ samples are widely varied depending on the final form and the preparation procedure. Therefore, it is important to invent a simple and single method to prepare MgB₂ in both single crystal and polycrystalline forms simultaneously in same process. This gives a great opportunity to study the reported discrepancies in their transport and magnetic properties. Also, the reported MgB₂ thin films prepared by magnetron sputtering are characterized by very low Tc (as compared to that of the bulk) or by an insulating thick layer for films annealed in-situ. This makes such thin films unsuitable for fabricating tunnel junctions. Therefore, a new method that eliminates these two problems is required.
Chapter 3
Experimental details

In this chapter we will show our procedure of preparing magnesium diboride in polycrystalline, single crystal and thin film forms. Also we will cover the details of preparing MgB₂/Pb planar tunnel junctions and the design of a cryogenic probe used in measuring the magnetic field effect on junctions.

3.1 Samples preparation

Reported properties of MgB₂ vary widely, depending on the form of the samples used in the measurements. For example, the anisotropy ratio of the upper critical field scatters between 1.1-13 for c-axis oriented films [39,86,87], aligned crystallites [36], and polycrystalline samples [42] but narrowed to 2.6-4.2 for single crystals [88,89]. The reported transport and magnetic properties of MgB₂ depend strongly on its form and more importantly, the procedure of preparation.

3.1.1 Preparation of single crystal and polycrystalline MgB₂

Polycrystalline form of MgB₂ can be prepared in bulk or wire forms. Bulk form can be prepared by sealing a mixture of Mg and B with Mg:B = 1:2 in a tantalum tube, then heating at 950 °C for 2 hours before quenching to room temperature [90]. Wires are prepared in a tantalum tube by exposing a boron filament to magnesium vapor and heating at 950 °C [91]. In general, the superconducting properties of polycrystalline MgB₂ gives the best T_c’s of about 39 K with sharp transition widths as compared to single crystals. However, reported data of critical current densities are inconsistent and depend strongly on the degree of coupling between grain boundaries. On the other hand, MgB₂ single crystals are synthesized mainly by heat treatment in sealed metal containers [88,92,93] or by sintering at high temperature (T > 1600 °C) and high pressure (GPa) [94-96].
Single crystals can be obtained in sub-millimeter size, and their shapes are in general irregular [88]. Single crystals have a wide transition and deficiency in Mg content. Their size, shape, and physical properties depend strongly on the details of preparation.

In the previous section we have pointed out the importance of finding a simple method to prepare high quality MgB$_2$ in both single crystal and polycrystalline forms in the same process. Here, we will describe our method of preparation [97].

According to Naslain [98], starting with the atomic ratio B/Mg =1.9 and heating at 1200-1400 °C assures an equilibrium between Mg vapor and liquid that generates an internal pressure. This pressure will be enough to form MgB$_2$ with the possibility of crystallization in the presence of a small temperature gradient. Accordingly, starting with a ratio of B/Mg = 1.9 and a total of about 2 gm of amorphous boron powder (99.99%, 325 mesh, Alfa Aesar) and Mg turnings (99.98%, 4 mesh, Alfa Aesar) are mechanically pressed and sealed in a tantalum tube (99.9%, 8.54 mm inner diameter and 0.16 mm thickness) at ambient pressure. The tantalum tube is then placed inside a quartz tube under vacuum and placed inside a box furnace in a nearly vertical position with Mg side at the top. The sample reached 1200 °C with heating rate of 700 °C/hr and stayed there for 30 min. It is then cooled down to 1000 °C with a rate of 10 °C/hr. Once the temperature reached 1000 °C, the cooling rate was further reduced to 2 °C/hr until temperature reached 700 °C when the furnace was turned off. While retrieving the material from the Ta tube, no leakage was observed indicating very good sealing of the tube. The sample consists of two separate portions. At the top of Ta tube, hundreds of shiny single crystals have been observed. This portion will be denoted as the S-sample. The base consists of one very dense polycrystalline piece with uniform golden-gray color. This portion will be donated as the P-sample.

Another method we employed to prepare polycrystalline samples is in accordance to Bud’ko et al. [90]. MgB$_2$ samples have been prepared by reacting Mg turnings (99.98%, 4 mesh, Alfa Aesar) and boron powder (99.99%, 325 mesh,
Alfa Aesar) with the stoichiometric composition 1:2, respectively. Magnesium and boron are mechanically pressed and vacuum-sealed in a tantalum tube (99.9%, 2.4mm ID). The tantalum tube is vacuum-sealed inside a quartz tube. It is then placed inside a box furnace at 950 °C for 2 hours before quenching to room temperature. In later chapter, we will discuss the differences in quality between samples prepared by Bud'ko method and our method. Our new method provides not only high quality MgB$_2$ single crystal samples, but also high quality polycrystalline MgB$_2$ with residual resistivity ratio as high as 16.6, and the lowest reported normal state resistivity $\rho_n(40 \, \text{K}) = 0.28 \, \mu\Omega \, \text{cm}$.

3.1.2 Thin film preparation

Preparation of superconducting MgB$_2$ thin films has two main problems: high probability of magnesium to oxidize and the large difference between its vapor pressure and that of boron. One way to overcome the first problem is by preparing films in ultra high vacuum chambers, while the second problem can be solved by using high Mg vapor pressure or by preparation at low temperatures. Thin films are prepared by different techniques on varieties of substrates as pulsed-laser deposition with both in-situ and ex-situ annealing [87,99-108], magnetron sputtering [109-112], molecular beam epitaxy [113,114], and chemical vapor deposition [115]. In general, the reported $T_c$ of MgB$_2$ thin films have a wide range that varies from 10 K to 39 K, depending on the technique in use and the procedure details.

We have attempted to prepare MgB$_2$ thin films by using MgB$_2$ (Superconductive Components, Inc. 99.5%) and Mg (Target Materials, Inc. 99.95%) targets so that we can have in-situ annealing using magnetron sputtering. This method did not work because of the difference in vapor pressure. We eventually have to prepare thin films by using one MgB$_2$ target followed by an ex-situ annealing. We used Al$_2$O$_3$ sapphire as a substrate. Our single crystal x-ray analysis of the substrate showed its lattice constants to be $a = b = 4.76 \, \text{Å}$ and $c = 13.005 \, \text{Å}$ with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. X-ray diffraction also showed...
the single crystals to be oriented with the c-axis making an angle of 34° with the normal to sapphire plane. Sapphire substrates have been cleaned by boiling it in acetone (HPLC grade) for 30 min, then in ultrasonic acetone bath for another 30 min. The same process was repeated again with methyl alcohol (HPLC grade). Substrates were then fixed to a sample holder which was separated by about 4" from the MgB₂ target. The sputtering chamber was pumped to 5.4x10⁻⁶ Torr, then high purity argon gas was released until the pressure inside the chamber reached 7.8x10⁻³ Torr. A power of 100 W was applied to the MgB₂ target sputtering gun for 5 min before opining the shutter for another 3 hours. Samples kept under vacuum until treated by ex-situ annealing in a Ta tube with Mg at 900 °C for 15 min before the furnace is turned off. Under optical microscope, these films have islands-like pattern of MgB₂ separated by Mg regions. However, the films were good enough for resistivity measurements while thickness was too thin for single crystal x-ray analysis or SQUID measurements.

3.2 Samples characterization

The polycrystalline MgB₂ prepared by the two techniques are characterized by powder x-ray diffractometer (Scintag PAD V with Cu Kα radiation), four probe resistivity, SEM and dc SQUID magnetometer (Quantum Design MPMS) measurements. Single crystals are studied by SQUID and SEM while thin films by resistivity measurement. All tunneling work is limited to polycrystalline samples.

