Penetration depth studies of unconventional superconductors

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2020

Sujith, K. S. (2020). Penetration depth studies of unconventional superconductors.
Doctoral thesis, Nanyang Technological University, Singapore.
<https://hdl.handle.net/10356/150687>

<https://hdl.handle.net/10356/150687>

<https://doi.org/10.32657/10356/150687>

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**PENETRATION DEPTH STUDIES OF UNCONVENTIONAL
SUPERCONDUCTORS**

KUNNINIYIL SUDHEESH SUJITH

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2020

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Abstract

A tunnel diode oscillator based system is used to measure the London penetration depth of unconventional superconductors. With noise levels less than 4 parts in 10^9 , high-resolution measurements of penetration depth can be made. Sample temperatures as low as 350 mK can be achieved using our helium-3 cryostat based setup. Information about the superfluid density and the superconducting order parameter, including the symmetry of the superconducting gap can be obtained from this data.

In this thesis, I present penetration depth data on single crystals of PdTe_2 , FeS , pure and doped CeCoIn_5 , and MoTe_2 intercalated with ionic liquid. For the topological superconductor candidate PdTe_2 , we find that the bulk is fully gapped with an isotropic s -wave like gap with moderate coupling. For FeS , our data indicates multi-gap superconductivity with the superfluid density preferring a $s + d$ gap model. The heavy fermion superconductor CeCoIn_5 exhibit power-law behaviour with exponent $n = 1.5$ at low temperatures, which is indicative of a d -wave gap with line nodes as expected. Doping with Sn or Cd suppresses superconductivity and the power law behaviour changes to $n > 2$. This, along with the superfluid density suggest an evolution of superconducting gap upon doping. Our measurements on ionic liquid intercalated MoTe_2 , which is a organic-inorganic hybrid superconductor, show power-law dependence hinting the presence of line nodes in the order parameter. A dirty d -wave model fits the data well at low temperatures.

Acknowledgements

First and foremost, I would like to thank my supervisor, Prof. Elbert Chia, for his support and guidance. His experience in the field and discussions helped me in my experiments and data analysis. I am grateful to him for giving me enough time to learn, perform experiments and analysis.

I would like to thank sample growers – Prof. Takao Sasagawa, Prof. Shiyun Li, Dr. Xiaofeng Lai, Prof. Tuson Park, and Prof. Shuyun Zhou for providing me with samples for the study. I would also like to thank Prof. Christos Panagopoulos and Prof. Wang Qijie for serving in my thesis advisory committee.

I would like to thank Dr. Sourav Mitra for teaching me the techniques and skills required for the experiments and data analysis. I would like to thank Dr. Xinbo Wang for his help in obtaining FeS samples and mounting them inside a glove box. I would also like to thank all the members of my group – Dr. Daming Zhao, Chang Qing, Dr. Cheng Liang, and Jiayun Liu for their help whenever I needed.

I would like to thank Dr. Alexander Petrovic for useful discussions and help in SQUID measurements. I would also like to express my gratitude to Li Yuanqing for his help in SQUID measurements and matters related to cryogenics.

I would like to thank all my friends for their company and support that helped me enjoy these years. I would like to express my special thanks to my girlfriend, Jiji, for all the love and support.

I would like to express my gratitude to my parents, whose love and sacrifices have made me what I am today. I would also like to thank my brother and extended family for their continuous support and love.

