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# STUDY OF UPPER CRITICAL MAGNETIC FIELD OF SUPERCONDUCTING HoM06SeS

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# STUDY OF UPPER CRITICAL MAGNETIC FIELD OF SUPERCONDUCTING $HoMo_6Se_8$

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# BAHIR DAR UNIVERSITY

# SCHOOL OF GRADUATE STUDIES

## Study of Upper Critical Magnetic Field of Superconducting $HoMo_6Se_8$

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## *Dedication*

*This work is dedicated to my Mother Hadase Gebremichael, my sisters Etsana Gebre and Kidsti Hatsey.*

# Table of Contents

# List of Figures

# Acknowledgements

First of all, thanks to God from the bottom of my heart who help me in any success in my life. God is with me every where.
I would like to begin by thanking my wonderful family, especially my Mother Hadase Gebremichael, my sisters Etsana Gebre and Kidsti Hatsey. I would like to thank my advisor and instructor Dr. Gebregziabher Kahsay for his encouragement and valuable comments through out the preparation of this thesis. I am grateful to all my friends for being with me for all the time. I am also thankful to Demisachew Shitaw for his great support to get journals. Finally, I would like to express my thanks to all my family members for their love and support.

Kindehafti Desalegn
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# Abstract

This work focuses on the study of mathematical aspects of upper critical magnetic field of superconducting $HoMo_6Se_8$. At zero external magnetic field, $HoMo_6Se_8$ was found to undergo a transition from the normal state to the superconducting state at $5.6K$ and returned to a normal but magnetically ordered state between the temperature range of $0.3K$ and $0.53K$. The main objective of this work is to show the temperature dependance of the upper critical magnetic field of superconducting $HoMo_6Se_8$ by using the Ginzburg-Landau(GL) phenomenological equation. We found the direct relationship between the GL coherence length($\xi_{GL}$) and penetration depth ($\lambda_{GL}$) with temperature. From the GL equations and the results obtained for the GL coherence length, the expression for upper critical magnetic field($H_{c2}$) is obtained for the superconducting $HoMo_6Se_8$.
The result is plotted as a function of temperature. The graph shows the linear dependance of upper critical magnetic field($H_{c2}$) with temperature(T) and our finding is in agreement with experimental observations.

**Key words**: Ginzburg-Landau equation, upper critical magnetic field and $HoMo_6Se_8$

# Chapter 1

# General Introduction to Superconductivity

## 1.1 Background of Superconductivity

Superconductivity is a phenomenon that occurs at very low temperatures. Every superconductor has a transition temperature($T_c$) below which it superconducts and above which it is a normal metal[1]. In the superconducting state, the material has no electrical resistance and thus conducts electricity with out losses. On the otherhand, in the normal state, the material does have resistance and the flow of electric current accompanies with the development of heat and the dissipation of energy[1].

The era of low-temperature physics began in 1908 when the Dutch physicist Heike Kamerlingh Onnes first liquefied helium which boils at 4.2K at standard pressure. Three years later, in 1911, Kamerlingh Onnes discovered the phenomenon of superconductivity while studying the resistivity of metals at low temperatures[1]. We now know that, the resistivity of a superconductor is zero. Soon after the discovery of superconductivity by Kamerlingh Onnes, many other elemental metals were found to exhibit zero resistance when their temperatures were lowered below a certain characteristic temperature of the material called the critical temperature($T_c$). Much to their surprise, the resistance of mercury sample dropped sharply at 4.2K to an unmeasurably small value. That is at the temperature of 4.2K, he observed that the resistance abruptly disappeared. It was quite natural that, Kamerlingh Onnes would choose the name superconductivity for this new phenomenon of perfect conductivity[1].

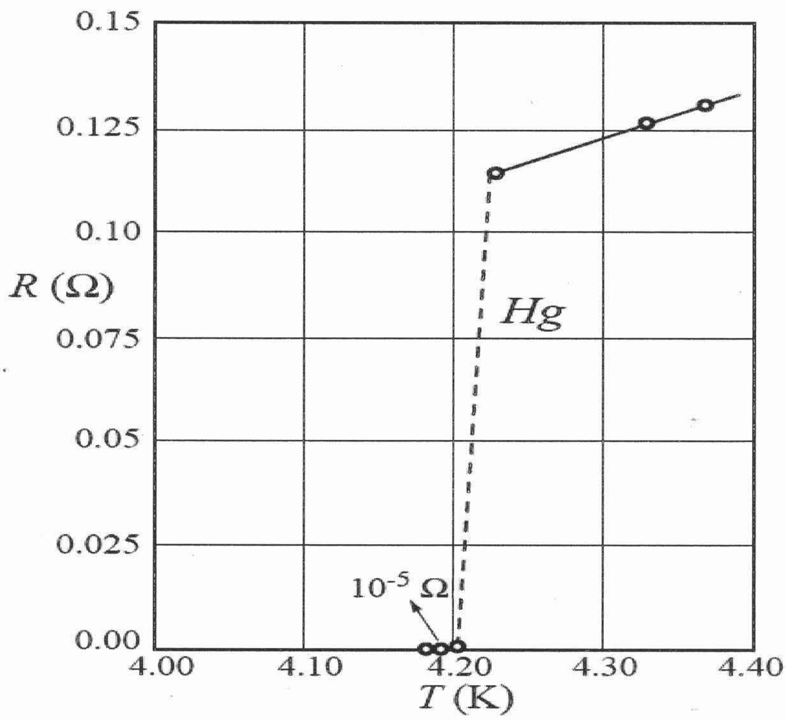


Figure 1.1: Experimental data obtained in mercury by H. Kamerlingh Onnes[2].

In subsequent years, superconductivity was found in several other materials. In 1913, lead was found to superconduct at 7.2K, 17 years later in 1930, niobium was found to superconduct at 9.2K[1]. The next important step in understanding superconductivity occurred in 1933, when Meissner and Ochsenfeld discovered that superconductors expelled applied magnetic fields, a phenomenon which has come to be known as the Meissner effect[1]. In 1935, F and H. London showed that, the Meissner effect was a consequence of the minimization of the electromagnetic free energy carried by superconducting current[1]. In 1941 niobium nitride was found to superconduct at 16K. In 1950, the phenomenological Ginzburg-Landau theory of superconductivity was devised by Landau and Ginzburg[3]. This theory, which combined Landau's theory of second-order phase transitions with a Schrdinger-like wave equation had great success in explaining the macroscopic properties of superconductors. In particular, Abrikosov showed that, Ginzburg-Landau theory predicts the division of superconductors into the two categories now referred to as Type-I and Type-II superconductors. Also in 1950, Maxwell and Reynolds et al.[1] found that the critical temperature of a superconductor depends on the isotopic mass of the constituent element. This important discovery pointed to the electron-phonon interaction as the microscopic mechanism responsible for superconductivity[1]. In 1953 Vanadium-Silicon displayed superconductive properties at 17.5K. The complete microscopic theory of superconductivity was finally proposed in 1957 by BCS[4]. This BCS theory explaines the superconducting current as a superfluid of Cooper pairs, pairs of electrons interacting through the exchange of phonons. The BCS theory was set on a firmer footing in 1958, when Bogoliubov showed that, the BCS wavefunction which had originally been derived from a variational argument could be obtained using a canonical transformation of the electronic Hamiltonian. In 1959, Gorkov showed that, the BCS theory reduced to the Ginzburg-Landau theory close to the critical temperature[5]. In 1962, the first commercial superconducting wire, a niobium-titanium alloy, was developed by researchers at Westinghouse[6]. In the same year, Josephson same year, Josephson made the important theoretical prediction that a supercurrent(paired electrons) can flow between two pieces of superconductors separated by a thin layer of insulator. This process which is nowadays known as the Josephson effect is exploited by superconducting devices such as superconducting quantum interference devices(SQUIDs)[6]. It is used in the most accurate available measurements of the magnetic flux quantum ($\phi_0 = \frac{hc}{2e}$) and thus (coupled with the quantum Hall resistivity) for Planck's constant(h). In 1986, Bednorz and Mueller discovered superconductivity in a lanthanum barium copper oxide compound(LaBaCuO) which had a transition temperature of 36K[7].

## 1.2 Types of Superconductors

The application of strong magnetic field destroys its superconducting state. According to the way superconductors behave in an applied magnetic field, they can be classified as type I and type II superconductors(also known as soft and hard superconductors) because of the dramatic difference in their magnetic and current-carrying properties. The main difference between these types of superconductors is their ability to expel magnetic field[5,8]. In type-I superconductors, the expulsion is complete up to a certain maximum or critical field($H_{c1}$) above which the superconductor returns to the normal state. Type-II superconductors also show complete expulsion up to a field $H_{c1}$, but now for higher fields magnetic flux starts to enter the superconductor in the form of small flux bundles, so-called vortices, crossing the interior of the superconductor. These vortices are like tubes having a non-superconducting core and carry a single quantum of flux($\phi_0 = \frac{hc}{2e}$). With increasing field, the density of vortices increases until a field $H_{c2}$ at which the superconductor becomes normal[1,8].

The value of the Ginzburg-Landau parameter $(\kappa) = \frac{\lambda_{GL}}{\xi_{GL}}$ determines the behavior of bulk superconductors in an applied magnetic field(H). All superconducting elements except Niobium(Nb), Vanadium (V) and Technetium(Tc) are type-I superconductors. Furtheremore, all superconducting alloys, chemical compounds and high temperature superconductors belong to type-II superconductors. For magnetic fields up to the lower critical field, both types of superconductors behave in the same way[8].

### 1.2.1 Type-I Superconductors

In type-I superconductors, the magnetic field(H) remains zero inside the superconductor until the superconductivity is suddenly destroyed[8]. The field where this happens is called the critical field($H_c$). There is no difference in the mechanism of superconductivity in type-I and type-II superconductors. Both types have similar thermal properties at the superconductor-normal transition in zero magnetic field. But the Meissner effect is entirely different. A good type-I superconductor excludes a magnetic field until superconductivity is destroyed suddenly and then the field penetrates completely[8].

The main difference between type-I and type-II superconductors is in the mean free path of the conduction electrons in the normal state. If the Ginzburg-Landau coherence length($\xi_{GL}$) is longer then the Ginzburg-Landau penetration depth ($\lambda_{GL}$) the superconductor will be type-I. Most pure metals have $\kappa < \frac{1}{\sqrt{2}}$ and are categorized as type-I superconductors. In this condition, the superconductor has no mechanism to carry flux and exhibits the Meissner effect, behaving like a type-I superconductor[8].

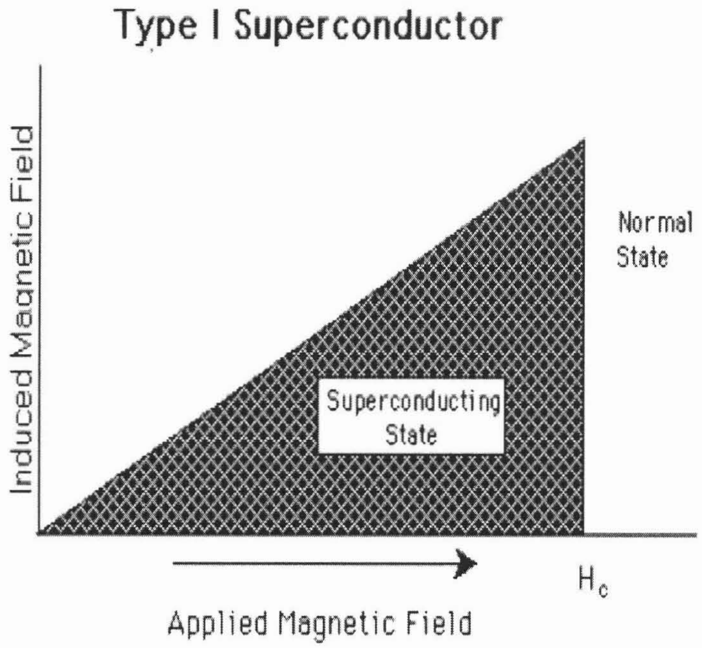


Figure 1.2: H-T phase diagram for type-I superconductors [9].