3.3 Planar Junctions preparation

One direct method to investigate whether the observed small energy gap (see for example Ref. [59]) is a real bulk property of MgB₂ or not is by measuring its temperature dependence by using tunneling technique. Why planar tunnel junctions? Tunneling techniques (like STM and point contact) are not suitable to study temperature and magnetic field dependence of the energy gap. The struct-
Figure 3.1: Preparation of MgB$_2$/Pb planar junctions. Two leads are attached to MgB$_2$ sample before molded them inside epoxy resin. The top is ground to expose the sample and then mechanically polished to a smoothness of 0.3 micron. Lead is deposited on top of sample as a counter electrode.

ure of these mechanical junctions is unstable against changes in temperature and/or magnetic field. The situation will be worse if the sample is not homogeneous and the gap value varies with the probe position. For instance, Zhang et al. [63] had studied the temperature dependence of MgB$_2$ energy gap by point contact method. He found out that the energy gap vanishes at $T = 29$ K, whereas a supercurrent was observed up to a temperature of 35 K (on the same junction) when the pressure between MgB$_2$ flakes was increased. Zhang et al. attributed the low $T_c$ to surface effects. Such phenomenon reflects the need to a stable junction to reveal the correct $\Delta(T)$ in MgB$_2$. The only reliable tunneling measurement for temperature dependence of energy gap is from sandwich-type planar junctions. For these junctions, any variation in the tunneling spectra will be a real result of the sample under study but not due to any structural changes in the junction. To the best of our knowledge, our work is the first reported work on MgB$_2$ energy gap by planar junctions.

MgB$_2$/Pb planar junctions are constructed (figure 3.1) by attaching two leads to MgB$_2$ sample and molded it inside epoxy resin. It is then ground to expose the sample and mechanically polished to a smoothness of 0.3 micron. Lead, a superconductor with $T_c \approx 7.2$ K and $H_c(0) \approx 0.08$ T, is then evaporated on the
top as a counter electrode. We used Pb to sharpen the peak features (SIS tunneling) and also as a control to monitor the tunneling conditions. In this work we will limit our analysis to the data when Pb is normal, which is simpler to understand. We have also attempted to grow artificial barrier by sandwiching a thin oxidized aluminum layer between the sample and Pb electrode. This will in general lead to very large junction resistance. So far, the best junctions are still those with natural barrier. Junctions show stability against any temperature changes in the full range from 4.2 K to room temperature. However, the performance against magnetic field changes is not perfect; they collapsed under an applied field of approximately 3.2 T or higher.

3.4 Design of cryogenic probe

Figure 3.2 shows the design of the cryogenic probe used to measure the magnetic effect on MgB$_2$ planar tunnel junctions. The magnetic field is produced by a superconducting coil. The figure shows also super insulated liquid He Dewar (by Cryomagnetics, Inc.) with a height of about 5 feet. At liquid helium temperature, the superconducting magnet can produce magnetic field up to 8 Tesla. The cryogenic probe is designed such that the sample is in middle of the magnet field to assure the most uniform magnetic field. The vacuum (brass) can is evacuated by a diffusion pump through the stainless steel central tube of the probe. The sample is placed inside high purity oxygen free copper can wrapped with a heater wire. One temperature sensing diode is attached close to the heater while another one is attached to the sample holder to assure an accurate and stable setting of the desired temperature. Sample holder and wiring are designed to measure up to three samples at the same time.
Figure 3.2: The cryogenics used for tunneling measurements under magnetic field. The vacuum can is evacuated by a diffusion pump through the central tube of the probe. Three stainless steel tubes are designed to carry wires. The four tubes pass through thin desk-like stainless steel sheets used for thermal insulations. The sample is placed inside a copper can wrapped with a heater wire. Two temperature sensing diodes are attached to the sample holder and heater.
Chapter 4

Results and discussions

Our goal here is to determine whether the small energy gap value $\Delta(0) \approx 2$ meV (which is substantially smaller than the BCS value) is a real bulk property of MgB$_2$ or a result of surface degradation as assumed by many groups, see e.g. [63]. One approach is to study the temperature dependence of the energy gap. Planar junctions are used to minimize any structural changes in junctions as temperature is varied. The results we show here are from MgB$_2$/Pb junctions (SIN junction) with polycrystalline MgB$_2$. Another aspiration is to study the gap nature of MgB$_2$, whether it is a single-gap, two-gap, or multi-gap. The effect of magnetic field on the energy gap will be investigated. We will also study the gap value from superconducting tunneling in weakly-linked junctions.

Finally, we will characterize MgB$_2$ in all polycrystalline, single crystal and thin film forms prepared by our simple techniques and compare their properties to the reported ones.

4.1 Temperature and field dependence of MgB$_2$ energy gap

Many techniques have been used to study the magnitude of MgB$_2$ energy gap and its temperature dependence. Examples are Raman spectroscopy, far-infrared transmission, specific heat, high-resolution photo emission and tunneling spectroscopy. Most tunneling data on MgB$_2$ are obtained from mechanical junctions like scanning tunneling microscope [45,59,60,67-69], point contact [46,62,65,70-80], and tunneling junctions [81-85,116].

At this point, it is important to briefly draw attention to the exotic property of MgB$_2$ energy gap. The situation can be summarized under three possible scenarios, namely, the one-gap [59,60,62], two-gap [43,45-48], and gap anisotropy [44] models. The reported one-gap data [59] shows a BCS quasiparticle DOS with $\Delta(0) = 2.0$ meV and no evidence of gap anisotropy, while
another value $\Delta(0) = 5.2$ meV has been reported by Karapetrov et al. [60]. On the other hand, the possibility of two distinct gaps with values $\Delta_1 = 2.8$ meV and $\Delta_2 = 7.0$ meV have been proposed [46]. Chen et al. [44] suggested an anisotropic s-wave pairing model with $\Delta_{xy} = 5.0$ meV and $\Delta_z = 8$ meV to best fit their tunneling data. Furthermore, a non BCS-like $\Delta(T)$ has been observed by Plecenik et al. [43] with $\Delta(0) = 4.2$ meV.

### 4.1.1 Samples characterization

The crystal structure of the polycrystalline MgB$_2$ sample is characterized by a powder x-ray diffractometer (Scintag PADV). This sample has been prepared following the procedure reported by Bud'ko et al. [90], see chapter 3 for details. As can be seen in figure 4.1b, all MgB$_2$ peaks are indexed and coincide with the standard diffraction pattern database shown in figure 4.1a. The figure includes also the peak positions and lattice constants in the inserted tables. Comparing the two charts, it is clear that x-ray pattern of the sample shows no presence of un-reacted Mg or other Mg-B phases. However, two low intensity MgO peaks (figure 4.1b) appear at $2\theta = 42.9^\circ$ and $62.4^\circ$ and can be attributed to oxidation in some Mg flakes. Resistivity measurement has been done by the conventional four probe technique. Figure 4.2 shows the normalized resistance versus temperature at zero-magnetic field. The sample has an onset critical transition temperature $T_{c \text{ onset}} = 39.5^\circ$K (as defined by 2% criteria) with a sharp transition width $\Delta T_c = 0.7$ K (10%-90% criteria). The sample has a Residual Resistivity Ratio $\text{RRR} = R(300)/R(T_c) = 8$. Later we will show how RRR can be enhanced by heat treatment and how this is reflected on the sample quality. Figure 4.3 (left) shows the temperature dependence of susceptibility for both zero-field cooled (ZFC) and field cooled (FC) modes at an applied field of 10 Oe for the same sample. The sample shows an onset of transition and a transition width as that reported from resistance measurements. Taking in account the demagnetizing factor of the measured cylindrical sample with $\gamma = 1$ (ratio of
Figure 4.1: (a) X-ray diffraction pattern for powder MgB$_2$ from the standard database, peaks characteristics and lattice constants are given in the inserted tables. (b) X-ray diffraction pattern for the prepared polycrystalline MgB$_2$.