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Chapter 1

Introduction and Background Knowledge

1.1 Introduction

Magnetic penetration depth is the consequence of one of the unique properties of superconducting state – the Meissner effect. Probing the penetration depth in the superconducting state can give information about the magnetic susceptibility, the superfluid density and the properties of the superconducting gap. This gives insight into the pairing mechanism and thus is an important tool in understanding the physics of superconductors. Even though the mechanism of superconductivity of some superconductors are understood by the Bardeen-Cooper-Schrieffer (BCS) theory, there are a group of superconductors called the unconventional superconductors whose microscopic mechanism behind their superconducting state is not well understood. Most of the type-II superconductors (such as the high temperature superconductors) with high potential for practical applications fall into this category, making the research in this topic very crucial. In this thesis, I first give a brief introduction to the topic, and then proceed to discuss our experimental setup which uses a tunnel-diode based resonant oscillator technique, how to analyze the data obtained to get quantities such as superfluid density, and how to interpret the obtained results. Then, I present the data on various samples listed below;

- PdTe_2 – A candidate for topological superconductivity.
- FeS – A simple iron-based superconductor with possibly multi-gap superconductivity.

- CeCoIn₅ – A heavy fermion superconductor. Sn, Cd doped and pure samples are measured and the data is compared.
- MoTe₂ intercalated with ionic liquid – An organic-inorganic hybrid superconductor.

In this chapter, we discuss some basic background knowledge needed for our study and the motivations for conducting the study. I give a brief introduction to superconductivity and explain some of the important concepts such as the energy gap, superfluid density, and penetration depth of a superconductor.

1.2 A brief introduction to superconductivity

Superconductivity was discovered in 1911 by Kamerlingh Onnes [2] (Nobel prize in 1913). He discovered that the resistivity of certain metals go to zero (*a perfect conductor*) at very low temperatures. He called this phenomenon *superconductivity* and found that it happens below a characteristic transition temperature (T_c) that is different for different metals. Later, he also discovered that the superconductivity is lost when high magnetic fields or high current densities are applied. In other words, superconducting state is characterized by a critical temperature and a critical magnetic field (H_c).

The phase diagram and the resistivity behavior for a typical superconductor is shown in Figure 1.1(a) and 1.1(b) respectively. The dashed line in Figure 1.1(b) shows the expected behavior of a normal metal and the solid line shows the behavior of a superconductor. The variation of critical field with temperature is found to be parabolic as

FIGURE 1.1: (a) The phase diagram and (b) The resistivity vs temperature of a typical superconductor. Adapted from [1].

shown in Figure 1.1(a) and is given by the empirical formula [1],

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \quad (1.1)$$

1.2.1 Meissner effect, London theory, and penetration depth

The next groundbreaking discovery in superconductivity came in 1933 when Meissner and Oschenfeld discovered *perfect diamagnetism* in the superconducting state [4]. It was discovered that a superconductor expels all magnetic flux from its bulk. In contrast to a perfect conductor that can expel time varying magnetic fields from its bulk (due to Faraday's law), the superconductor expels static magnetic fields as well. This phenomenon is illustrated in Figure 1.2. Magnetic field can penetrate through the bulk in normal state ($T > T_c$), but is expelled in the superconducting state ($T < T_c$). The Meissner effect makes it possible for a superconducting sample to levitate over a magnet.

FIGURE 1.2: The Meissner effect. Adapted from [3].

The Meissner effect was first explained by brothers F. and H. London in 1935 [5]. They proposed a phenomenological theory in which the electric and magnetic fields in a superconductor are governed by the two equations:

$$\vec{E} = \frac{\partial}{\partial t} (\Lambda \vec{J}_s) \quad (1.2)$$

$$\vec{H} = -c \left[\nabla \times (\Lambda \vec{J}_s) \right] \quad (1.3)$$

where $\Lambda = 4\pi\lambda^2/c^2 = m/(n_s e^2)$ is a phenomenological parameter. The first equation explains infinite conductivity and the second showed that the electromagnetic free energy in a superconductor is minimized when,

$$\nabla^2 \vec{H} = \frac{\vec{H}}{\lambda^2} \quad (1.4)$$

where $\vec{H}$ is the magnetic field and λ is called the London penetration depth or the magnetic penetration depth or simply the **penetration depth** which is given by (in cgs units),

$$\lambda = \sqrt{\frac{mc^2}{4\pi n_s e^2}} \quad (1.5)$$

FIGURE 1.3: Penetration of magnetic field inside a superconductor.

where n_s is the number density of superconducting electrons (also known as the superfluid density), m is the mass and e is the charge of an electron. As $T \rightarrow T_c$ from below, the number density of superconducting electrons approaches zero ($n_s \rightarrow 0$), hence the penetration depth diverges.