### 1.2.2 Type-II Superconductors

Type-II superconductors behave much differently as compare to type-I superconductors. For this variety, the magnetic field begins to penetrate at a lower critical magnetic field($H_{c1}$) and continues to grow which increases in the applied magnetic field($H_{app}$) until it reaches the value of the upper critical magnetic field($H_{c2}$). This removes the superconducting state of the entire material. For applied magnetic fields below $H_{c1}$, there is no flux penetration inside the material[1]. The vortex density increases with increasing magnetic field strength[8]. At a higher critical magnetic field($H_{c2}$), superconductivity is completely destroyed[8]. For type-II superconductors, there are two critical magnetic fields, lower($H_{c1}$) and upper critical($H_{c2}$). If

$H_{c1} < H_c < H_{c2}$ it is called vortices(mixed) state. A good type-II superconductor excludes the magnetic field completely up to a field $H_{c1}$[8,10]. Above $H_{c1}$ the field is partially excluded, but the specimen remains electrically superconducting. In other words, type-II superconductors can conduct electricity with out resistance in a relatively high magnetic field(H). At a much higher critical magnetic field($H_{C2}$), the flux penetrats the region completely and superconductivity vanishes[8,10]. In a type-II superconductor, the Ginzburg-Landau coherence length($\xi_{GL}$) is smaller than the Ginzburg-Landau penetration depth($\lambda_{GL}$) and $\kappa > \frac{1}{\sqrt{2}}$. An external magnetic field(H) between the lower and upper critical magnetic fields ($H_{c1}$ and $H_{c2}$) respectively do not penetrate uniformly through the sample[11].

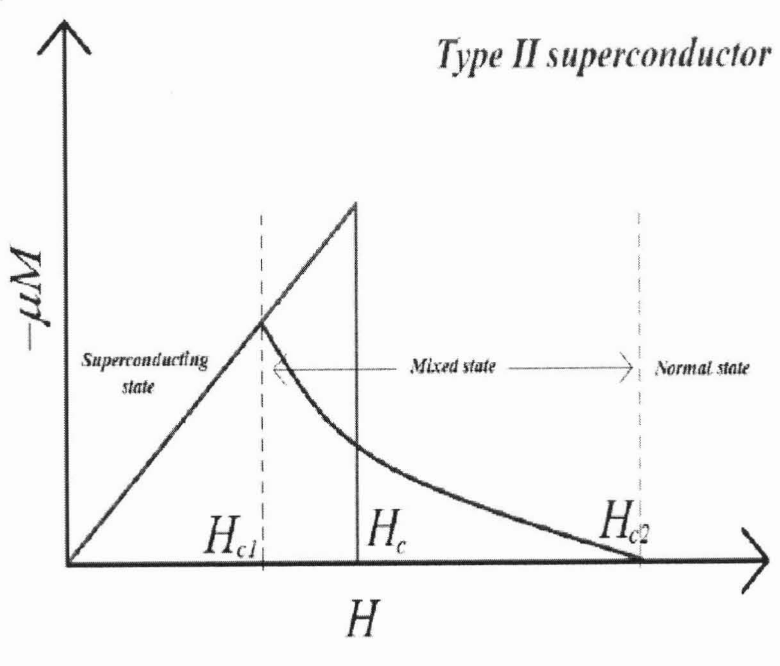


Figure 1.3: Applied magnetic field versus Magnetization for type-II superconductors[10].

## 1.3 Properties of Superconductors

Most of the fundamental properties of superconductors vary from material to material. The superconducting state, as any state of matter has its own basic properties. So, any superconductor independent of the mechanism of superconductivity and the material will exhibits these properties. The basic properties of the superconducting state are: zero resistance, Meissner effect, magnetic flux quantization, Josephson effects, the BCS theory, Cooper pair, appearance of an energy gap in elementary excitation energy spectrum, Isotope effect and the proximity effect. Every superconducting transition is marked by a jump in specific heat. In the mixed state, the behavior of type-II superconductors has the same pattern[6,8].

### 1.3.1 Isotopic Effect

Superconductivity is due to the electron-phonon interaction between conduction electrons and lattice vibrations(phonons) which provides some background on the nature of isotopes[1]. These vibrations can also exhibit particle like properties with localized regions of vibration moving about the lattice and perhaps being scattered by obstacles that are encountered. For example, an earthquake(seismic wave) forms a localized region of earth vibrations that acts like a giant particle as it moves at the speed of sound. A localized lattice vibration exhibiting particle like properties is called a phonon[8].

In 1950, the theorist Herbert Frohlich concluded that, vibrating atoms of a material must play an important role causing it to superconduct[1]. Frohlich proposed that, an electron-phonon interaction between electrons carrying the supercurrent and the lattice that vibrates brings about superconductivity[1]. He knew that, no one could accept his conjecture unless it were supported by an experiment and he also knew from infrared spectroscopy that, the frequency of vibration of an atom in a solid is proportional to the reciprocal of the square root of its mass. The isotope effect, dependence of infrared vibrational frequencies on atomic mass was a well-known phenomenon among spectroscopists[1]. Accordingly, Frohlich proposed that, searching for an isotope effect in superconductors would establish whether or not lattice vibrations play an important role in the interaction responsible for the onset of superconductivity[1,2]. They found that, the transition temperature decreased when the mercury atom became heavier and the change was proportional to the reciprocal of the square root of the mass of the atom which is in agreement with infrared spectroscopic results[1]. These experimental results convinced physicists that a microscopic theory of superconductivity must involve the electron-phonon interaction to explain the isotope effect. However, the phenomenological theories just described did not accomplish this. Knowing the basic mechanism provided theorists were motivated to searched for a fundamental theory. In 1956 Leon Cooper showed that, two conduction electrons in the presence of very weak electron-phonon interaction are capable of forming the stable paired state referred to as a Cooper pair. This provided the final fact needed to formulate a microscopic theory of superconductivity[8].

### 1.3.2 Meissner Effect

In 1933 Meissner and Ochsenfeld discovered that, when a superconducting metal is placed in a magnetic field and then cooled below the transition temperature, the magnetic field is expelled i.e superconductor exhibits perfect diamagnetism, B = 0 inside the superconductor. It turns out that, no magnetic field is allowed inside a metal when it is in the superconducting state, a phenomenon known as the Meissner effect[1]. Another property discovered by Onnes, shortly after his observation of the disappearance of resistance below $T_c$ was that, small magnetic fields destroy superconductivity. In 1938 the London brothers, Fritz and Heinz, provided an explanation for the Meissner effect. They applied the well-known theory of electromagnetism based on Maxwell's equations to the case of a superconductor. They showed that, an applied magnetic field($B_{app}$) induces a surface current. This surface current in turn produces an internal magnetic field that exactly cancels the applied field within the superconductor, so that no magnetic field is present in its interior. In other words, the induced internal field is equal in magnitude and opposite in direction to the applied field($B_{app}$), so the two fields cancel each other.

A more detailed analysis of this situation shows that, some magnetic fields do indeed penetrate surface layers of the superconductor and it is present where the surface currents flow. Probably, the most spectacular demonstration of the Meissner effect is the levitation effect. A small magnet above $T_c$ simply rests on the surface of a superconductor having dimensions larger than those of the magnet. If the temperature is lowered below $T_c$, the magnet will float above the superconductor. The gravitational force exerted on the magnet is compensated by the magnetic pressure occurring due to supercurrent circulation on the surface of the superconductor[8,12].

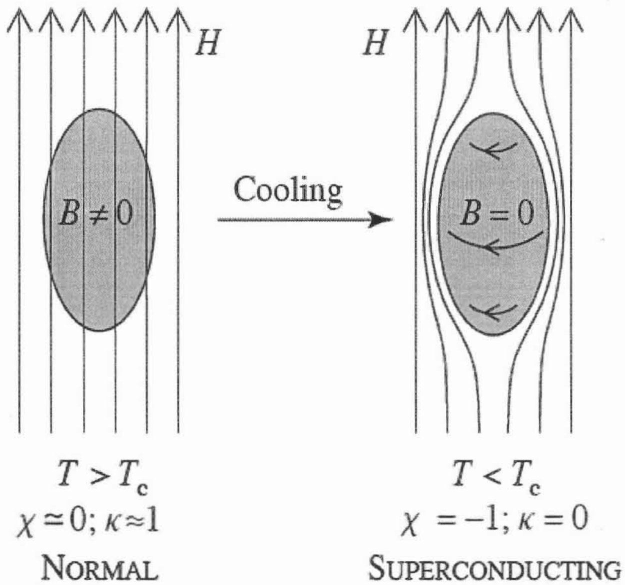


Figure 1.4: Meissner effect in a superconducting sphere cooled in a constant applied magnetic field;on passing below the transition temperature[13].

### 1.3.3 The BCS Theory

In 1957, more than 40 years after the discovery of conventional superconductivity, Bardeen, Cooper and Schrieffer(BCS) found the theoretical explanation to superconductivity in metals[4]. In a theoretical model, they proposed an explanation such that electrons form pairs before forming a collective quantum wave[1].

The theory describes superconductivity as a microscopic effect caused by a condensation of Cooper pairs into a boson-like state[1]. The theory is also used in nuclear physics to describe the pairing interaction between nucleons in an atomic nucleus. The BCS theory starts from the assumption that, there is some attraction between which can overcome the Coulomb repulsion[1,4]. In most low temperature superconductors, this attraction is brought about indirectly by the coupling of electrons to the crystal lattice. However, the results of BCS theory do not depend on the origin of the attractive interaction. The original results of the BCS theroy described as s-wave superconducting state which is the rule among low-temperature superconductors but is not realized in many unconventional superconductors such as the d-wave high-temperature superconductors[1,4].

Generally, the BCS theory is a microscopic field theoretical frame work of superconductivity. The basic principle of the BCS theory is that electrons(fermions) pair up via phonon coupling and the pairs(bosons) condense into a single microscopic quantum state and travel together cooperatively and coherently through the crystal lattice without scattering[4,8].

### 1.3.4 The Cooper Pairs

It was developed by Lion Cooper in 1956[1,8]. Cooper pair is the binding of two electrons(fermions) at low temperatures in a certain manner[1]. Cooper showed that an arbitrarily small attraction between electrons in a metal can cause a paired state of electrons to have a lower energy than the Fermi energy which implies that the pair is bound[1]. In conventional superconductors, this attraction is due to the electron-phonon interaction[1]. The Cooper pair state is responsible for superconductivity as described in the BCS theory[4]. Although Cooper pairing is a quantum effect, the reason for the pairing can be seen from a simplified classical explanation[1]. An electron in a metal normally behaves as a free particle. The electron is repelled from other electrons due to their negative charge but it also attracts the positive ions that make up the rigid lattice of the metal. This attraction distorts the ion lattice, moving the ions slightly toward the electron, increasing the positive charge density of the lattice in the vicinity[1]. This positive charge can attract other electrons. At long distances, this attraction between electrons due to the displaced ions can overcome the electrons repulsion due to their negative charge and cause them to pair up[1]. The strict quantum mechanical explanation shows that, the effect is due to electron-phonon interactions[1,4]. The energy of the pairing interaction is quite weak, of the order of $10^{-3}$eV and thermal energy can easily break the pairs[1]. The electrons in a pair are not necessarily close together, because the interaction is long range, paired electrons may still be many hundreds of nanometers apart. This distance is usually greater than the average interelectron distance, so many Cooper pairs can occupy the same space[14]. Electrons have spin half, so they are fermions, therefore a Cooper pair is a composite boson as its total spin is integer (0 or 1)[4]. This means, the wave functions are symmetric under particle interchange and they are allowed to be in the same state. The tendency for all the Cooper pairs in a body to 'condense' into the same ground quantum state is responsible for the peculiar properties of superconductivity[1,4]. Here, the pairing is supported by web in an optical lattice.