Figure 4.2: Normalized resistance versus temperature for MgB$_2$ at a constant current of 50 mA and zero-magnetic field.
Figure 4.3: (Left) Temperature-dependence of susceptibility for both zero-field cooled (ZFC) and field cooled (FC) modes at 10 Oe for polycrystalline MgB$_2$. (Right) FC and ZFC curves at $H = 100$ Oe for commercial MgB$_2$ powder.

Figure 4.4: Magnetization curve $M(H)$ for MgB$_2$ at 5 K. The insert is a close up that shows the sample to have an estimated lower critical field $H_{c1}(5K) = 0.2$ T.
length to diameter), the sample shows a perfect diamagnetic shielding $M/H = -1$. The small FC (less than 1% of ZFC signal) susceptibility signal observed here is a common feature for such polycrystalline MgB$_2$ samples sintered around 950 °C or higher [117,118]. This can be attributed to large trapping of flux attributable to good grain coupling [119]. MgB$_2$ powder has a poor grain coupling, its Magnetization curve (figure 4.3, right) shows a $T_c = 38.5$, $\Delta T_c = 16.5$ K, and a large FC magnetization signal which is 63% of ZFC signal. In addition to low $T_c$ and wide transition, the FC signal for MgB$_2$ powder is much greater than that for the polycrystalline sample (less than 1%). This is due to the fact that a high quality polycrystalline sample has well coupled grain boundaries that will trap magnetic flux inside them and consequently a small FC signal is observed. From figure 4.4 we can also estimate the lower critical field $H_{c1}$ at 5 K to be about 0.2 T. $H_{c1}$ is defined as the value of field at which a deviation from straight line behavior takes place. Our reported value is significantly larger than those reported by other groups [117,120].

4.1.2 Temperature dependence of the energy gap of MgB$_2$ (I)

Now we will study the temperature dependence of the energy gap, $\Delta(T)$, for MgB$_2$/Pb planar junctions. The choice of Pb ($T_c \approx 7.2$ K and $H_{c}(0) \approx 0.08T$) as the counter electrode is to sharpen the peak features at temperatures below Pb $T_c$. In that case, the measured energy gap will be the sum of Pb gap and MgB$_2$ gap. Furthermore, the choice of Pb will enable us to monitor the tunneling condition as it switches from SIS behavior (when $T < T_c$ of Pb) to SIN ($T > T_c$ of Pb). Figure 4.5 shows the conductance spectra evolution with temperatures below Pb $T_c$ for MgB$_2$/Pb junction. For such SIS junction we can roughly estimate the energy gap $\Delta$ of MgB$_2$. It is clear that spectra are sharpened significantly as the Pb gap is opening up. The peak position of the 4.2 K curve is at 3.2 meV and it can be considered as the half sum of gaps. Since $\Delta_{Pb}$ (4.2 K) is about 1.1 meV, we can estimate $\Delta_{MgB2}(4.2$ K) to be about 2.1 meV. This gives a value of only 1.2 for $2\Delta$(MgB$_2$)/k$T_c$, which is much smaller than the BCS value for weak coupling
Figure 4.5: Conductance spectra temperature-evolution normalized to the conductance at $T = 40$ K versus bias voltage for temperatures below $T_c$ of Pb for MgB$_2$/Pb SIS junction.
Figure 4.6: Conductance spectra temperature-evolution normalized to the conductance at $T = 40$ K versus bias voltage for temperatures above $T_c$ of Pb for MgB$_2$/Pb SIN junction. Solid curves are the fitting curves using BTK model. Curves are vertically shifted for clarity purposes.
superconductors. This is consistent with most small gap results from tunneling measurements, see, e.g., Rubio-Bollinger et al. [59].

Figure 4.6 shows the temperature-evolution of conductance spectra normalized to the conductance at $T = 40$ K. Curves (except the $T = 7.78$ K curve) are shifted vertically for clarity purposes. Solid curves are the fitting curves using BTK model (discussed below). Figure 4.7 overlays these curves (along with the corresponding BTK fitting) together without such a shift.

We have used Blonder, Tinkham, and Klapwijk (BTK) [121] model to analyze the curves when Pb is normal, i.e. for SIN junction. This model gives a unified treatment (applicable for different barrier strengths) for SIN interface (handled by using Bogoliubov equations). When an electron inside N (with $E > \Delta$) incident on the interface, there will be four processes that may take place. The electron can suffer ordinary reflection back to N (with probability amplitude $B(E)$), or reflected as a hole on the other side of Fermi surface (Andreev reflection with probability amplitude $A(E)$). The other two possibilities are the transmission through the interface on the same side of Fermi surface (with probability amplitude $C(E)$) or by crossing it (i.e. as a hole) with a probability amplitude $D(E)$. Probability conservation requires $A + B + C + D = 1$. The energy dependence of the parameters $A, B, C,$ and $D$ can be written as

\[
A = \frac{u_o^2v_o^2}{(u_o^2 + Z^2(u_o^2 - v_o^2))^2}, \quad B = \left(\frac{u_o^2 - v_o^2}{(u_o^2 + Z^2(u_o^2 - v_o^2))^2}\right)^2 Z^2 \left(1 + Z^2\right) E > \Delta
\]

\[
C = \frac{u_o^2(u_o^2 - v_o^2)(1 + Z^2)}{(u_o^2 + Z^2(u_o^2 - v_o^2))^2}, \quad D = \frac{v_o^2(u_o^2 - v_o^2)Z^2}{(u_o^2 + Z^2(u_o^2 - v_o^2))^2} E > \Delta
\]

If the electron energy is less than the gap value, there will be no quasiparticle transmission ($C = D = 0$) and $B = 1 - A$, where

\[
A = \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)^2} \quad E < \Delta
\]
Figure 4.7: Temperature-evolution of conductance spectra normalized to the conductance at \( T = 40 \) K. Solid curves are the fitting curves using BTK model. There is no BTK fitting for the curve at 4.2 K, SIS junction. This curve is included to illustrate the degradation of the energy gap as the junction switch from SIS to SIN.

The dimensionless parameter \( Z \) represents the SIN barrier strength, no barrier corresponds to \( Z = 0 \). Parameters \( u_0 \) and \( v_0 \) are known as the Bogoliubov factors, defined as

\[
  u_0^2 = 1 - v_0^2 = \frac{1}{2} \left( 1 + \left( \frac{E^2 - \Delta^2}{E^2} \right) \right)^{1/2}
\]

As indicated by our fitting, the barrier strength \( Z \) of our junction is not strong enough to prevent Andreev reflection from happening. A depairing term \( \Gamma \) is also included because of shortening in quasiparticle lifetime by different scattering processes. Dynes et al. [122] introduced the thermal smearing parameter \( \Gamma \) to account for the inverse dependence of recombination time of quasiparticles (to condensate) at the gap edges with temperature. Therefore, the
BCS density of states as defined in equation (1.23) should be modified through replacing $E$ by $(E-i\Gamma)$ and so the modified DOS will have the form

$$\rho(E,\Gamma) = \frac{1}{(E-i\Gamma)^2 - \Delta^2}$$

(4.1)

The measured conductance corresponds to the real part of equation (4.1) with $\Gamma$ taken into consideration. At high temperatures, temperature smearing at the gap edges will be strong and therefore it will be difficult to measure the gap from peak positions because of broadening. Therefore, we use BTK model to fit our data and extract the energy gap value.

It is clear that there is a smaller peak around 9 meV (figure 4.6) in the low temperature curves. Assuming the two gap model, if we attribute this small peak to another energy gap $\Delta_2$ in MgB$_2$, then the curve will be best fitted if we assign a small percentage of tunneling $C_2$ for $\Delta_2$ and $C_1=1-C_2$ for the smaller gap $\Delta_1$. Parameters $\Gamma$, $Z$, $\Delta_1$, $\Delta_2$, $C_1$ and $C_2$ are used to best fit the curve at 7.78K and their values are 0.95 meV, 1.33, 1.75 meV, 8.2 meV, 0.94 and 0.06, respectively. After this, the parameters $\Gamma$, $Z$, $C_1$ and $C_2$ are kept constant for all higher temperature curves with $\Delta$'s as the only adjusting parameters. From the quality of the fittings, it is justifiable to say that $\Gamma$, $Z$ and $C$'s are independent of energy and temperature within the range of our measurement. Furthermore, the zero bias offset is purely a result of Andreev reflection at the barrier.