Assuming a vacuum-superconductor interface at origin, the solution of the London equation 1.4 inside the superconductor will be an exponentially decaying function given by,

$$\vec{H}(x) = \vec{H}(0) \exp\left(-\frac{x}{\lambda}\right) \quad (1.6)$$

This shows that the magnetic field penetrates the surface of a superconductor but is expelled from the bulk. The spatial extent of penetration is given by a characteristic length λ – the penetration depth. This is shown in Figure 1.3. This phenomenon of zero magnetic field in the bulk is achieved by setting up supercurrents¹ on the surface of the sample which creates an opposite magnetic field inside, effectively expelling the flux from the bulk and increasing the flux outside.

1.2.2 The BCS theory and the energy gap

The microscopic theory of (conventional) superconductivity was proposed in 1957 by John Bardeen, Leon Cooper and Robert Schrieffer [7] (Nobel prize in 1972). According to this theory, at sufficiently low temperatures, electrons can pair up overcoming the Coulombic repulsion to form *Cooper pairs* due to a weak attractive potential between the electrons. These Cooper pairs are bosons since electrons are fermions with half-integer spins and when two of them pair up, the resulting particle will have an integer

¹Since the resistance is zero, these currents won't decay, hence the name.

spin. Unlike fermions which follow the Pauli exclusion principle where no more than two particles can exist in a single state, any number of bosons can occupy a single energy state. The Cooper pairs condense into the lowest energy state forming a Bose-Einstein condensate. Since the condensate has a collective behavior, it is energetically stable and resists all minor energy fluctuations. Therefore, it can have a collective ordered motion without any resistance.

The weak attractive potential required for the pairing of electrons to happen arises from electron-phonon coupling. A simplified model for this is illustrated in Figure 1.4. The grey balls are lattice ions and the pink balls are electrons. When an electron moves through the lattice, the positive charges around it are attracted to it causing a distortion in the lattice. As the lattice relaxation is slower compared to the movement of the electron, there is a temporary uncompensated positive charge at the site after the electron has moved away. This attracts another electron to the site. This process continues in the lattice effectively pairing up the electrons to behave like a single particle. In other words, a moving electron creates a phonon which attracts another electron, effectively binding the two electrons together.

FIGURE 1.4: The electron-phonon coupling. Adapted from [6].

As we have already seen, the electrons pair up and condense to a lower energy state leaving an energy gap at the Fermi surface. Elementary excitations above this ground state are called Bogoliubov quasiparticles. **The Energy Gap** is defined as the energy difference between the superconducting ground state and the smallest quasiparticle excitation [1]. If Δ is the energy gap, then the energy required to break a Cooper pair into two quasiparticles will be 2Δ . The energy gap is regarded as the order parameter of superconducting state. The order parameter distinguishes two different phases. Δ is zero above the transition temperature and nonzero below it. The temperature dependence of the energy gap will be discussed later.

FIGURE 1.5: The quasiparticle density of states for a superconductor.

The quasiparticle density of states (DOS) of a superconductor is shown in Figure 1.5. As the energy gap opens up, the states that were previously at the gap are pushed to the

edge giving distinct peaks in the DOS spectrum. At $T=0$ K, all the available states below E_F are filled and all of those above it are empty.