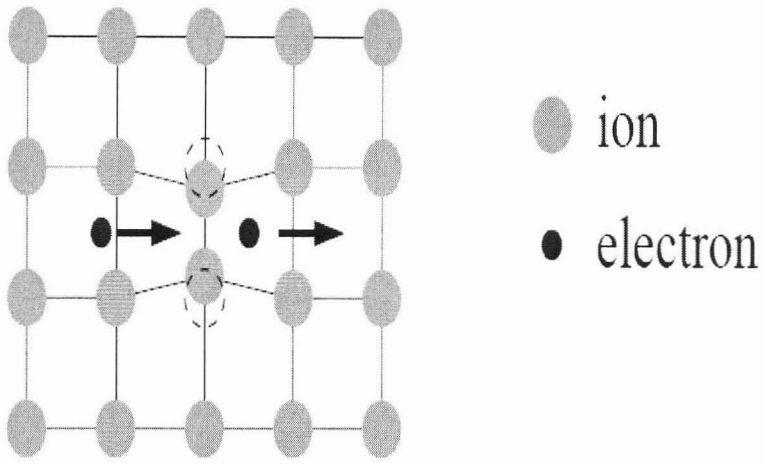


Figure 1.5: The figure shows how electrons form Cooper pairs. There is time-retarded, effective attraction between two electrons in a crystal lattice(virtual electron-phonon interaction)[5].

## 1.4 High temperature Superconductor(HTS)

High-temperature superconductors are materials that behave as superconductors at unusually high temperatures[8]. The Ginzburg-Landau coherence length for HTS materials is far smaller than for low temperature superconductors(LTS)[8].

After the discovery of the first high-$T_c$ superconductor by Bednorz and Mueller[7], the compound yttrium barium copper oxide(YBaCuO) was discovered in 1987 with $T_c$ of 92K[7]. However, several iron-based compounds are now known to be superconducting at high temperatures. In 1988 bismuth strontium calcium copper oxide(BiStCaCuO) discovered with $T_c$ up to 108K and thallium calcium-cooper oxide(TiCaCuO) discovered to have $T_c$ of 127K[7,15]. As of 1993, the highest-temperature superconductor is mercury barium calcium copper oxide ($HgBa_2Ca_2Cu_3O_x$) around 138K and is held by a cuprate-perovskite material, which possibly reaches 160K under high pressure[7,16].

# Chapter 2

# Literature Review

## 2.1 Introduction

In this chapter, literature which are related to our research work will be reviewed. $HoMo_6Se_8$ crystallizes in a hexagonal-rhombohedral structure.

$HoMo_6Se_8$ compound is building blocks of the Chevrel-phase crystal structure[13]. The discovery in 1984 of the new superconducting $HoMo_6Se_8$ gave rise to a renewed interest in the interplay of magnetism and superconductivity. From the experimental results, a magnetic phase transition($T_m$=0.53K) to a long-period magnetic states has been observed via neutron scattering in the superconductor $HoMo_6Se_8$($T_c$=5.6K)[17]. The characteristic wave vector($q_c$) is strongly temperature dependent and there is no observation of higher-order satellites.

The rare occurrence of ferromagnetism as found in $HoMo_6Se_8$ and $HoMo_6S_8$, revealed the strongly competitive nature of these two cooperative phenomena in the form of long-wavelength at low oscillatory magnetic temperature(<1K) and a ferromagnetic lock-in transition that quenches the superconductivity. No sign of reentrant behavior (in zero field) was observed down to 0.04K[17,18]. Ternary rare-earth superconductors which display a propensity for ferromagnetism has received considerable experimental as well as theoretical attention recently. In the case of the new superconductors, $HoMo_6Se_8$ were observed despite the presence of the holmium moment of the rare earth ion in each unit cell. These compounds did not destroy the property of superconductivity at low temperature. In $HoMo_6Se_8$, the domain coexistence phase survives till T= 0.3K (the exchange interaction is weaker and the coexistence persists down to T=0.3K)[19]. In addition to the superconducting and ferromagnetic domains, a coexistence region was observed in $HoMo_6S_8$ in which the superconducting state coexists with a long range modulated magnetic order in a narrow region above the reentrant temperature $Tc_2$.

The behavior of superconductivity $HoMo_6Se_8$ compound is quit similar to $HoMo_6S_8$ but a higher $T_{c1}$ is equal to 5.6k and in the superconducting phase also the higher nonuniform magnetic structure with wave vector q=0.09$\mathring{A}^{-1}$ appears at $T_m$=0.53k[20,21]. Unlike $HoMo_6S_8$, however, the superconductivity is not destroyed in $HoMo_6Se_8$ and the higher nonuniform magnetic structure coexists with it[18,19].

At low temperature ($T > T_{c2} \simeq 0.4{-}0.5K$) the wave vector(q) decreases from 0.09$\mathring{A}^{-1}$ down to 0.06$\mathring{A}^{-1}$[22]. As shown in figure 2.1, temperature increases as the magnetic intensity decreases and the characteristic wave vector increases[17].

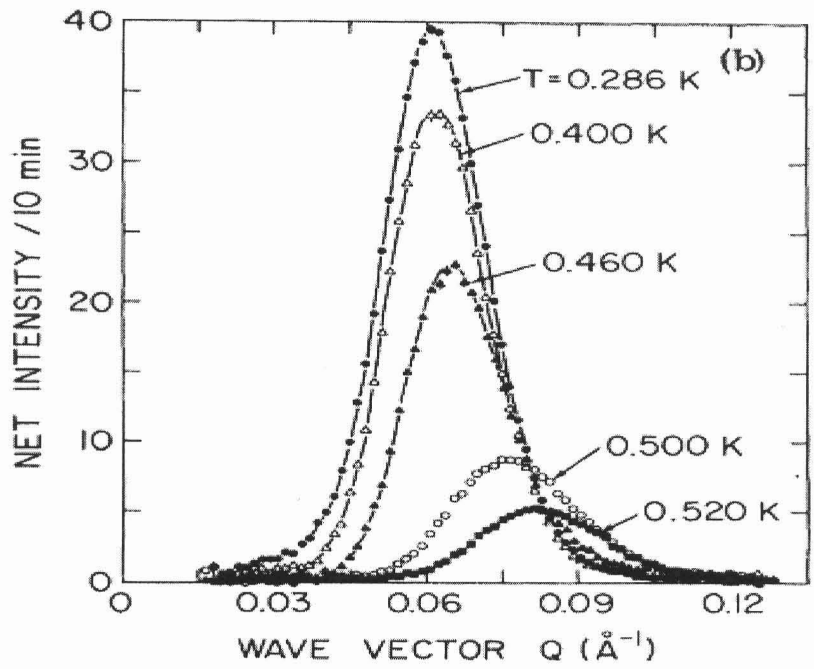


Figure 2.1: The figure shows the temperature dependence of the scattering on several temperatures. Note that, the position of the peak shifts to large q(wave vector) with increasing temperature[17].

## 2.2 Superconducting and Magnetic properties of $HoMo_6Se_8$

In solid state physics, magnetic superconductors are especially interesting because of the competition between magnetic order and superconductivity[23]. Important progress in the field started with the discovery of the magnetic superconductors $REMo_6Se_8$ and $REMo_6S_8$, where the rare earth ions(RE) are regularly distributed in the crystal lattice. After intensive experimental investigation, it is turned out that, in many of these systems, superconductivity coexists with antferromagnetic ordering[3]. One usually has $T_N < T_c$. $HoMo_6Se_8$ and $HoMo_6S_8$ are in fact, under certain physical conditions, ferromagnetic order is transformed into a spiral(domain-like magnetic structure) in the presence of superconductivity properties. In the same manner, the superconducting order parameter is suppressed at the presence of the modified ferromagnetism which coexists in temperature even down to $T_{c2}$=0.3K in $HoMo_6Se_8$ depending on system parameters[19].

From the experiment of small angle neutron scattering(SANS), the properties of two ferromagnetic Chevrel-type of superconductors are studied by means of electrical and neutron scattering measurements[18]. The superconductivity properties are quite similar but behavior of the coexistence phase are quite different in these compounds. The behavior of the coexistence phase and superconductivity of $HoMo_6Se_8$ ($T_{c1} = 5.6K$) undergoes a transition ($T_m = 0.53K$) to an oscillatory magnetic state which coexists with ferromagnetic order at least down to $T_{c2} = 0.3K$ and superconductivity was observed down to 0.04K and presumably represents the ground state behavior[18,19]. In the absence of an applied magnetic field, the scattering pattern in the ordered state is isotropic about the forward scattering direction[18]. The net magnetic scattering due to the modulated state at low temperatures then forms a ring of constant intensity on the area detector with a radius corresponding to q. There is no evidence for a ferromagnetic component to the scattering at any temperature in zero magnetic field. With a magnetic field applied perpendicular to the neutron beam, an asymmetric pattern is observed with an additional small-q component to the scattering. In a zero magnetic field, $HoMo_6Se_8$ was found to undergo a normal to superconducting state transition at 5.6K($T_{c1}$) and to return to a normal but magnetically ordered state at 0.3K($T_{c2}$)[18,19]. The Neutron Scattering experiments indicate that, the magnetic ordering occurring at $T_{c2}$ is ferromagnetic and thermodynamically of second order.

In interesting case of a ferromagnetic state like $HoMo_6Se_8$, there is a strong coupling in the superconducting state that originates from the generation of internal magnetic field[19]. The wave vector $q_c$ of $HoMo_6Se_8$ in the sinusoidal state is strongly temperature dependent with the full available holmium moment developing in this phase. Thus, there was no genuine(q=0) ferromagnetic component (in zero applied field) at any temperature and the superconductivity persists to law temperature[17].

Neutron scattering experiments were carried out at the National Bureau of Standards Research Reactor. Field-dependent diffraction and inelastic scattering data were collected above the magnetic phase transition with the use of convention triple-axis spectrometers. Furthermore, the saturation magnetic moment per $Ho^{3+}$ is found from neutron diffraction experiments $\mu_z = 6\mu B$[17]. To study the low-temperature magnetic state, the sample was mounted in a pumped $^3Ho$ cryostate. The width of the scatterining in fact increases very rapidly above $T_m$ and for $T$ >0.56K, there is no peak in the scattering at finite q. No higher-order satellites where detected at any temperature. In addition, we found no evidence for a ferromagnetic component to the magnetization. With increasing temperature, the magnetic intensity decreases and the characteristic wave vector increases.

There are four basic states which have been proposed as possibilities for these ferromagnetic superconductors. These are spontaneous vortex, laminar state, linearly polarized state and spiral state. The spontaneous vortex does not believe that such a model is appropriate for $HoMo_6Se_8$. This then allows the spiral state or the linearly polarized state. We emphasize that, our diffraction data are consistent with either model. It is not possible to determine directly which state is realized experimentally from powder data alone. Energetically, the linearly polarized state is stabilized if sufficient magnetic anisotropy is present, but how much anisotropy is sufficient for the present system of interest is not known[17].

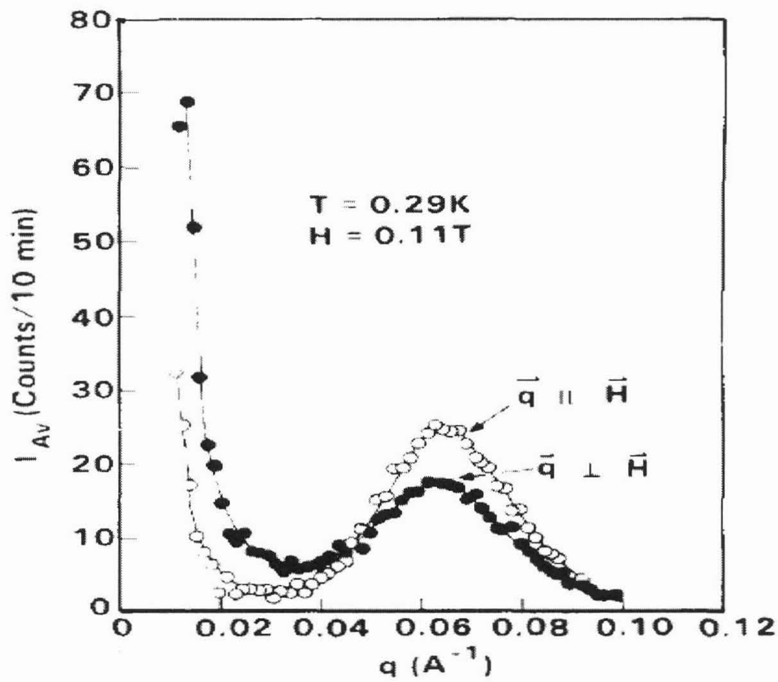


Figure 2.2: The figure shows Intensity versus wave vector in a field of 0.11 T (T= 0.29 K), with averages calculated separately for sectors parallel and perpendicular to the applied field [18].