Before proceeding further with data analysis, we should point out that our data surely present a two-gap behavior and the peak around 9 meV is not an experimental artifact. First, the $\Delta_2$ conductance peak can be seen for the few curves above Pb $T_c$ (figure 4.6) and more clearly for all curves below Pb $T_c$ (figure 4.5). Second, even the peak can not be easily recognized at higher temperatures due to its small weight, its effect on the tunneling spectra is unmistakable. To further demonstrate this, we can compare the fitting between using only one single-gap (i.e. with $C_2=0$) and two-gap (even with $C_2$ as small as 0.06). Figure 4.8 shows such simulation with the same fixed parameters we used to fit our tunneling data. As can be seen, the effect of the large gap $\Delta_2$ (even with its small weight) can easily be recognized and distinguished from the single-
gap case. The presence of the big gap is demonstrated not only by the presence of its peak at all temperatures, but in its effect on the overall shape of the tunneling curves as well.

Let us now investigate the temperature-dependence of the two gaps obtained from our fitting with BTK model. Figure 4.9 shows the absolute values of the two gaps, while figure 4.10 shows both gaps normalized to their values at $T = 7.78$ K along with the BCS expected behavior (solid line). Both $\Delta_1$ and $\Delta_2$ survive to the $T_c$ of bulk MgB$_2$ in fair agreement with $\Delta_{BCS}(T)$. Since the tunneling features are mainly due to $\Delta_1$ ($C_1=0.94$) and it survives up to $T_c$ of MgB$_2$, it is justifiable to be considered as a true bulk property of this superconductor and not due to surface degradation or other defects as assumed by other groups. This two-gap fitting gives $\Delta_2(0)/\Delta_1(0) = 8.2/1.8 \approx 4.5$, close to both theoretical predicted [123] and experimental suggested [55] values. Nevertheless, there are still unexplained problems with this two-gap model. For example, why the larger gap contributes that little to tunneling, $C_2 = 0.06$, for a polycrystalline sample? As an attempt to answer this question we refer to Brinkman et al. [124] on the conditions for observing one or two gaps in MgB$_2$ tunneling experiments. To observe one gap or two gaps in conductance measurements depends on the direction in which tunneling takes place, because of the Fermi surface (FS) geometry in MgB$_2$. In more detail, two peaks will be clearly visible for tunneling in the $a$-$b$ direction where tunneling in that direction will have contributions not only from 2D Fermi surface but from 3D tubular surface as well. On the other hand, for tunneling in the $c$-direction only one peak will appear in the conductance spectrum because no contribution is expected from 2D FS. In the following paragraph we will explain the nature of FS in more detail.

The two-gap concept in MgB$_2$ has been theoretically proposed by Kortus et al. [125] and Liu et al. [123]. The study of electronic structure by Kortus and co-workers showed that MgB$_2$ is held together by interplane and intraplane B-B covalent bonds and B-Mg ionic bonds. Also, Mg is fully ionized and it is the electron donor of the system and the electronic states near the Fermi level are
Figure 4.8: BTK theoretical curves of normalized conductance versus bias voltage at the given fitting parameters. Every set of two curves are at the corresponding temperature for the two cases of one-gap and two-gap assumptions. Curves are vertically shifted for clarity purposes.
Figure 4.9: Temperature-dependence of the absolute values of the two energy gaps $\Delta_1$ and $\Delta_2$ of MgB$_2$/Pb planar junction. The two gap values are calculated by using the BTK model.

Figure 4.10: Temperature-dependence of the two gaps $\Delta_1$ and $\Delta_2$ of MgB$_2$/Pb planar junction. Values of two gaps are normalized by their values at $T = 7.78$ K. The solid line represents the expected BCS $\Delta(T)/\Delta(0)$ with $T_c = 39.5$ K.
primarily due to boron, figure 4.11. The Fermi surface of MgB$_2$ is shown in figure 4.12. It consists of two nearly-cylindrical (blue and green) sheets (hole-like) at the corners originated from the $p_{xy}$ bond with a quasi-2D character. The blue tubular network (hole-like) comes from the $p_z$ bond, and the red (electron-like) tubular network from the anti $p_z$ bond. These tubular network have a 3D character. Liu et al. [123] predicted MgB$_2$ to have two different superconducting order parameters in the case of clean limit. The smaller order parameter is associated with the 3D FSs while the larger one with the 3D FSs with a ratio of approximately one third.

4.1.3 Field dependence of the energy gap of MgB$_2$

To further characterize the junctions, we have also studied the field dependence of the tunneling spectra at 4.2 K, figure 4.13. The junction in an external field normal to the barrier is not as stable as its performance against temperature changes. It experiences slight changes even when a small field is applied. This can be seen from the development of the zero bias conductance peak, similar to that observed by Schmidt and co-workers [62]. This could be explained by enhancement of microshorts through the barrier as a result of the applied field. Furthermore, most junctions collapse and the tunneling spectra transit from quasiparticle to Josephson tunneling at fields of about 3.2 T. Now we will focus only on quasiparticle tunneling spectra while Josephson tunneling will be discussed later. It can be seen from figure 4.13 that the quality of the spectra has severely degraded when $H$ exceeds $H_c$ of Pb ($H_c(0) \approx 0.08$T). The curve at $0.43$ T is more severely smeared and depressed as compared to the curve at $T = 7.78$K (figure 4.6). This reflects the fact that this field is already greater than $H_c$ of Pb. Using the peak position of the small gap $\Delta_1$, we can roughly estimate its dependence on $H$ as shown on figure 4.14. It is worth noting that $\Delta_1(0T)-\Delta_1(0.43T)>\Delta_{Pb}$. This supports the above argument of the condition of the curve at $0.43$T to be at a field much greater than $H_c$ of Pb. The dependence of
Figure 4.11: Mg, B, interstitial, and total density of states (down to up, respectively) of MgB$_2$ compound [125].

Figure 4.12: The Fermi surface of MgB$_2$. Green and blue cylinders (hole-like) come from the bonding $p_{xy}$ bands, the blue tubular network (hole-like) from the bonding $p_z$ bands, and the red (electron-like) tubular network from the antibonding $p_z$ band. The last two surfaces touch at the K-point [125].
energy gap on magnetic field is similar to that observed by other group [116] and further investigation is required to explain this dependence.

Since MgB$_2$ is a type II superconductor, the effect of magnetic field is to produce vortices and hence the order parameter on the surface is not homogeneous anymore when $H > H_{c1}$. In a simple model, the tunneling spectrum is an ensemble of all different gap values sampled within the junction area (0.05 mm$^2$). If we consider the vortex core as normal region, and the number of vortices is proportional to the applied normal field, then the zero-bias conductance should be proportional to that field [126]. To study this dependence, we have fitted the tunneling spectra within the gap by a parabola to remove the zero conductance peak. The resulting conductance at $V = 0$ can then be estimated from the parabola. We have plotted this resulting conductance versus the external applied field (figure 4.15, main panel). It is clear that the zero-bias offset increases linearly with the external field. By extrapolation we can estimate $H_{c2}$ of MgB$_2$ to be about 5.6 T, where $H_{c2}$ is the field at which the zero-bias offset equals to the normal conductance. This value is in agreement with $H_{c2}$ of bulk MgB$_2$ measured by tunneling spectroscopy as reported by many groups, e.g., Karapetrov et al. [60]. From figure 4.15 we can also estimate the SIN zero-bias offset at zero field to be around 2.1 mS. This agrees with the zero-bias offset in the zero-field conductance curve at $T = 7.78$ K (figure 4.15, inset). We should keep in mind that the normal conductance value is around 2.5 mS (main panel) rather than 3.5 mS (inset) due to instability of junction against magnetic field as we pointed out earlier. Why the upper critical field measured from transport measurements is about three times greater than that from tunneling measurements is an open question that needs more investigation to be answered.
Figure 4.13: Magnetic-field dependence of the experimental tunneling conductance spectra normalized by the conductance at 15 mV of MgB$_2$/Pb junction. Magnetic field is applied normal to the plane of the junction barrier. Measurements take place at a temperature of 4.2 K. Curves above $H = 0.06$ T are vertically shifted for clarity purposes.
Figure 4.14: The field dependence of $\Delta_1$ as measured from peaks positions for MgB$_2$/Pb planar junction at 4.2 K. Magnetic field is applied normal to the plane of the junction barrier. The sudden drop in the energy gap value around 0.43 T is due to switching from SIS to SIN when the magnetic field is greater than $H_c$ of Pb.