1.2.3 Ginzburg-Landau theory and coherence length

The Ginzburg-Landau (GL) theory [8] is a phenomenological theory of superconductivity proposed in 1950 (Nobel prize in 2003). This theory treats the superconducting transition as a second order phase transition (or first order in some cases). An order parameter (ψ), which is the superconducting wave function, is defined as zero in the normal state (disordered state) and finite in the superconducting state (ordered state). It then uses thermodynamic arguments such as minimization of free energy and the surface energies to find the characteristics of order parameter. According to the theory, the free energy of the superconducting state (f_s) in absence of magnetic field is,

$$f_s = f_n + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 \quad (1.7)$$

where f_n is the free energy of normal state, $|\psi|^2 = n_s$ is the number density of superconducting electrons, α is a parameter dependent on temperature, and β is a constant. By minimizing f_n , they showed that when $\alpha < 0$ and $\beta > 0$, a superconducting order can exist with $|\psi|^2 = n_s = -\alpha/\beta$. Predictions of critical magnetic field and critical currents can be made using this theory.

A similar approach is used for transitions in presence of a magnetic field and along with the penetration depth that London introduced (equation 1.5), Ginzburg-Landau theory introduces a characteristic length known as the *coherence length* (ξ) given by,

$$\xi = \frac{\hbar^2}{2m|\alpha|} \quad (1.8)$$

$\hbar$ is the reduced Planck's constant and m is effective mass. Physically, coherence length is the distance over which the superconducting wave function can vary. In the BCS limiting case, this is related to the size of a Cooper pair. The ratio of the two lengths $\kappa = \lambda/\xi$ is called the *Ginzburg-Landau parameter*. This parameter has profound implications in the physics of the superconductors that one classification of superconductors (see section 1.2.4.1) is based on it. The phenomenological (GL) and microscopic (BCS) theories were shown to be equivalent in some limiting cases by Gor'kov [9], which sparked considerable interest. He showed that the superconducting energy gap explained in the BCS theory (Δ) and the GL wave function (ψ) are related by a proportionality constant. ψ can be interpreted as the Cooper pair wave function. Many extensions of this theory followed, having varying levels of successes. This theory is used to explain the behavior of a class

of superconductors called the type-II superconductors (section 1.2.4.1). It is also used to explain the symmetry of the order parameter and the pairing mechanism (see section 1.3) in another class of superconductors called unconventional superconductors which cannot be explained using the BCS theory.

1.2.4 Classification of superconductors

1.2.4.1 Type-I and type-II superconductors

This classification is based on the phase diagram. Type-I superconductors have a normal phase and a superconducting phase characterized by a critical temperature and a critical magnetic field as shown in Figure 1.1a. Type-II superconductors have a mixed phase as shown in Figure 1.6, where there are physically separated superconducting and normal domains in the sample. Generally speaking, there are two critical magnetic fields (H_{c1} , H_{c2}) for type-II superconductors which characterizes the transitions from superconducting to mixed and from mixed to normal phases respectively. Since the H_{c2} is much greater than H_c of type-I superconductors, type-II superconductors are of more practical importance such as in making strong superconducting magnets, carrying high currents, etc.

The existence of type-II superconductors can be explained by the Ginzburg-Landau theory (section 1.2.3). Superconductors that have a Ginzburg-Landau parameter $\kappa < 1/2$ are type-I ($\lambda \ll \xi$) and that with $\kappa \geq 1/2$ are type-II ($\lambda \gg \xi$). This is due to the

FIGURE 1.6: Typical phase diagram for a type-II superconductor. Magnetic flux behaviour at different phases is also shown. Adapted from [1].

competition of two energies at superconductor-normal interfaces: (i) the energy gained (negative) by being in a superconducting state and (ii) the energy penalty (positive) for excluding the field. This is illustrated in Figure 1.7. The total surface energy of systems with $\lambda \gg \xi$ at these boundaries becomes negative in presence of magnetic fields and therefore they prefer to make mixed systems with many of these interfaces. Net energy for systems with $\lambda \ll \xi$ at boundaries is positive and hence they cannot afford to be in a mixed state.

FIGURE 1.7: Illustration of competing surface energies. (a) and (c) shows the magnetic field and superconducting wave function along with their characteristic length scales for type-I ($\lambda \ll \xi$) and type-II ($\lambda \gg \xi$) superconductors respectively. (b) and (d) shows respective energy contributions and the net surface energy. Adapted from [1, 10].