### 2.2.1 The influence of magnetic field on single crystal of Superconducting $HoMo_6Se_8$

Magnetic field increases the temperature $T_{c2}$ of (domain-like magnetic structure)$DS \rightarrow FN$(ferromagnetic normal state) transition due to the strong lowering of the $FN-phase$ free energy in comparison with $DS-phase$[19]. The complete destruction of $DS-phase$ in favour of $FN-phase$ occurs in a rather weak magnetic field with direction along the easy axis. The effect of perpendicular field (relative to the easy axis) is much weaker owing to the small susceptibility of localized moments(LM) for this direction[24]. The theoretical description of the effect of magnetic field on $DS - phase$ is given in ferromagnetic normal state. Experimentally the suppression of $DS - phase$ by magnetic field was observed by Pynn et al.[21] in the polycrystalline samples of $HoMo_6Se_8$. Fields as small as 100-200 Oe were sufficient to decrease the intensity of peak Q. Also, the remarkable anisotropy of the intensity of peak Q was observed for different orientations of the scattering wave vector q with respect to the magnetic field direction H. The effect of the field $H \parallel q$ was weaker than the effect of perpendicular field $H \perp q$. To explain this anisotropy we remark that, at $q \parallel H$ the scattering comes from the crystallites with wave vector $Q \parallel H$ in $DS - phase$. Here the magnetization and easy axis are perpendicular to Q and H owing to the transverse type of the domain magnetic structure in the coexistence phase. So, the magnetic field is perpendicular to the easy axis in crystallites under consideration and its effect on $DS - phase$ is weak. Contrary, in the case $q \perp H$ there is parallel (to the easy axis) component of magnetic field. It suppresses the $DS - phase$ more effectively in those crystals which give contribution to the scattering with $q \perp H$. Besides, below $T_m$ the value Q should diminish as a magnetic field grows. By applying the sufficiently strong magnetic field below $T_M$, the complete destruction of $DS - phase$ should occur. After switching off the magnetic field the reentrant formation of $DS - phase$ could be very slow[19].

## 2.3 Crystal structure of $HoMo_6Se_8$

The crystal structure of $HoMo_6Se_8$ is a hexagonal-rhombohedral structure which is similar to Chevrel phase compunds[13]. These are ternary molybdenum chalcogenides of composition $MMo_6X_8$, where X is one of the chalcogenes S, Se, or Te. M can be one of the many different metals(rare earth elements). The most remarkable property of these compounds is the possession of high critical magnetic field[13].

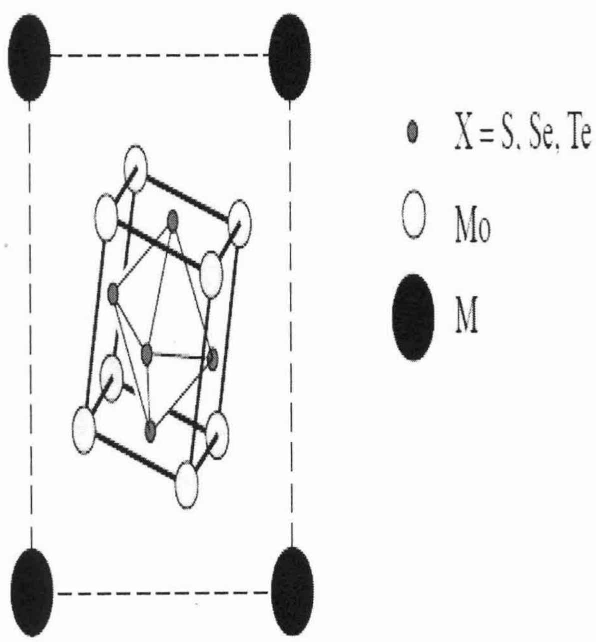


Figure 2.3: The figure shows the structure of the Chevrel phase compounds[13].

## 2.4 Superconducting and Normal state properties of $HoMo_6Se_8$

The study of superconducting and Normal state properties with the formula $REMo_6Se_8$ were reported by Matthias et al. with RE= Ho, to become either superconducting or ferromagnetic[22]. The Ho members of the series were found to exhibit ferromagnetism and reported to become superconducting. Fertig et al.[22] showed that, the transition from the normal state to the superconducting state at $T_{c1} = 5.6K$ in $HoMo_6Se_8$ a thermally hysteretic superconducting to normal state transition occurred at $T = 0.3K$. The transition at $T_{c2}$ was assign to the long-range ordering of the $Ho^{3+}$ holmium moments as indicated by a lambda-type specific heat anomaly at $T_{c2}$ as well as a decrease in the low-field ac magnetic susceptibility below $T_{c2}$. Subsequent neutron scattering experiments showed the ordering of ferromagnetic in nature and found the magnetic transition to exhibit smooth second-order behavior with no hysteresis, in contrast to the resistive behavior. The sample is a polycrystalline material with a superconducting transition of $T_{c1}$=5.6K as measured by susceptibility techniques. When the behavior of superconductivity was observed down to 0.04K, there is no reentrant behavior at zero field. If $T > T_{c1}$ it shows the complete normal state property of $HoMo_6Se_8$[18,19].

## 2.5 Pairing mechanism of $HoMo_6Se_8$

The early stages of superconductors occur with the consideration of electron pairing. These electron pairs, known as Cooper pairs[25], can be in state of either total spin, S=0 (spin singlet) or S=1 (spin triplet). In the standard S-wave pairing(conventional superconductors), the electron pairs are formed by an attractive electron-electron interaction(a virtual phonon exchange).

In 1972, unconventional superfluidity due to a p-wave (spin triplet) Cooper pairing of $^3He$ atom was experimentally predicted[26]. In this case, the accepted mechanism of Cooper pair is based on attraction between the fermion ($^3He$ atom) due to a virtual exchange of spin fluctuations. For unconventional superconductors, Cooper pairing is assumed as being mediated by spin fluctuation, similar to bosonic excitation of phonons. $HoMo_6Se_8$ is one types of Chevrel-phase compounds having a few known ferromagnetic reentrant superconductors, upper critical temperature($T_{c1} = 5.6K$), Curie temperature equals to the oscillatory magnetic temperature($T_m = 0.53K$) and reentering into a normal ferromagnetic state at $T_{c2} = 0.3K$.

## 2.6 Upper critical and Critical Magnetic field of $HoMo_6Se_8$

The upper critical magnetic field is a very important magnetic superconductivity parameter. Therefore, starting from its discovery as a superconducting material, experiments were carried out to analysis the upper critical magnetic field($H_{c2}$) of $HoMo_6Se_8$.

According to magnetization measurements, on both poly and single crystalline samples of the ferromagnetic superconducting $HoMo_6Se_8$, the upper critical magnetic field is a turning point from the superconducting state to the normal state. The first-order phase transition is the inter changing point of the superconducting state to the normal state observed when the external field H is applied parallel to the magnetically easy axis (a axis of the hexagonal-rhombohedral crystal lattice structure).

### 2.6.1 Critical Magnetic field of $HoMo_6Se_8$

The critical magnetic field in type-I superconductor is the inter changing point of superconducting state into normal state. From Maxwell's equation, $\nabla XE = -\frac{\partial B}{\partial t}$, when the magnetic field is frozen, the field is expelled from the interior of the superconductors, otherwise superconductivity will be destroyed by a critical magnetic field($H_c$), such that

$$H_c(T) = H_{c(0)}\Big[1 - \Big(\frac{T}{T_c}\Big)^2\Big] \tag{2.6.1}$$

Equation (2.6.1) yields the expression of thermodynamic critical magnetic field($H_c(T)$)[27]. (For derivation of equation(2.6.1) see appendix).

## 2.7 Temperature dependence of Energy Gap in Superconducting $HoMo_6Se_8$

In solid state physics, energy gap is an energy range in a solid where no electron states can exist. The superconducting energy gap is a process of controlling or altering how strongly the electrons of a substance are bound or coupled inside a Cooper pair. So, the energy gap is a major factor determining the electrical conductivity of a Cooper pair. The superconducting energy gap plays a role when considering the electrons at the Fermi surface which mediate the magnetic coupling. Direct evidence was provided for energy gap by measurement of the absorption of electro magnetic wave[23,28]. That is, at $T << T_c$, the absorption of electrons is very small and frequency($\nu$) is law. But frequency increases sharply as the photon energy sufficiently excites electrons across the energy gap[23]. The frequency of absorption is given by;

$$h\nu = 2\triangle_0 \tag{2.7.1}$$

Now, let us define $\triangle$ (energy gap) as follows,

$$\triangle_k = -\sum_{kk'} V_{kk'} \frac{\triangle_{k'}}{2E_{k'}} tanh(\frac{\beta E_{k'}}{2}) \tag{2.7.2}$$

where $V_{kk'}$ is the effective interaction potential between electrons with wave vector k and k', $\beta = \frac{1}{k_B T}$ , $E_{k'} = \sqrt{E_k^2 + \triangle_k^2}$ and is the energy of excitation.

when $T = T_c$ , $\triangle$=0 and $E_{k'} = E_k = E$

For the BCS approximation, we have;

$V_{kk'} = -V$ and $\triangle_k = \triangle_{k'} = \triangle$

Thus, equation(2.7.2) becomes,

$$\frac{1}{V} = \sum \frac{tanh}{2E_{k'}} (\frac{E_{k'}\beta}{2}) \tag{2.7.3}$$

This yields an implicity temperature dependence of the energy gap parameter. For $\omega_D < E_{k'}$ and changing summation to integration and introducing the density of state at the fermi level $N(0)$, eq(2.7.3) becomes,

$$1 = N(0)V \int_0^{\hbar\omega_D} \frac{dE}{2E} tanh(\frac{\beta E_{k'}}{2}) \tag{2.7.4}$$

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{dE}{2E} tanh(\frac{\beta E_{k'}}{2}) \tag{2.7.5}$$

If $T \to 0$ and $\beta \to \infty$

Thus, $\triangle$ at the ground state (the energy gap at zero temperature($\triangle(0)$) can be evaluated in the weak coupling limit (BCS model) to be,

$$\triangle(0) = 2\hbar\omega_D \exp(-\frac{1}{N(0)V}) \tag{2.7.6}$$

where $\omega_D$ is the Debye frequency and V is the electron-lattice interaction potential.

$$\triangle(0) = 2\hbar\omega_D \exp(-\frac{1}{\lambda}) \quad (2.7.7)$$

where $\lambda = N(0)V$.

The prediction of the BCS theory of an energy gap depends on temperature. $\triangle(T)$ is created from the minimum required energy of a single electron(hole) excitation from the superconducting ground state. The estimation of the BCS theory at zero temperature energy gap $2\triangle(0)$, becames;

$$\triangle(0) = 1.74K_BT_c \quad (2.7.8)$$

From equation(2.7.8), $\triangle(T)$, becomes

$$\frac{\triangle(T)}{\triangle(0)} = 1.74(1 - \frac{T}{T_c})^{1/2} \quad (2.7.9)$$

$$\triangle(T) = 1.74\triangle(0)(1 - \frac{T}{T_c})^{1/2} \quad (2.7.10)$$

$$\frac{2\triangle(0)}{K_BT_c} = \frac{2(1.74)K_BT_c}{K_BT_c} = 3.53 \quad (2.7.11)$$

The ratio of $\frac{2\triangle(0)}{k_BT_c}$ is the fundamental expression for superconductor and has a universal constant value equals to 3.53 which is obtained within weak coupling approximation in the BCS theory. Regarding the energy gap between superconductor and semiconductor materials, even though in both materials there exists energy gap between valance and conduction bands, the energy gap in superconductor materials is smaller and more dependent on temperature. For $T \to T_c$, $\triangle(T) \to 0$[2].