Figure 4.15: Dependence of minimum conductance on the applied magnetic field. The linear fit intersects the normal conductance line in a point corresponding to $H_{c2} \approx 5.6$ T. The intersection with the vertical axis matches the minimum conductance offset of the spectrum at 7.78 K and 0.0 T (inset).
4.1.4 Temperature dependence of the energy gap of MgB$_2$ (II)

Let us now show a set of tunneling data from another planar junction that *looks* very different and see how a second gap can influence the spectra for energies $eV > \Delta$. Figure 4.16 shows tunneling conductance at different temperatures. Different from the junction we have discussed, there are no peaks at 9 meV. Does this imply a single-gap scenario? Also, a zero-bias peak develops when $T < 7.2$ K. What is the origin of this zero-bias peak? Let us try to answer these two questions here. We start with BTK fitting for $T > T_c$ of lead, i.e. when MgB$_2$/Pb is still an SIN junction. As a first attempt, we tried to fit the conductance curves with only one-gap ($C_2 = 0.0$). Figure 4.17 shows the data (open circles) of normalised conductance curve at 7.89 K (from figure 4.16) versus bias voltage. BTK fitting curves for different Z's (0.80 and 0.83) are denoted by dashed lines. As can be seen, the fit is not satisfactory. Although both curves fit the data for $V < \Delta/e$, they fail to do so for $V > \Delta/e$. The fitting is improved by assuming another gap, even with a very small weight. This fitting curve is denoted by the solid (red) line in figure 4.17. In this case, the conductance for $V > \Delta/e$ as well as $V < \Delta/e$ can be easily fitted. The parameters used to best fit the curve at 7.89 K (figure 4.17) are $\Gamma$, $Z$, $\Delta_1$, $\Delta_2$, $C_1$ and $C_2$ with 2.0 meV, 0.8, 1.86 meV, 5.6 meV, 0.94 and 0.06, respectively. As before, all these parameters except $\Delta$'s are kept constant for all higher temperature curves so that the energy gap values $\Delta_1$ and $\Delta_2$ are the only adjusting parameters. Figure 4.18 shows some of tunneling curves along with the BTK fitting (solid line). Comparing with the pervious junction parameters, the barrier strength $Z$ is about 60 %, $\Delta_1(0)$ is almost unchanged, whereas $\Delta_2(0)$ is about 68 %. The reduction in the value of $\Delta_2(0)$ could be attributed to the fact that this gap is associated with the quasi-2D FS. For this junction, it was difficult to track $\Delta_2(T)$ for higher temperatures, while the small gap $\Delta_1(T)$ survives up to $T_c$ of MgB$_2$ and in good agreement with the expected BCS behavior at high temperatures (figure 4.19). In summary, these results support the two-gap model rather than the one-gap scenario. To answer the second question, the observed zero-bias peak could be interpreted as a Josephson
Figure 4.16: Conductance spectra temperature-evolution versus bias voltage for MgB$_2$/Pb planar junction. For the given temperature range, the junction has both SIS and SIN character. Conductance scale is for the curve at 4.2 K with normal conductance of about 0.8 mS. Curves at higher temperatures are vertically shifted for clarity purposes.
Figure 4.17: Normalised conductance versus bias voltage for curve at $T = 7.9$ K (circles). BTK fitting curves at different $C$’s and $Z$’s are shown. Dashed lines are for the one-gap ($C_1 = 0$) at $Z = \text{test}$. The best fitting curve (solid line) is for $C_2 = 0.06$ (two-gap test) and $Z = 0.8$. The other fitting parameters are kept constant.

Figure 4.18: Conductance spectra temperature-evolution normalized to the conductance at $T = 40$ K versus bias voltage for temperatures above $T_c$ of Pb of MgB$_2$/Pb SIN junction. Solid curves are the fitting curves using BTK model. Curves are vertically shifted for clarity purposes.
Figure 4.19: Temperature-dependence of $\Delta_1$ normalized by their values at $T = 7.9$ K. The solid line represents the expected BCS $\Delta(T)/\Delta(0)$ with $T_c = 39.5$ K. The inset shows the absolute values of $\Delta_1(T)$.

peak. This interpretation is supported by the fact that the peak disappeared when $T \geq T_c$ of lead. Furthermore, the barrier strength $Z$ is reduced by 40% (in comparison to the previous junction) and this enhances the possibility of weak link at low temperatures.

4.2 Josephson tunneling in MgB$_2$/Pb junctions

In the previous section we have studied quasiparticle tunneling in MgB$_2$/Pb SIN junctions with magnesium diboride as the superconductor and lead as the normal counter electrode. We have also shown that the major peak features are mostly due to the small energy gap at 1.8 meV. We have pointed out that junctions were not very stable to magnetic field changes. Such instability caused the switching of tunneling mechanism from quasiparticle tunneling to Josephson tunneling with I-V behavior (figure 4.20) similar to that shown in figure 1.12. Such observed "collapse" of our junctions took place at an applied magnetic field of about 3.2 T normal to the junction plane and this is an irreversible change. In other words, for fields equal to or greater than 3.2 T we have a new junction that shows Josephson tunneling rather than quasiparticle tunneling. Figure 4.20 shows I-V
curves of the Josephson junction at different temperatures. The calculated characteristic voltage $I_cR_N$ versus temperature for this junction is shown in figure 4.21. On the other hand, figure 4.22 shows the I-V curves of another Josephson junction along with the $I_cR_N$ as a function of temperature (figure 4.23).

Before commenting on these figures, let us try to understand Josephson I-V characteristics (Figs. 4.20 and 4.22) and the related characteristic voltage $I_cR_N$. Consider a constant current $I$ is applied to the junction and the voltage $V$ is measured as a function of $I$. At $V = 0$, a superconducting current can tunnel through the interface if chemical potentials on two sides are equal. If $I$ increases, the phase difference $\delta$ will increase because $I = I_c \sin \delta$ (equation 1.35). As $I$ increases further, an upper limit of supercurrent ($I = I_c$) will be reached at $\delta = \pi/2$. Any further increase in $I$ will kill the supercurrent and single particle tunneling takes place as in an ordinary NIN junction. This is the dc Josephson effect.

The product $I_cR_N$ is known as the characteristic voltage of the junction, $V_C$. $I_c$ is the maximum (critical) supercurrent that the weak link junction can support and $R_N$ is the normal resistance. A weak link can be either a thin insulating layer, normal layer by proximity effect, or a constriction between two superconductors. $V_C$ depends mainly on the critical temperature of the superconductors and also on the operating temperature, $T$.

Tunneling between two superconductors has been studied by Ambegaokar and Baratoff (A-B theory) in 1963 (Ref. [127] and the errata). For two superconductors with energy gaps $\Delta_1$ and $\Delta_2$ where $\Delta_1 < \Delta_2$ and both measured in electron volts, the characteristic voltage is given by

$$I_cR_N = \Delta_1(T)\Delta_2(T) \frac{\pi}{e\beta_n} \sum_{n=0,1,2,...} \left( \omega_n^2 + \Delta_1^2(T) \right) \left( \omega_n^2 + \Delta_2^2(T) \right)^{1/2}$$

where $\omega_n = \pi(2n+1)/\beta$ and $\beta = 1/k_BT$. When $\Delta_1 = \Delta_2 = \Delta$ (two identical BCS superconductors on both sides of the junction), equation (4.2) takes the form

$$I_cR_N = \frac{\pi}{2e} \Delta(T) \tanh \left( \frac{\beta\Delta(T)}{2} \right)$$
Figure 4.20: I-V Josephson tunneling at different temperatures as a result of junction collapse after applying magnetic field normal to the interface. The listed temperatures are in the same order as the curves presented.

Figure 4.21: \( I_{CRN} \) versus temperature of MgB\(_2\)/Pb Josephson junction. \( I_{CRN} \) value is 1.16 mV for the curve at \( T = 4.2 \) K. The junction has a nearly temperature-independent normal resistance \( R_N = 65 \Omega \).
Figure 4.22: Josephson tunneling of MgB$_2$/Pb planar junction at different temperatures. The listed temperatures are in the same order as the curves presented. The critical current at T = 4.2 K has a value of 210 µA. The junction has a nearly temperature-independent normal resistance $R_N = 10 \, \Omega$. 
Figure 4.23: $I_C R_N$ versus temperature of MgB$_2$/Pb planar tunnel junction. At $T = 4.2$ K, junction has a characteristic voltage $I_C R_N = 2.1$ mV.

At $T = 0$, equation (4.3) reduces to the simple form

$$I_C R_N = \pi \Delta(0)/2e.$$

(4.4)

On the other hand, numerical calculations are required to determine the temperature dependence of the critical current when $\Delta_1 \neq \Delta_2$.

Josephson tunneling in MgB$_2$ has been studied by many groups using different kinds of junctions like break junctions [128,129], point contact [63], and thin film nanobridges [130]. Gonnelli et al. [128] have constructed a MgB$_2$ break junction with normal resistance $R_N \approx 0.1-11$ Ω. For a break junction, both sides are made from the same type of superconductor (MgB$_2$) and $V_C$ is given by equation (4.3). Gonnelli observed $I_C R_N = 0.3-1.7$ mV for junctions with $R_N \leq 1$ Ω. These junctions showed a $T_c$ of MgB$_2$ at 26.5 K. Changing the pressure between the two MgB$_2$ pieces leads to $I_C R_N = 3.2-3.8$ mV and $R_N = 1-11$ Ω.

Josephson tunneling in figure 4.20 is between MgB$_2$ and Pb when the temperature is below $T_c$(Pb) = 7.2 K. Normal resistance ($R_N = 65$ Ω) varies very slightly with temperature and can be considered constant. The presence of a finite slope at $V = 0$ can be attributed to the imperfect 4-point measurement for bulk samples. It is not clear if magnetic field plays a role or not in causing this finite slope. The critical current in such case could be roughly estimated by the
value of current corresponds to intersection of the extrapolated lines at high and low voltages. Figure 4.21 shows the variation of $I_cR_N$ with temperature. The characteristic voltage is estimated to be about 1.18 mV for the curve at 4.2 K. For two different superconductors with energy gaps $\Delta_1$ and $\Delta_2$, the critical voltage $V_C$ takes the approximate form

$$I_cR_N \approx \frac{\pi \Delta_1 \Delta_2}{e (\Delta_1 + \Delta_2)}.$$  \hspace{1cm} (4.5)

Using equation (4.5) we can roughly estimate $\Delta_1$ for MgB$_2$ to be 0.58 meV, by taking $\Delta_{Pb}(at \ 4.2K) \approx 1.08$ meV. This result is about 1/3 the value from quasiparticle tunneling discussed before. This discrepancy can be attributed to inaccuracy in the evaluation of normal resistance and critical current.

Let us evaluate the gap value for another junction (figure 4.22) that shows a typical I-V Josephson behavior [139]. In this figure, we can clearly see the absence of any zero-bias resistance in the junction. The normal resistance for this junction is about 10.5 Ω and the characteristic voltage is 2.1 mV (figure 4.23), higher than the junction observed in figure 4.21. Using (4.5), the estimated $\Delta_1$ for MgB$_2$ is 1.75 meV which is consistent with our previous result from quasiparticle tunneling. A similar $I_cR_N$ temperature dependence has been observed in MgB$_2$ break junctions by Gonnelli et al. [131]. By using equations (1.16) and (4.4), the expected BCS value for $V_C$ in MgB$_2$/I/ MgB$_2$ planar junction at low temperatures is given by

$$I_cR_N = \frac{3.51 \pi kT_c}{4} = 9.3 \text{ mV}.$$ \hspace{1cm} (4.6)

The characteristic voltage observed by many groups in different tunnel junctions is much less than the BCS expected value, equation (4.6). For instance, Tao et al. [129] have observed $V_C = 1.44$-4.2 mV in different break junctions. Mijatovic et al. [132] have referred the observed small $V_c$ to barrier inhomogeneity and reduction in $T_c$ in thin film tunnel junctions.

Analysis of the temperature dependence of characteristic voltage in our junctions requires further work due to the difficulty of using two different superconductors. In case of identical superconductors, the analysis is easier and
it is possible to identify the nature of the weak link. For instance, the behavior of $I_c$ (for identical superconductors) near near $T_{cJ}$ ($T_c$ of the junction) has been used to identify whether the junction is SIS, SINS, or SNS. Close to $T_{cJ}$, $I_c$ can be described as $I_c(T) \propto (1-T/T_{cJ})^N$, where $N$ is a fitting parameter. For $N = 1$, the weak link is a SIS type, while $N = 2$ corresponds to SNS weak link. When the value of $N$ is between 1 and 2, the weak link has SINS character [132].

4.3 Characterization of polycrystalline, single crystal, and thin film MgB$_2$ prepared by new methods

In this section we will characterize magnesium diboride in polycrystalline, single crystal, and thin film forms prepared by our simple methods. Details of preparation procedures have been given in chapter 3. Polycrystalline samples are characterized by x-ray, resistivity, SEM, and SQUID measurements. Single crystals are characterized by SEM and SQUID, while thin films by resistivity measurements. Limitations on characterization techniques on single crystals are due to its small size, while thin films are too thin to give reasonable signals in x-ray and SQUID measurements. Our samples are compared to those reported by different groups.

4.3.1 Characterization of polycrystalline and single crystal MgB$_2$.

The discovery of MgB$_2$ has brought great deal of attention in the scientific community because MgB$_2$ can be a promising candidate for technical applications. We will give here the results for MgB$_2$ prepared with a new method [97]. This method, indeed, enhances the transport properties of MgB$_2$ as the lowest reported normal state resistivity $\rho_0(40 \text{ K}) = 0.28 \mu\Omega\text{cm}$ with RRR = 16.6. This make MgB$_2$ magnet wires able to handle quenching more efficiently than many superconductors used in practice.

On the other hand and as we have already mentioned in chapter 2, the reported properties on polycrystalline, thin film, and single crystal MgB$_2$ samples
are widely varied depending on the form and the preparation procedure. Since we have prepared both single crystal and polycrystalline forms in same treatment, this will give us a great opportunity to study the published discrepancies in transport and magnetic properties.