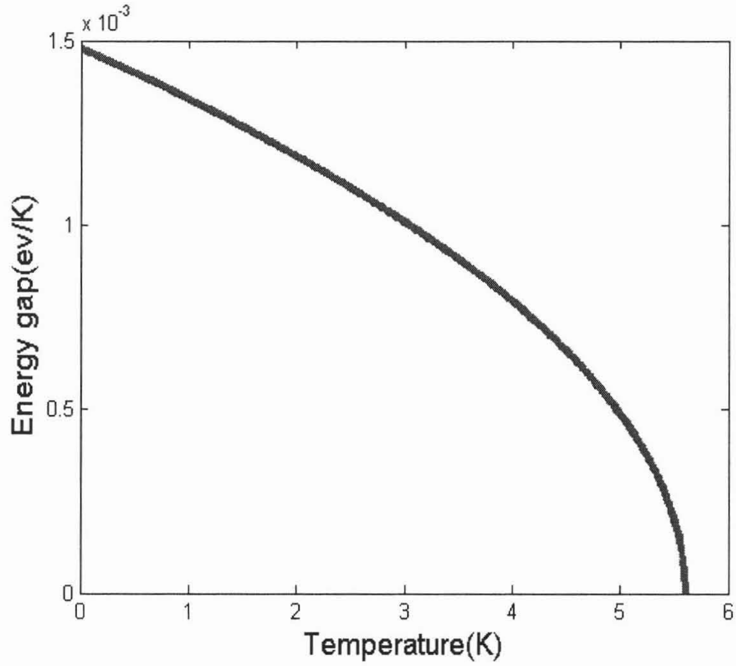


Figure 2.4: The figure shows the Temperature versus Energy gap.

As we can see from figure(2.4), as temperature increases, the energy gap(△) decreases. We already know that, in order to break a Cooper pair and create two elementary excitations, the energy 2△ is needed. If the temperature T is such that $k_BT \sim \triangle$, it is evident that, many Cooper pairs will be broken through thermal processes. Accordingly, a large number of states in momentum space will be filled by elementary excitations(single electrons). But, this implies that, these states can no longer participate in the pairs transition. Therefore, it cannot contribute to the net reduction of the superconductor energy. Accordingly, the energy of the superconductor has to increase. These states will likewise be unable to participate in forming the energy gap. If the number of broken pairs grow, the number of elementary excitation increases and decreases the energy gap(2△).

# Chapter 3

# Mathematical formulations to find the upper critical magnetic field of $HoMo_6Se_8$

## 3.1 The basic Ginzburg-Landau theory

Ginzburg-Landau(GL) theory is a mathematical theory used to describe superconductivity. Ginzburg-Landau(GL) theory is used to explain the difference between Type-I and Type-II superconductors and enables the calculation of two critical magnetic fields $H_{c1}$ and $H_{c2}$[29]. Ginzburg-Landau theory was derived from the BCS microscopic theory by Lev Gorkov, showing that it also appears in some limit of microscopic theory and applying microscopic interpretation of all its parameters. Ginzburg and Landau can be expressed in terms of a complex order parameter($\psi$). The parameter $|\psi(r)|^2$ represents the local density of superconducting electrons($n_s(r)$). In the framework of the two-fluid model, in a superconductor below $T_c$, there are superconducting and normal electrons[2,30].

We introduce the ordered parameter $\psi$ with the property that

$$\psi^*(r)\psi(r) = n_s(r) \tag{3.1.1}$$

Equation(3.1.1) is the local concentration of superconducting electrons. Now, starts form the Gibb's free energy density($F_s(r)$) of superconductors, such that:

$$F_s = F_n + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}|\Big(-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big)\psi|^2 + \frac{|H|^2}{8\pi} \tag{3.1.2}$$

where $\alpha$ and $\beta$ are phenomenological parameters, ($\beta$ is positive and the sign of $\alpha$ is temperature dependent), $m^* = 2m$ is an effective mass, $e^* = q^* = 2e$ is the charge of an electron, $\vec{A}$ is the magnetic vector potential and $\vec{B} = \nabla X\vec{A}$ is the magnetic field[13,29].

If $\psi = 0$, equation(3.1.2) reduces to the free energy of the normal state; $F_n + \frac{|H|^2}{8\pi}$.

Let us now consider the three terms that describe the property of superconductivity. In the absence of magnetic fields and neglecting gradient terms, we have

$$F_s - F_n = \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 \tag{3.1.3}$$

Equation(3.1.2), is the expression of free-energy expansion which depends on two cases whether $\alpha$ is positive or negative. If $\alpha$ is positive, the minimum free energy occurs at $|\psi|^2 = 0$ which corresponds to the normal state of the superconductor($T > T_c$). On the other hand, if $\alpha$ is negative, the minimum free energy occurs at $|\psi|^2 = -\frac{\alpha}{\beta}$. If the value of $\psi = 0$, equation(3.1.2) becames

$$F_s - F_n = -\frac{|H|^2}{8\pi} \tag{3.1.4}$$

Now, by minimizing the free energy with respect to fluctuations in the order parameter and the vector potential, one arrives at the Ginzburg-Landau equations given by :

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m^*}\Big(-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big)^2\psi = 0 \tag{3.1.5}$$

The current density from the Hamilton's energy of particles is given by;

$$H = \frac{1}{2}m^*v_d^2 = \frac{1}{2m^*}\Big[\vec{p} - \frac{e^*}{c}\vec{A}\Big]^2$$

$$v_d^2 = \frac{1}{m^{*2}}\Big[\vec{p} - \frac{e^*}{c}\vec{A}\Big]^2$$
$$v_d = \frac{1}{m^*}\Big[\vec{p} - \frac{e^*}{c}\vec{A}\Big]$$

where $\vec{p} = -i\hbar\nabla$

$$v_d = \frac{1}{m^*}\Big[-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big]$$
$$\vec{J_s} = e^* n_s v_d$$

where $n_s = \psi(r)^*\psi(r)$

$$\vec{J_s} = \frac{e^*}{m^*}\Big[-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big]\psi(r)^*\psi(r)$$
$$\vec{j_s} = \frac{e^*}{m^*}\Big[\psi^*\Big(-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big)\psi + \psi\Big(-i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big)\psi^*\Big] \tag{3.1.6}$$
$$\vec{j_s} = \frac{e^*}{m^*}\Big[\psi^*\Big(\frac{\hbar}{i}\nabla - \frac{e^*}{c}\vec{A}\Big)\psi + \psi\Big(\frac{\hbar}{i}\nabla - \frac{e^*}{c}\vec{A}\Big)\psi^*\Big] \tag{3.1.7}$$

where $\vec{j_s}$ is supercurrent density.

Equation(3.1.5) determines the order parameter $\psi$ based on the applied magnetic field and equation(3.1.7) yields the superconducting current density. The Ginzburg-Landau equation provides a complete information about the superconducting state $\psi(r)$ that gives the spatial distribution of the Cooper pair density taking into account a possible variation in their concentration, where as $\vec{A}(r)$ describes the local distribution of the magnetic field in the superconductor.

In the absence of external magnetic field (at free surface), there will not be superconducting current(current flow) and the equation for $\psi$ becomes:

$$F_s - F_n = \alpha\psi + \beta|\psi|^2\psi \tag{3.1.8}$$

This equation has a trivial solution $\psi = 0$ and it corresponds to normal state of $T > T_c$. Below superconducting transition temperature($T_c$), equation(3.1.8) is expected to have a non-trivial solution (i.e $\psi \neq 0$) and the equation can be rearranged into:

$$|\psi|^2 = -\frac{\alpha}{\beta} \tag{3.1.9}$$

If the second part of equation(3.1.5) is positive, then there is a non zero solution for $\psi$ and this can be achieved by assuming the temperature dependence of $\alpha$ such that $\alpha(T) = \alpha_0(T - T_c)$ with $\frac{\alpha_0}{\beta} > 0$ and $n_s = \propto (T_c - T)$. For $T > T_c$, the expression $\frac{\alpha(T)}{\beta}$ is positive and the second part of equation(3.1.5) is negative and only $\psi = 0$ solves the Ginzburg-Landau equation. For $T < T_c$, the second part of equation(3.1.5) is positive and there is a non-trivial solution for $\psi$. Thus equation(3.1.9) can be expressed as:

$$|\psi|^2 = \frac{\alpha_0(T_c - T)}{\beta} \tag{3.1.10}$$

$$|\psi| = \Big(\frac{\alpha_0(T_c - T)}{\beta}\Big)^{\frac{1}{2}} \tag{3.1.11}$$

Equation(3.1.11) yields Ginzburg Landau order parameter[13,31].

## 3.2 Calculation of Ginzburg-Landau coherence length

In superconductivity, the superconducting coherence length($\xi$) is the characteristic exponent of the variations of the density pairs of superconducting, which is reduced in a normal surface. The Ginzbrug-Landau coherence length($\xi_{GL}$) is a measure of the distance in the superconducting electron concentration that can not change drastically in a spatially-varying magnetic field. The Ginzbrug-Landau coherence length($\xi_{GL}$) is a temperature-dependent as well as a material dependent quantity. We will now demonstrate how it may be derived from the GL-theory, even with out the presence of a magnetic field[8,13]. In this case the GL Free energy(GL-I) equation becomes;

$$\alpha\psi + \beta|\psi|^3 + \frac{1}{2m^*}\Big(-i\hbar\nabla\Big)^2\psi = 0 \tag{3.2.1}$$

Now, let us consider a wave function that varies only in the z-direction with zero applied magnetic field. In this case, the first GL equation is one dimensional.

i.e,

$$\alpha\psi + \beta|\psi|^3 - \frac{\hbar^2}{2m^*}\frac{d^2\psi}{dx^2} = 0 \qquad (3.2.2)$$

Assuming $\psi$ is real and neglecting the term $\beta|\psi|^3$ in comparison with $\alpha$, equation(3.2.2), becomes:

$$\alpha\psi = \frac{\hbar^2}{2m^*}\frac{d^2\psi}{dx^2} \qquad (3.2.3)$$

For the plane wave function, the solution of equation(3.2.3) is in the form of,

$$\psi(x) = e^{\left(\frac{ix}{\xi_{GL}}\right)} = exp\left(\frac{ix}{\xi_{GL}}\right) \qquad (3.2.4)$$

Substituting the value of plane wave function into equation(3.2.3)(in terms of $(\psi(x))$), we get,

$$\alpha exp\left(\frac{ix}{\xi_{GL}}\right) = \frac{\hbar^2}{2m^*}\frac{d^2}{dx^2}\left[exp\left(\frac{ix}{\xi_{GL}}\right)\right] \qquad (3.2.5)$$

$$\alpha exp\left(\frac{ix}{\xi_{GL}}\right) = \frac{\hbar^2}{2m^*}\left(\frac{i}{\xi_{GL}}\right)^2 exp\left(\frac{ix}{\xi_{GL}}\right) \qquad (3.2.6)$$

$$\frac{\hbar^2}{2m^*}\left(\frac{i^2}{\xi_{GL}^2}\right)\psi = \alpha\psi \qquad (3.2.7)$$

This implies that,

$$\frac{\hbar^2}{2m^*}\left(\frac{1}{\xi_{GL(T)}^2}\right) = \alpha \qquad (3.2.8)$$

Solving for $\xi_{GL}$ at superconducting state that means, where $\alpha$ is negative yields,

$$\xi_{GL(T)} = -\sqrt{\frac{\hbar^2}{2m^*|\alpha|}} = \sqrt{\frac{\hbar^2}{2m^*|\alpha_0(T_c - T)|}} \qquad (3.2.9)$$

where $\alpha = \alpha_0(T - T_c)$, $-\alpha = \alpha_0(T_c - T)$ and $\xi_{GL(0)} = \sqrt{\frac{\hbar^2}{2m^*|\alpha_0|T_c}}$

Equation(3.2.9) yields the GL coherence length[2,13]. Since $\alpha$ depends on temperature as $\alpha \propto (T - T_c)$, the coherence length varies as a function of temperature.

For superconducting state($T < T_c$),

$$\xi_{GL(T)} = \xi_{GL(0)}\Big(1 - \frac{T}{T_c}\Big)^{-\frac{1}{2}}; \tag{3.2.10}$$

and

For normal state($T > T_c$),

$$\xi_{GL(T)} = \xi_{GL(0)}\Big(\frac{T}{T_c} - 1\Big)^{-\frac{1}{2}}; \tag{3.2.11}$$

The length $\xi_{GL(0)}$ is known as the zero temperature GL coherence length. Of course, the GL theory is not valid at T = $T_c$ and the logic of the name comes from the fact that $\xi_{GL(0)}$ is the zero temperature extrapolation of the GL result[2,13]. The physical importance of $\xi_{GL(0)}$ is that, it sets the basic length scale of the healing process[2].