Crystal structure of P-sample (see chapter 3) is characterized by powder x-ray diffractometer, (see figure 4.24a). All MgB$_2$ peaks are indexed and they coincide with standard diffraction pattern shown in figure 4.24c. X-ray pattern shows no presence of un-reacted Mg or other Mg-B phases. However, two low intensity MgO peaks (figure 4.24a) appear at $2\theta = 42.9^\circ$ and $62.4^\circ$. Existence of MgO may be a result of starting with excess Mg and/or surface oxidation of some Mg turnings. Resistivity measurements were performed by the conventional four-probe technique. Figure 4.25 shows zero-field temperature dependence of resistivity $\rho(T)$ for P-sample at a constant current of 53 mA. As can be seen, P-sample has a normal state resistivity $\rho_n(40 \text{ K}) = 0.28 \mu\Omega\text{cm}$, the lowest reported value for MgB$_2$. In addition, P-sample has a transition temperature $T_c = 38.4 \text{ K}$ (2% criteria) with transition width $\Delta T_c = 0.2 \text{ K}$ (10% - 90% criteria) and residual resistivity ratio RRR ($R_{300K}/R_{40K}$) = 16.6.

While MgB$_2$ single crystals have RRR $\approx 5$ [41,88,133], polycrystalline samples have reported values of RRR $\geq 20$ [91,134]. There are two main interpretations to explain such a discrepancy. Jung et al. [135] studied the effect of Mg-content on electrical properties of polycrystalline MgB$_2$ and referred the observed high RRR (as compared to RRR of single crystals) to the presence of Mg impurities with its very large RRR. Accordingly, they considered such high RRR of polycrystalline MgB$_2$ as an extrinsic property. On the other hand, Ribeiro et al. [136] have studied the effect of boron purity, boron isotope, and Mg content on RRR of polycrystalline MgB$_2$. In that paper, they have considered using boron isotope $^{11}\text{B}$ (RRR $\approx 18$ for Mg$^{11}\text{B}_2$) rather than natural boron B (RRR $\approx 7$ for MgB$_2$) as the main key to achieve high quality samples with high RRR. Therefore, the observed high RRR in their polycrystalline Mg$^{11}\text{B}_2$ has been accounted as an intrinsic property of magnesium diboride. To clarify the nature of high RRR in

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Figure 4.24: X-ray diffraction pattern for (a) P-sample, (b) polycrystalline MgB$_2$ mentioned in our Ref. [81] and (c) powder MgB$_2$ from standard database for easy comparison, its full characteristics are given in the inserted table of figure 4.1.
polycrystalline MgB₂, it is noteworthy to share our experience in this issue. In a previous article [81], we have prepared polycrystalline MgB₂ following Bud’ko et al. procedure [90]. As mentioned in that paper, our sample showed a residual resistivity ratio of about 8. This value is close to both RRR = 7.25 reported by Lee et al. [137] (for their best single crystals) and RRR ≈ 7 on polycrystalline MgB₂ prepared under similar conditions [136] and with boron powder of same quality we have used (99.99%, 325 mesh, Alfa Aesar). Figure 4.24b shows the x-ray spectra of that sample, while that of the P-sample is shown in figure 4.24a. It is clear from the two charts (Figs. 4.24a and 4.24b) that both samples almost have same MgO content that be attributed to surface oxidation of Mg turnings. Also, both samples show no noticeable trace of un-reacted Mg or other Mg-B phases. The only difference between our previously prepared sample (RRR = 8) and the P-sample (RRR = 16.6) is in the heat treatment. Therefore, under no circumstances could the high RRR of P-sample be attributed to excess magnesium impurities (compare Figs. 4.24(a) and (b)). Therefore, we agree with Ribeiro et al. [136] in considering high RRR as an intrinsic property, but with different interpretation. This interpretation based on the simple result we pointed out above, namely, using the exact starting materials the residual resistivity ratio can be tuned as a result of heat treatment. We believe that both ρ₀ and RRR can
be enhanced by improving the coupling of grain boundaries. This enhancement of coupling (will be confirmed later by SEM imaging) is a direct result of the new heat treatment we have employed and reflected by the very low value of normal state resistivity \(\rho_o(40 \text{ K}) = 0.28 \mu\Omega\text{cm}\) and the high residual resistivity ratio (RRR = 16.6).

To confirm the quality of grains coupling, we characterized our samples with SEM. Figure (4.26, left) shows scanning electron microscope (SEM) picture for P-sample without any treatment of the sample’s surface. A close up of a selected area (400 \(\mu\text{m}^2\)) of that figure is given in figure (4.26, right). As can easily be seen, the images reveal a single crystal-like grains. Surface morphology reflects the polycrystalline, dense character, and well coupling of grains (no clear boundary is observed). This point will be more clear by comparing our SEM pictures to previously reported SEM ones by Rhyee et al. [138] (figure 4.27) and Gümbel et al. [140], figure 4.28. In both cases, we can easily identify both grain boundaries and sizes. For polycrystalline MgB\(_2\) with Mg:B = 1:2 (figure 4.27, right), grains with an average sizes of just 5 \(\mu\text{m}\) can be seen, while for Mg:B = 1.3:2 (figure 4.27, right) grains sizes shrink to about 1 \(\mu\text{m}\). These still better than milled and then hot pressed MgB\(_2\) sample, where grains with a size of 40–100 nm have been formed (figure 4.28).

Although sub-millimeter single crystals have the advantage of size, they have many shortcomings resulted mainly from their preparation under high pressure and temperature. For instance, MgB\(_2\) single crystals grown under high pressure have a deficiency in Mg by 4 \% [141]. Furthermore, the high temperature gradient used to grow sub-millimeter crystals causes growing instabilities that leads to irregularity in shape [137]. Therefore, we believe that the reported discrepancies on transport and magnetic properties of sub-millimeter single crystals are structurally-related and optimizing their growing techniques is still a challenge. Figure 4.29 shows SEM picture for S-sample where superconductivity in these single crystals has been proven by magnetization measurements. SEM picture shows our single crystals to have an average diagonal length of 50 \(\mu\text{m}\) and thickness of about 10 \(\mu\text{m}\). Angles formed by the surfaces reveal the
Figure 4.26: Scanning electron microscopy image for (a) polycrystalline MgB$_2$ (P-sample) with a close up of selected $20 \times 20$ $\mu$m$^2$ area. White bar (left image) represents a length of 20 $\mu$m.

Figure 4.27: Scanning electron microscopy image of polycrystalline MgB$_2$ prepared with Mg:B = 1:2 (right) and Mg:B = 1.3:2 (left). White bars represent 1.0 $\mu$m in length [138].
Figure 4.28: Scanning electron microscopy image of a milled and then hot pressed MgB₂ sample. Grains with a size of 40–100 nm and nearly uniform spherical shape are observed [140].

hexagonal structure of MgB₂ crystals. In comparison with some previously reported MgB₂ single crystals (see, e.g., references [41,93,142-144]), our single crystals have unique and regular shape. Both the small size and regular shape of our single crystals can be attributed to the expected low growing rate due to both low sintering temperature and small temperature gradient (see chapter 3 for preparation details). Figure 4.30 shows SEM pictures of MgB₂ crystals [137]. These single crystals reveal different shapes and sizes according to the employed heat treatment. Needle-like crystals (top left picture), thin plate-like crystals (bottom left), hexagonal-like shape (top right) and thick bar-like crystals (bottom right) have been observed by Lee et al. [137].

Superconductivity in polycrystalline MgB₂ (P-sample) is confirmed by SQUID measurements of the temperature and field dependence of magnetization, M(T) and M(H) respectively. Figure 4.31 shows M(T) at low field of 100 Oe for P-sample. The sample shows a transition temperature Tc = 39.1 K (2% criteria) and a sharp transition of ΔTc = 0.7 K (10%-90%), indicating bulk superconductivity. Field-cooled (FC) mode gives a very small magnetization signal which is less than 0.4 % of zero –field-cooled (ZFC) signal. This can be attributed to large flux trapping in grain boundaries. This reflects the well coupling of grains [119] as well, compare with figure (4.2, right). The high quality of P-sample is also
Figure 4.29: Scanning electron microscopy image for MgB$_2$ single crystals (S-sample) with an average diagonal length of 50 $\mu$m and thickness of about 10 $\mu$m. Angles formed by the surfaces reveal the hexagonal structure of MgB$_2$ crystals. White bar represents 25 $\mu$m length.