### 3.2.1 The range of validity for the Ginzburg-Landau coherence length

The relation between the zero temperature GL coherence length($\xi_{GL(0)}$) and the BCS coherence length($\xi_0$) is obtained by Gorkovos formulation of the BCS theory for conventional low $T_c$ superconductors.

Let us now consider two cases:

a). In the clean limit when the electron mean free path($l_{el}$) is much larger than the size of the Cooper pair($l_{el} >> \xi_0$), the Ginzburg-Landau theory is valid if $\xi_{GL}(T) >> \xi_0$. Since $\xi_{GL(T)} \sim \xi_0(1 - \frac{T}{T_c})^{\frac{-1}{2}}$

$$\xi_{GL(0)} = 0.74\xi_0 \tag{3.2.12}$$

b). In the dirty limit($\xi_0 >> l_{el}$), the validity interval for the Ginzburg-Landau theory is much wider than that for clean superconductors. For dirty superconductors, the characteristic scale of inhomogeneity is the mean free path. This means that, the Ginzburg-Landau theory can be applied if $\xi_0 >> l_{el}$. Since $\xi_{GL(T)} \sim (\xi_0 l_{el})^{\frac{1}{2}}(1 - \frac{T}{T_c})^{\frac{-1}{2}}$ the condition $\xi_0 >> l_{el}$ is reduced to $(\xi_0 l_{el}) >> (1 - \frac{T}{T_c})$.

i.e.

$$\xi_{GL(0)} = 0.85\sqrt{\xi_0 l_{el}} \tag{3.2.13}$$

Now, substituting the values of $\xi_{GL(0)}$ for pure and dirty materials, the expression of GL coherence length for clean(pure) and dirty materials respectively become:

$$\xi_{GL(T)} = 0.74\xi_0\left(1 - \frac{T}{T_c}\right)^{-\frac{1}{2}} \tag{3.2.14}$$

and

$$\xi_{GL(T)} = 0.855\sqrt{\xi_0 l_{el}}\left(1 - \frac{T}{T_c}\right)^{-\frac{1}{2}} \tag{3.2.15}$$

Clearly the overall length scale for healing is the size of a Cooper pair. Of course, the divergence of $\xi_{GL(T)}$ as T $\rightarrow T_c$ means that the slowly varying approximation of the GL theory is always valid near $T_c$ [2].

## 3.3 Calculation of Ginzburg-Landau penetration depth

The surface current flows in a very thin layer of thickness($\lambda_{GL}$) which is called the Ginzburg-Landau penetration depth[2]. The temperature and magnetic field dependence of the penetration depth appear quite naturally in Ginzburg-Landau(GL) theory. Like the London model, the GL model is independent of the underlying mechanism for superconductivity. Ginzburg-Landau theory is strictly valid only in superconducting phase boundary and is thus not generally applicable at low temperatures[2]. In the Ginzburg-Landau theory, a complex order parameter($\psi$) is a function of temperature, magnetic field and the spatial coordinates[13,29]. The total free energy per unit volume of the superconducting state in the presence of a magnetic field is minimizing this expression with respect to the first GL equation and with respect to $\vec{A}$ the current density(GL-II) equation;

$$F_{GL} = \frac{1}{2m^*}| - i\hbar\nabla - \frac{e^*}{c}\vec{A}|^2\psi + \alpha\psi + \beta|\psi|^2\psi = 0 \tag{3.3.1}$$

where $m^* = 2m$ and $e^* = 2e$.

$$|\psi| = |\psi_0| = \sqrt{\frac{-\alpha}{\beta}} \tag{3.3.2}$$

Using equation(3.3.1), we get the expression for current density, as follows

$$\vec{J_s} = -\frac{e^*\hbar i}{m^*}\left[\psi^*\nabla\psi + \psi\nabla\psi^*\right] - \frac{e^{*2}}{m^*c}\vec{A}|\psi|^2 \tag{3.3.3}$$

since $|\psi|^2 = n_s = |\psi_0|^2$

$$\vec{J_s} = -\frac{e\hbar i}{m^*}\left[\psi^*\nabla\psi + \psi\nabla\psi^*\right] - \frac{e^{*2}}{m^*c}\vec{A}|\psi|^2 \tag{3.3.4}$$

Neglecting $\nabla\psi$ and $\nabla\psi^*$ equation(3.3.4), becomes;

$$\vec{J_s} = -\frac{e^{*2}}{m^*c}|\psi|^2\vec{A} \tag{3.3.5}$$

Using Maxwell's equation:

$$\nabla X\vec{B} = \frac{4\pi}{c}\vec{J_s} \tag{3.3.6}$$

Taking the curl on both sides of equation(3.3.6), we get

$$\nabla X\nabla X\vec{B} = \frac{4\pi}{c}\left(\nabla X\vec{J_s}\right) \tag{3.3.7}$$

$$\nabla\left(\nabla.\vec{B}\right) - \nabla^2\vec{B} = \frac{4\pi}{c}\left(\nabla X\vec{J_s}\right) \tag{3.3.8}$$

where $\nabla.\vec{B} = 0$, $\nabla X\vec{J_s} = -\frac{e^{*2}}{m^{*}c}|\psi|^2\nabla X\vec{A}$ and $\vec{B} = \nabla X\vec{A}$

From equation(3.3.6) and equation(3.3.8), we get

$$\nabla X\vec{J_s} = -\frac{e^{*2}}{m^{*}c}|\psi|^2\nabla X\vec{A} = -\frac{4e^2}{m^{*}c}|\psi|^2\vec{B} \tag{3.3.9}$$

$$\nabla^2\vec{B} = -\frac{4\pi}{c}\left(\nabla X\vec{J_s}\right) = -\frac{16\pi e^2}{m^{*}c}n_s\vec{B} \tag{3.3.10}$$

Since $|\psi|^2 = n_s = \frac{-\alpha}{\beta}$ and $\lambda^2_{GL(T)} = \frac{m^{*}c^2}{16\pi e^2 n_s}$, we get

$$\nabla^2\vec{B} = -\frac{4\pi}{c}\left(\nabla XJ_s\right) = \frac{\vec{B}}{\lambda^2_{GL(T)}} \tag{3.3.11}$$

Therefore,

$$\lambda^2_{GL(T)} = \frac{m^{*}c^2}{16\pi e^2 n_s} = \frac{m^{*}c^2\beta}{16\pi e^2\alpha} \tag{3.3.12}$$

$$\lambda_{GL(T)} = \sqrt{\frac{m^{*}c^2\beta}{16\pi e^2|\alpha|}} = \sqrt{\frac{m^{*}c^2}{16\pi e^2 n_s}} = \sqrt{\frac{mc^2}{8\pi e^2 n_s}} \tag{3.3.13}$$

where $m^{*} = 2m$ and $n_s = -\frac{\alpha}{\beta} = \frac{\alpha_0(T_c - T)}{\beta}$.

Therefore,

$$\lambda_{GL(T)} = \sqrt{\frac{mc^2\beta}{8\pi e^2\alpha_0(T_c - T)}} \tag{3.3.14}$$

For

$$\lambda_{L(0)} = \sqrt{\frac{mc^2\beta}{8\pi e^2\alpha_0 T_c}} \tag{3.3.15}$$

from equation(3.3.14)[27] it follows that, the Ginzburg-Landua penetration depth($\lambda_{GL(T)}$) varies as a function of temperature as:

$$\lambda_{GL(T)} \propto [(1 - (\frac{T}{T_c})]^{-\frac{1}{2}} \tag{3.3.16}$$

$$\lambda_{GL(T)} = \lambda_{L(0)}\left[1 - \left(\frac{T}{T_c}\right)^4\right]^{-\frac{1}{2}} \tag{3.3.17}$$

where $\lambda_{L(0)}$ is the London penetration at absolute zero temperature[27].

### 3.3.1 The range of validity of Ginzburg-Landau penetration depth

In the clean limit when the electron mean free path is much larger than the size of the Cooper pair, ($l_{el} >> \xi_0$), the Ginzburg-Landau theory is valid if $\lambda_{GL(T)} >> \xi_0$. The superconductor is of London type.

Since

$$\lambda_{GL(T)} \propto \left[\left(1 - \left(\frac{T}{T_c}\right)\right]^{-\frac{1}{2}} \tag{3.3.18}$$

$$\lambda_{GL(T)} = \frac{\lambda_{L(0)}}{\sqrt{2}}\left[\left(1 - \left(\frac{T}{T_c}\right)\right]^{-\frac{1}{2}} \tag{3.3.19}$$

In the dirty limit ($l_{el} << \xi_0$) or ($\xi_0 >> l_{el}$), the validity interval for the Ginzburg-Landau theory is much wider than that for clean superconductors. For dirty superconductors, the characteristic scale of inhomogeneity is the mean free path($l_{el}$). This means that, the Ginzburg-Landau theory can be applied if $\lambda_{GL(T)} >> l_{el}$[2].

$$\lambda_{GL(T)} = \frac{\lambda_{L(0)}}{\sqrt{\frac{\xi_0}{1.33 l_{el}}}}\left(1 - \frac{T}{T_c}\right)^{-\frac{1}{2}} \tag{3.3.20}$$

## 3.4 Flux quantization of a superconducting ring

Flux quantization inside the superconducting rings of current provides evidence for the existence of paired electrons as predicted by Cooper. It is found that, flux is quantized in units of $\phi_0 = \frac{hc}{2e} = \frac{hc}{e^*}$[6]. This also implies that, the electric current vanishes[8]. The current is expressible in terms of the superconducting order parameter $\Psi = \psi_0$. Flux quantization can be derived by considering a superconducting ring with a thickness much larger than the London penetration depth. The expression of the superconducting current density with, $|\psi^2| = n_s$, the flow of particles characterized by a wave function(order parameter) $\psi$ is described by a current density vector.

$$|\psi^2| = \psi^*\psi = n_s \tag{3.4.1}$$

where $\psi = n_s^{\frac{1}{2}} exp(i\theta)$ and $\psi^* = n_s^{\frac{1}{2}} exp(-i\theta)$

The velocity of particles is obtained from Hamilton's equation as follows;

$$v = \frac{1}{m^*}\Big(p - \frac{e^*}{c}\vec{A}\Big) = \frac{1}{m^*}\Big( - i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big) \tag{3.4.2}$$

$$\psi^* v\psi = \frac{n}{m^*}\Big(p - \frac{e^*}{c}\vec{A}\Big) = \frac{|\psi|^2}{m^*}\Big( - i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big) \tag{3.4.3}$$

$$\vec{J} = e^*\psi^* v\psi = \frac{e^*}{m^*}|\psi^2|(\hbar\nabla\theta - \frac{e^*}{c}A) \tag{3.4.4}$$

Inside a superconductors, J = 0. Hence equation(3.4.4), becomes

$$\hbar\nabla\theta = \frac{e^*}{c}\vec{A} \tag{3.4.5}$$

Integrating equation(3.4.5) around a closed path of the superconducting ring, we get

$$\hbar \oint \nabla\theta.d\vec{l} = \frac{e^*}{c} \oint \vec{A}.d\vec{l} \tag{3.4.6}$$

But due to the single-valuedness of the wave function,

$$\oint \nabla\theta.d\vec{l} = \theta_2 - \theta_1 = 2\pi n \tag{3.4.7}$$

where n is an integer and $\theta_2 - \theta_1 = 2\pi n$[13].

The total flux contained inside a superconducting ring is evaluated by changing the right hand side of equation(3.4.6), into surface integral, that is:

$$\frac{e^*}{c} \oint \vec{A}.d\vec{l} = \frac{e^*}{c} \int\int (\nabla X\vec{A}).d\vec{s} \tag{3.4.8}$$

From the fact that $\nabla X\vec{A} = \vec{B}$ and

$$\int\int \vec{B}.d\vec{s} = \Phi = 2\pi n\hbar \tag{3.4.9}$$

we get;

$$\frac{e^*}{c}\int\int \vec{B}.d\vec{s} = \frac{e^*}{c}\Phi \tag{3.4.10}$$

Here s is the surface spanning the hole and $\Phi$ is the flux through the hole. Combining the results of equations(3.4.9) and (3.4.10), we get:

$$2n\pi\hbar = \frac{e^*}{c}\Phi \tag{3.4.11}$$

Rearranging equation(3.4.11) and substituting the value of $e^*$, we have

$$\Phi = 2\pi\hbar\frac{c}{2e}n \tag{3.4.12}$$

Since $2\pi\hbar = h$, eq.(3.4.12) can be written as:

$$\Phi = n\frac{hc}{2e} \tag{3.4.13}$$

$$\Rightarrow \Phi = n\phi_0 \tag{3.4.14}$$

where $\phi_0 = \frac{hc}{2e}$ is a flux quantum. If the magnetic flux enclosed in the hole is quantized then, the current circulating around the hole cannot be of an arbitrary magnitude and cannot change continuously and is also quantized[13,29].