Figure 4.30: SEM pictures of MgB$_2$ crystals mechanically extracted from the bulk sample with different shapes that depend on heat treatment. Needle-like crystals (top left picture, white bar represents 10 $\mu$m and 100 $\mu$m for the rest), thin plate-like crystals (bottom left), hexagonal-like shape (top right) and thick bar-like crystals (bottom right) has been observed [137].
Figure 4.31: Temperature-dependent magnetization curves for polycrystalline MgB$_2$ (P-sample). ZFC and FC curves are measured at an applied field of $H = 100$ Oe. The insert shows the hysteresis curve in the first quadrant at $T = 25$ K.

evidenced by SEM picture (figure 4.26) and by the low normal state resistivity (figure 4.25). These properties put polycrystalline MgB$_2$ as a potential candidate in high current applications. The insert of figure 4.31 shows the first quarter $M(H)$ at $T = 25$ K, a lower critical field $H_{c1} \approx 0.1$ T has been determined as the field value at which $M$ deviates from straight line behavior.

Superconductivity in S-sample has been proved by measuring the temperature–dependence of magnetization. Due to the small size of single crystals, we collected about 200 randomly oriented crystals on a non-magnetic strip. Figure 4.32 shows $M(T)$ behavior for both ZFC and FC modes at low field of 100 Oe. As can be seen, single crystals have a superconducting transition width $\Delta T_c = 4.6$ K (10%-90% criteria) and $T_c = 38.5$ K (2%). Although this transition width is much greater than that of the P-sample, it is much less than that reported for single crystals by other groups. For instance, Xu et al. [88] prepared MgB$_2$ single crystals in mm-range with estimated transition width $\Delta T_c \approx 17$ and 10 K (10%-90%) for magnetic fields parallel and perpendicular to ab-plane, respectively. The observed broad transition in S-sample (compared to
Figure 4.32: Temperature-dependent magnetization curves of randomly oriented single crystal (S-sample). Measurements of ZFC and FC curves take place at an applied field of 100 Oe.

P-sample) can be attributed to the randomly oriented character of S-sample. This view is supported by a study of Eltsev *et al.* [145] in which they have found the transition width to depend on the direction of magnetic field relative to MgB$_2$ ab-plane. As can be seen from figure 4.32 and in contrast to P-sample, the FC signal is about 65% of ZFC signal. This indicates the flux pinning in single crystals is very weak due to absence of impurities or any other flux trapping centers, which in turn requires our single crystals to be very clean.

### 4.3.2 Characterization of MgB$_2$ thin films

The critical temperature for thin films is in general lower than that reported for polycrystalline and single crystal samples. For example, thin films prepared by Pulsed Laser Deposition (PLD) [102,107,108] have $T_c$ values in the range of 11-30 K, while $T_c$ as low as 11-18 K has been reported for ion beam synthesis technique [146]. There are also reports that thin films can be prepared with higher $T_c$, for example thin films prepared by chemical vapor deposition technique have zero resistance at 36 K [115]. Thin films prepared by magnetron sputtering have inconsistent $T_c$s depending on the details of preparation. For
Figure 4.33: Normalized resistance versus temperature for MgB$_2$ thin film prepared by magnetron sputtering technique. The inset is a close up of the transition region. Thin film has a residual resistivity ratio of 1.54, an onset of transition at 35.2 K, and a transition width of about 1 K.

example, thin films deposited on SrTiO$_3$ and Al$_2$O$_3$ substrates showed zero resistivity at about 10-15 K [110]. A better result was achieved by using single crystal Al$_2$O$_3$ substrates with an onset of transition at around 28 K [111]. Peng et al. [146] studied the effect of annealing on $T_c$ and concluded that the observed suppression of $T_c$ in thin film samples can be attributed to the small grain size of MgB$_2$.

We have prepared MgB$_2$ thin films by using single MgB$_2$ target in a magnetron sputtering chamber, followed by ex-situ annealing. Oriented sapphire (its c-axis makes an angle of 34° with the normal to its plane) is used as a substrate. Films are good enough for resistivity measurements while the thickness was too thin for x-ray analysis or SQUID measurements. Resistivity measurements are done by the conventional four probe technique. Figure 4.33 shows the normalized resistance versus temperature, the inset is a close up of the transition region. As seen, the thin film shows a residual resistivity ratio of 1.54, an onset of transition at 35.2 K, and with width of 1 K (10%-90%). Vaglio et al. [112] reported a similar result to ours, their best films showed a maximum onset transition at around 35 K with transition width of 0.5 K. These films were prepared on sapphire and MgO substrates followed by in-situ annealing. According to Ueda et al. [147], our thin films are more suitable for tunnel junction
fabrication than the films prepared by in-situ annealing, as in-situ annealed films have a nonsuperconducting surface on the top.

In summary, we have studied the energy gaps of MgB$_2$ and their temperature and magnetic field dependence. We used sandwich-like MgB$_2$/Pb planar junctions to offer a stable and reliable measurement of the temperature dependence of energy gap. The study of the temperature dependence showed polycrystalline MgB$_2$ to have two energy gaps (many models have been suggested by different groups) with a gap ratio of about 4.5 and a weight of 6% for the large gap. Also, we showed that the small energy gap value (reported by many groups and explained as a result of surface degradation) is a true bulk property of MgB$_2$. Both gaps have been found to obey the BCS prediction of the energy gap temperature-dependence. This supports the pairing mechanism in MgB$_2$ to be phonon mediated. We showed also that, the observed conductance tunnel spectra with no peak features around the large gap value can be best fitted with assuming two energy gaps rather than a one-gap model.

On the other hand, the study of magnetic field (applied normal to the junction barrier) effect on the junctions gave an estimation of the upper critical field of about 5.6 T, in consistence with many reported values from tunneling measurements. The dependence of energy gap on the field has been studied as well. While our junctions show stability against temperature changes, they collapsed when a magnetic field higher than 3.2 T was applied. This resulted in an irreversible structural change in the junctions and switched the tunneling mechanism from quasiparticle tunneling into Josephson tunneling. For these collapsed junctions, Josephson I-V curves at different temperatures have been studied and both the characteristic voltage and energy gap have been estimated. Josephson tunneling has also been observed in weak link junctions. The estimated MgB$_2$ energy gap from supercurrent tunneling agrees very well with that from quasiparticle tunneling in these junctions.

Polycrystalline and single crystal MgB$_2$ have inconsistent reported properties. This motivated us to look for a new heat treatment to prepare high
quality polycrystalline and single crystal MgB$_2$ in the same process. A second motivation is to improve the coupling of grain boundaries in polycrystalline MgB$_2$ (has the lowest normal state resistivity in comparison to many other practical superconductors) which will be of practical interest. We invented a new and simple heat treatment to prepare single crystals (neither high pressure cells nor very high sintering temperatures were required) and polycrystalline MgB$_2$ in same process. This method gives high quality and dense polycrystalline MgB$_2$ with the lowest reported normal state resistivity of 0.28 $\mu$Ωcm and a residual resistivity ratio of 16.6. The obtained single crystals are in high quality and have an average diagonal of 50 $\mu$m and 10 $\mu$m thickness with a unique shape that resembles the hexagonal crystal structure. As a future work, preparing both polycrystalline and single crystal MgB$_2$ in same process will give a great opportunity to study inconsistencies in their properties. We also improved the electrical properties of magnesium diboride thin films (prepared by using magnetron sputtering technique) by using new preparation conditions. The prepared thin films (ex-situ annealed) have a transition temperature of about 35.2 K. These thin films will be promising in fabricating tunnel junctions in contrast to films treated by in-situ annealing.
References:


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List of Publications


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