## 3.5 Calculation of the upper critical magnetic field using Ginzburg-Landau theory

The upper critical magnetic field(UCMF) is the magnetic field which completely suppresses superconductivity in type-II superconductors. More properly, the UCMF is a function of temperature(and pressure) and if not specified absolute zero and standard pressure are implied. Supercondcting region nucleates spontaneously within a normal conductor when the applied magnetic field is decreased below a value denoted by $H_{c2}$[8]. At the onset of superconductivity, $|\psi|$ is small and we linearize the GL equations as follows;

$$H\psi = \frac{1}{2m^*}\Big( - i\hbar\nabla - \frac{e^*}{c}\vec{A}\Big)^2\psi = -\alpha\psi = E\psi \tag{3.5.1}$$

Since $m^* = 2m$, $e^* = 2e$, $\nabla = \frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}$ and $E = E_x + E_y + E_z$.

The upper critical magnetic field($H_{c2}$) can be calculated by linearizing equation(3.5.1) and substituting the value of $\nabla$ as:

$$\frac{1}{2m^*}\Big[ - i\hbar\Big(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}\Big) - \frac{e^*}{c}\vec{A}\Big]^2\psi = -\alpha\psi \tag{3.5.2}$$

The magnetic field in a superconducting region at the onset of superconductivity is just the applied field, so that $\vec{A} = \vec{B}(0, x, 0) = \vec{B}x$ and equation(3.5.2) becomes

$$\frac{1}{2m^*}\Big[ - i\hbar\Big(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}\Big) - \frac{e^*}{c}\vec{B}x\Big]^2\psi = -\alpha\psi \tag{3.5.3}$$

where $\vec{P} = -i\hbar\nabla = -i\hbar\Big(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}\Big)$ and $\vec{P}\psi = \hbar k\psi = \hbar\Big(k_x + k_y + k_z\Big)\psi$ where the eigne value of momentum crystal is $\hbar k$.

Therefore,

$$\frac{1}{2m^*}\Big[ - i\hbar\Big(\frac{\partial}{\partial x} + k_y + k_z\Big) - \frac{e^*}{c}\vec{B}x\Big]^2\psi = -\alpha\psi \tag{3.5.4}$$

Since the expression of the Hamiltonian's energy given in equation(3.5.4)) does not depend on coordinates(y and z) the corresponding momentum components($k_y$, $k_z$) are conserved.

$$E_x\psi = -\alpha\psi - \frac{\hbar^2}{2m^*}\Big(k_y^2 + k_z^2\Big)\psi \tag{3.5.5}$$

$$E_x\psi = -\Big[\frac{1}{2m^*}\Big[ - i\hbar\Big(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\Big) - \frac{e^*}{c}\vec{B}x\Big]^2\psi\Big] - \frac{\hbar^2}{2m^*}\Big(k_y^2 + k_z^2\Big)\psi \tag{3.5.6}$$

$$E_x\psi = \frac{\hbar^2}{2m^*}\Big(\frac{\partial^2}{\partial x^2}\Big)\psi + \frac{m^*}{2}\Big(\frac{e^*\vec{B}x}{m^*c}\Big)^2\psi \tag{3.5.7}$$

The largest value of the magnetic field($\vec{B}$) for which the solution of equation(3.5.7) of the lowest eigenvalue is given by

$$E_n = \Big(n + \frac{1}{2}\Big)\hbar\omega_c = \Big(n + \frac{1}{2}\Big)\frac{\hbar e^* \vec{B}_{max}}{m^* c} = -\alpha - \frac{\hbar^2 {k_z}^2}{2m^*} \qquad (3.5.8)$$

Let us take the smallest eigenvalues n=0 and $K_z = 0$ corresponding to the highest field in which superconductivity can nucleate in the interior of a bulk sample which occurs with the upper critical magnetic field in the coefficients change of sign. From equation(3.5.8), we have;

$$\frac{1}{2}\hbar\omega_c = \frac{\hbar e^* \vec{B}_{max}}{2m^* c} = -\alpha \qquad (3.5.9)$$

where $\omega_c$ is the cyclotron frequency and is given by

$$\omega_c = \frac{e^* \vec{B}_{max}}{m^* c} = -\frac{2\alpha}{\hbar} \qquad (3.5.10)$$

since $\vec{B}_{max} = H_{c2}$, solving for $H_{c2}$, we get:

$$H_{c2} = -\frac{2m^* c}{\hbar e^*}|\alpha| \qquad (3.5.11)$$

From the relation $\alpha = \alpha_0(T - T_c)$ that means $-\alpha = \alpha_0(T_c - T) = \frac{\hbar^2}{2m^*}\Big(\frac{1}{\xi^2_{GL(T)}}\Big)$, $\xi_{GL(T)} = \xi_{GL(0)}\Big[\Big(1 - \frac{T}{T_c}\Big)\Big]^{-\frac{1}{2}}$ and $\xi^2_{GL(T)} = \frac{\xi^2_{GL(0)}}{\Big(1-\frac{T}{T_c}\Big)}$.

we obtain the expression of the temperature dependent upper critical magnetic field($H_{c2}$),

$$H_{c2} = \Big(\frac{2m^* c}{\hbar e^*}\Big)\Big(\frac{\hbar^2}{2m^* \xi^2_{GL(0)}}\Big)\Big[(1 - \frac{T}{T_c})\Big]$$

$$H_{c2} = \frac{\hbar c}{e^* \xi^2_{GL(0)}}\Big(1 - \frac{T}{T_c}\Big)$$

$$H_{c2} = \frac{\phi_0}{2\pi\xi^2_{GL(T)}} = \frac{\phi_0}{2\pi\xi^2_{GL(0)}}\Big(1 - \frac{T}{T_c}\Big) \qquad (3.5.12)$$

where $\hbar = \frac{h}{2\pi}$ or $2\pi\hbar = h$ and $\phi_0 = \frac{hc}{2e} = \frac{2\pi\hbar c}{e^*}$

$$\frac{\phi_0}{2\pi} = \frac{hc}{2\pi e^*} = \frac{\hbar c}{e^*}$$

### 3.5.1 Anisotropic mass tensor model

Now, consider anisotropy in mass, by introducing the effective mass tensor to the kinetic energy term of the GL equation(3.1.5)

i.e

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m^*}(-i\hbar\nabla - \frac{e^*}{c}A)^2\psi = 0 \qquad (3.5.13)$$

where $m^*$ is an effective mass tensor which is given by,

$$m^* = \begin{bmatrix} m_x & 0 & 0 \\ 0 & m_y & 0 \\ 0 & 0 & m_z \end{bmatrix}$$

Since the coherence length $\xi_{GL(0)}$ depends on the effective mass as $\xi_{GL(T)} \propto \frac{1}{\sqrt{m}}$, the resulting equation is formally identical with the Schrödinger equation of a particle with charge $e^* = 2e$, an isotropic mass tensor $m^* = 2m$ in a uniform magnetic field $H$ and the energy levels that have the harmonic oscillator are given by;

$$-\alpha = \left(n + \frac{1}{2}\right)\hbar\omega_c(\theta) \qquad (3.5.14)$$

Let us consider Newton's law of motion under the influence of lorentz force

i.e.

$$F_l = m^*.\dot{v} = \frac{e^*}{c}vXH \qquad (3.5.15)$$

where $v$ is the velocity.

The upper critical magnetic field can be expressed by using cyclotron frequency with the lowest free energy;

$$-\alpha = \frac{1}{2}\hbar\omega_{c(\theta)}$$

The solution of upper critical magnetic field by applying elliptical orbits traversed with cyclotron frequency is given by,

$$\omega_{c(\theta)} = \frac{|e^*|B_{max}}{c}\Big(\frac{\sin^2\theta}{m_x m_z} + \frac{\cos^2\theta}{m_x}\Big)^{\frac{1}{2}} \tag{3.5.16}$$

The solution of the lowest free energy corresponds to $n = 0$ and by using equation(3.5.16), we gat

$$\frac{1}{2}\hbar\omega_{c(\theta)} = -\alpha = \frac{1}{2}\hbar\Big[\frac{|e^*|B_{max}}{c}\Big(\frac{\sin^2\theta}{m_x m_z} + \frac{\cos^2\theta}{m_x}\Big)^{\frac{1}{2}}\Big]$$

where $\theta$ is the angle of the magnetic field that makes with the z-axis $-\alpha = -\alpha_0(T - T_c) = \alpha_0(T_c - T)$.

$$H_{c2} = \frac{2c\alpha_0\Big(T_c - T\Big)}{\hbar e^*\Big[\frac{sin^2\theta}{m_x m_z} + \frac{cos^2\theta}{m_x}\Big]^{\frac{1}{2}}} \tag{3.5.17}$$

From the general expression of coherence length equation(3.5.12) we have,

$$\xi_x = \Big[\frac{\hbar^2}{2m_x\alpha_0(T_c - T)}\Big]^{\frac{1}{2}} \tag{3.5.18}$$

$$\xi_z = \Big[\frac{\hbar^2}{2m_z\alpha_0(T_c - T)}\Big]^{\frac{1}{2}} \tag{3.5.19}$$

Using the expression for the flux quantization, $\phi_0 = \frac{hc}{|e^*|}$ and equation(3.5.12), $H_{c2}$ can be expressed as,

$$H_{c2} = \frac{\phi_0}{2\pi\Big[\frac{sin^2\theta}{\xi_x^2\xi_z^2} + \frac{cos^2\theta}{\xi_x^4}\Big]^{\frac{1}{2}}} \tag{3.5.20}$$

For fields parallel and perpendicular to the symmetry plane we can write equation(3.5.20) as:

$$H_{c2}|| = \frac{\phi_0}{2\pi\xi_z\xi_z} \tag{3.5.21}$$

and

$$H_{c2}\perp = \frac{\phi_0}{2\pi\xi_x^2} \tag{3.5.22}$$

Equations(3.5.21) and (3.5.22) are the mathematical expressions of the upper critical magnetic field($H_{c2}$) for fields parallel and perpendicular to the symmetry axis[8].

# Chapter 4

# Results and discussion

In this chapter, we focus on the results of the upper critical magnetic field of superconducting $HoMo_6Se_8$ by using the GL equation.

i.e,

$$-\frac{\hbar^2}{2m^*}\Big[\nabla - \frac{ie^*}{\hbar c}\vec{A}\Big]^2\psi + \alpha\psi + \beta|\psi|^2\psi = 0$$

First, we determined the temperature dependence of GL coherence length($\xi_{GL}$) which is expressed as:

$$\xi_{GL(T)} = \xi_{GL(0)}\Big(1 - \frac{T}{T_c}\Big)^{-\frac{1}{2}}$$

where $\xi_{GL(0)}$ is the zero temperature GL coherence length and $T_c$ is the transition temperature. In figure(4.1), we plot the graph that shows the relationship between the GL coherence length and temperature(T).

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$$\xi_{GL(T)} = \xi_{GL(0)}\left(1 - \frac{T}{T_c}\right)^{-\frac{1}{2}}$$

where $\xi_{GL(0)}$ is the zero temperature GL coherence length and $T_c$ is the transition temperature. In figure(4.1), we plot the graph that shows the relationship between the GL coherence length and temperature(T).

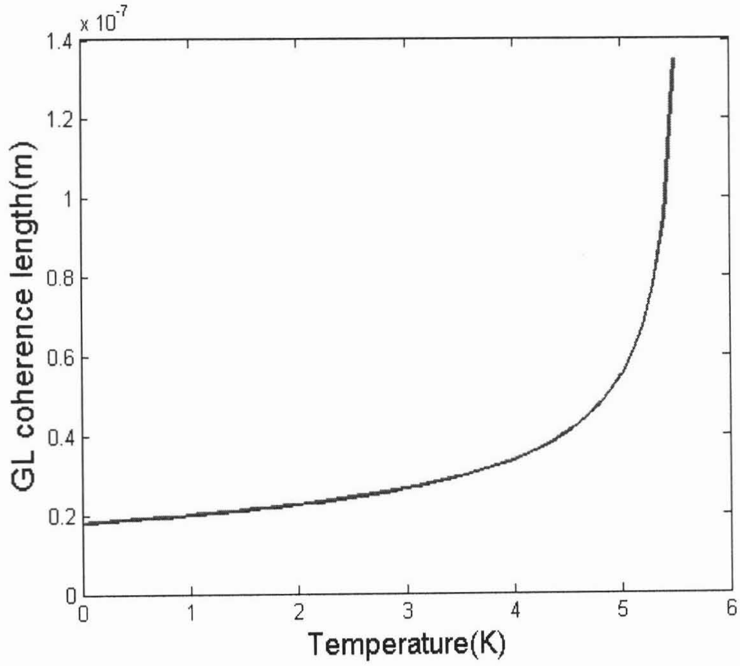


Figure 4.1: GL coherence length versus temperature(T)

As can be see from figure(4.1), the GL coherence length increases with temperature and diverge as $T \longrightarrow T_c$. $\xi_{GL(0)}$ has the same value with the BCS coherence length i.e $\left(\xi_{GL(0)} = \xi_0\right)$[2].

We have already calculated the GL penetration depth in chapter three and obtained to be:

$$\lambda_{GL(T)} = \lambda_{L(0)} \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right]^{-\frac{1}{2}}$$

The relationship between the GL penetration depth and temperature(T) is shown in figure(4.2). From figure(4.2), we observe the increase of the GL penetration depth with temperature(T).

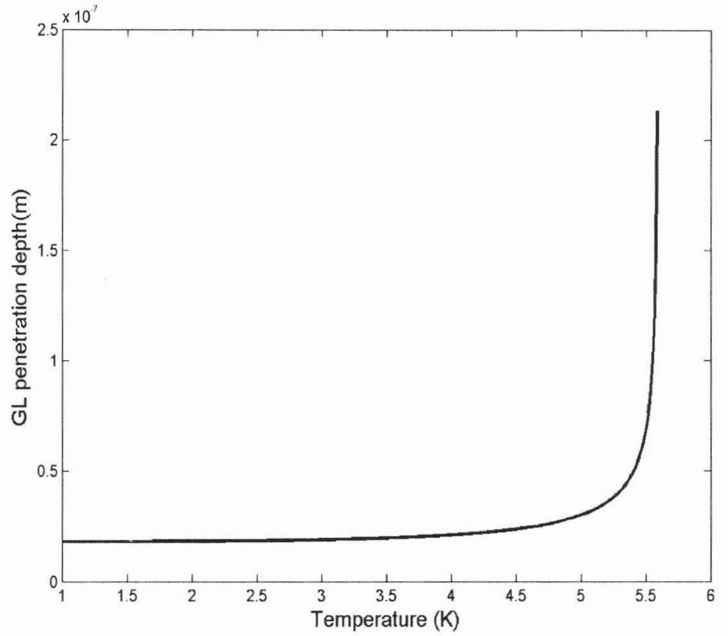


Figure 4.2: GL penetration depth versus temperature(T).

Generally, we observe that, the penetration depth rises asymptotically as the temperature approaches $T_c$. Thus, the penetration of field increase as the temperature approaches to $T_c$.

We finally determined the expression for upper critical magnetic field of superconducting $HoMo_6Se_8$ using the GL equation:

$$H_{c2} = \frac{\phi_0}{2\pi\xi^2_{GL(0)}}\left(1 - \frac{T}{T_c}\right)$$

where all the parameters have their usual meaning.

Considering anisotropic mass tensor, the expression for the upper critical field of superconducting $HoMo_6Se_8$ is obtained. In this case, anisotropic mass is combined with the kinetic energy term of the GL equation and the equation for the upper critical field becomes:

$$Hc_{c2} = \frac{\phi_{(0)}}{2\pi\left(\frac{\sin^2\theta}{\xi_x^2\xi_z^2} + \frac{\cos^2\theta}{\xi_x^4}\right)^{1/2}}$$

For fields parallel and perpendicular to the symmetry of the above equation reduces to :

$$H_{c2} \parallel = \frac{\phi_0}{2\pi\xi_x\xi_z}$$

and

$$H_{c2} \perp = \frac{\phi_0}{2\pi\xi_x^2}$$

By taking experimental data and upper critical magnetic fields for parallel and perpendicular, we plot the upper critical fields at parallel and perpendicular to the symmetry axis as shown in figure(4.3)[17,18].

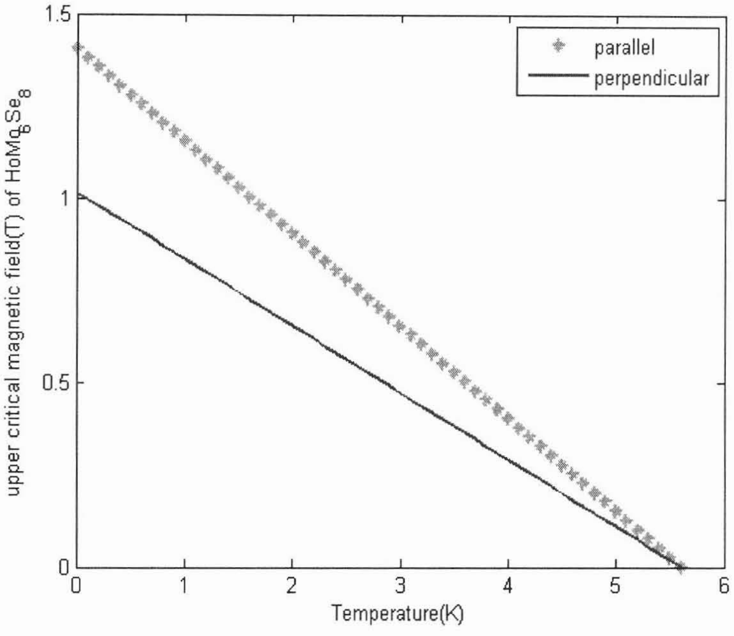


Figure 4.3: upper critical magnetic field parallel and perpendicular to the symmetry axis versus temperature(T)

From figure(4.3), we can see that, the upper critical magnetic field decreases as temperature increases and reaches to zero at the critical temperature of superconducting $HoMo_6Se_8$, which agrees with the experimental observations[17]. As can be seen from figure(4.3), the upper critical magnetic field($H_{c2}$) parallel and perpendicular to the symmetry axis of superconducting $HoMo_6Se_8$ is inversely proportional to the GL coherence length and fits.

# Chapter 5

# Conclusion

In the first chapter of this work, we discussed the general introduction of superconductors, types of superconductors and property of superconductors.

In chapter two we reviewed literature that are related to our research work.

In the third chapter, the expression of upper critical magnetic field($H_{c2}$) is obtained mathematically by using the basic GL theory. At the same time, the expressions for GL coherence length, GL penetration depth and flux quantization which are necessary to obtain the expression of $H_{c2}$ are determined.

The fourth chapter deals with the results which are obtained in the third chapter and figures are plotted by using MATLAB scripts. From the figures plotted in this chapter, it can be concluded that, the upper critical magnetic field of superconducting $HoMo_6Se_8$ is inversely related to temperature which is in agreement with experimental observations[17].

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# Appendix

From Maxwell's equation, $\nabla X E = -\frac{\partial B}{\partial t}$, when the magnetic field is frozen, the field is expelled from the interior of the superconductors, otherwise superconductivity will be destroyed by a critical magnetic field($H_c$), such that

$$f_s = F_n - \frac{H_c^2}{8\pi} \Longrightarrow F_s + \frac{H_c^2}{8\pi} = f_n \tag{5.1.1}$$

$$f_s - F_n = \frac{H_c^2}{8\pi} \tag{5.1.2}$$

where $f_{s,n(T)}$ are the densities of free energy in the superconducting state at zero magnetic field and the density of the free energy in the normal state. By the Gorter-Casimir model[27], we have the following expression for free energy of the electron

$$f(x,T) = \sqrt{x} f_n(T) + (1-x) f_s(t) \tag{5.1.3}$$

where $f_n(T) = \frac{-\gamma}{2} T^2$ and $f_s(T) = -\beta$

$$\frac{\partial f(x,T)}{\partial x} = \frac{\partial}{\partial x}\Big[(\sqrt{x} f_n(T)) + (1-x) f_s(T)\Big] = 0 \tag{5.1.4}$$

$$f_n \frac{\partial \sqrt{x}}{\partial x} + f_s(T) \frac{\partial (1-x)}{\partial x} = 0 \tag{5.1.5}$$

$$\frac{f_n(T)}{2\sqrt{x}} - f_s(T) = 0 \tag{5.1.6}$$

$$\frac{f_n(T)}{2\sqrt{x}} = f_s(T) \tag{5.1.7}$$

$$f_n(T) = 2\sqrt{x}f_s(T) \tag{5.1.8}$$

$$f_n^2(T) = 4xf_s^2(T) \tag{5.1.9}$$

$$x = \frac{f_n^2(T)}{4f_s^2(T)} \tag{5.1.10}$$

Now substitute the value of $f_n(T)$ and $f_s(T)$, we get

$$x = \frac{\gamma^2}{16\beta^2T^4} \tag{5.1.11}$$

We see that at x = 1 at the critical temperature $T_c$, we get

$$T_c^2 = \frac{4\beta}{\gamma} \tag{5.1.12}$$

and

$$\gamma = \frac{4\beta}{T_c^2}$$

Therefore, by using equation(5.1.12), we get

$$x = \frac{16\beta^2T^4}{16\beta^2T_c^4} \Longrightarrow \left(\frac{T}{T_c}\right)^4 \tag{5.1.13}$$

Substituting this into Gorter Casmir mode, the corresponding value of the free energy is obtained to be

$$f_s(T) = -\beta\left[1 + \left(\frac{T}{T_c}\right)^4\right] \tag{5.1.14}$$

From equation(5.1.1), we have

$$f_n(T) = -\frac{\gamma T^2}{2} = 2\beta\left(\frac{T}{T_c}\right)^2 \tag{5.1.15}$$

also by using equation(5.1.1), we get

$$-\beta\left[1 + \left(\frac{T}{T_c}\right)^4\right] + \frac{H_c^2}{8\pi} = -2\beta\left(\frac{T}{T_c}\right)^2 \tag{5.1.16}$$

From equation(5.1.2), we have

$$H_c^2(T) = 8\pi\Big[f_n(T) - f_s(T)\Big] \tag{5.1.17}$$

$$H_c^2(T) = 8\pi\left[\beta\left(1 + \left(\frac{T}{T_c}\right)^4\right) - 2\beta\left(\frac{T}{T_c}\right)\right]^2 \tag{5.1.18}$$

$$H_c^2(T) = 8\pi\beta\left[1 - 2\left(\frac{T}{T_c}\right)^2 + \left(\frac{T}{T_c}\right)^4\right] \tag{5.1.19}$$

$$H_c^2(T) = 8\pi\beta\left[1 - \left(\frac{T}{T_c}\right)^2\right]^2 \tag{5.1.20}$$

$$H_c(T) = \left[8\pi\beta\left(1 - \left(\frac{T}{T_c}\right)^2\right)^2\right]^{\frac{1}{2}} \tag{5.1.21}$$

where $H_c(0) = \sqrt{8\pi\beta}$

Therefore,

$$H_c(T) = H_{c(0)}\left[1 - \left(\frac{T}{T_c}\right)^2\right] \tag{5.1.22}$$

Equation(5.1.22) yields the expression of thermodynamic critical field($H_c(T)$)[27].

# Declaration

I, hereby declare that this thesis is my original work and has not been presented for a degree in any other university, and that all sources of materials have been duly acknowledged.

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Date: 14-10-2005 EC

This thesis has been submitted for the examination with my approval as a University advisor.

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