In the mixed state, the system allows magnetic flux to pass through certain regions called vortices (See Figure 1.6). Each of these vortices have a core with normal phase and carry a quantum of flux ($\phi_0 = hc/2e$). Hence, the number of vortices in the system is dependent on the applied magnetic field. The vortices are maintained by the same phenomenon that expels magnetic field from superconducting regions – super-currents circulating around the vortex.

1.2.4.2 Conventional and Unconventional superconductors

This classification is based on our understanding of the physics of superconductors. Conventional superconductors are those whose physics can be explained by the BCS theory or its extensions, ie, Cooper pair formation due to electron-phonon coupling. Almost all type-I superconductors [most pure metals such as Al (1.2 K), Hg (4.15 K),

Mo (0.92 K), Pb (7.19 K), etc] and some type II superconductors [Nb (9.26 K), V (5.3 K), Nb-Ti (9.2 K), MgBi₂ (39 K) etc] fall into this category.

Unconventional superconductors are those which cannot be explained by the BCS or variations of BCS theory. There is no common consensus on the mechanism of Cooper pair formation in these systems. The intriguing physics of these systems will be introduced in the subsequent sections. Most of the type-II superconductors such as the heavy fermion superconductors [LaCuSi₂ (0.5 K), UBe₁₃ (0.85 K), UPt₃ (0.54 K), CeCoIn₅ (2.3 K), etc], high temperature superconductors including the copper oxide based superconductors [LaBaCuO₄ (35 K), YBa₂Cu₃O_{7-x} (YBCO) (90 K), Tl_mBa₂Ca_{n-1}Cu_nO_{2n+2} (TBCCO) (125 K)], and iron-based superconductors [LaOFeAs (26 K), SmFeAsO (55 K), FeSe (27 K)]², etc fall under this category. Understanding the physics of unconventional superconductors is not only interesting, but also has high practical and industrial importance since these materials have the potential to revolutionize industry, especially the energy sector.

1.3 Energy gap, coupling strength, and pairing symmetry

The temperature dependence of the superconducting energy gap according to BCS theory in the weak-coupling limit is shown in Figure 1.8. At temperatures close to 0 K, the gap is almost a constant because of the low number of thermally excited quasiparticles. As the temperature increases and there are enough number of these thermally excited quasiparticles, the gap begins to shrink rapidly and closes at $T = T_c$.

This temperature dependence of the order parameter ($\Delta(T)$) is approximated by Gross *et al.* [11] as,

$$\Delta(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\} \quad (1.9)$$

where $\delta_{sc} \equiv \Delta(0)/k_B T_c$ is called the gap ratio. $\Delta(0)$ is the value of gap at $T = 0$ K, k_B is the Boltzmann constant, T_c is the transition temperature, a is a constant, and $\Delta C/C$ is the electronic specific heat jump at T_c . For the BCS weak coupling limit, the values for the parameters are $\delta_{sc} = 1.76$, $a = 2/3$, and $\Delta C/C = 1.43$.

FIGURE 1.8: Temperature dependence of the BCS Gap.

²might be doped to achieve these T_c .

The gap ratio is widely regarded as the measure of coupling strength (between electrons to form a Cooper pair) in the superconductor. The prediction of 1.76 in the weak-coupling limit is one the major achievements of BCS theory. The gap ratio increases monotonically with the coupling strength of superconductor. For conventional superconductors, the gap ratios lie close to the predicted value of 1.76, while in unconventional superconductors, the gap ratios range from 1.4 to 5 [12]. The electronic specific heat jump ($\Delta C/C$) can also be used as an indicator of coupling strength. This is related to T_C and the Sommerfeld coefficient (γ_n) as $\Delta C/C = \Delta C/\gamma_n T_C$, and this value increases monotonically with the coupling strength. In unconventional superconductors, $\Delta C/C$ ranges from 0.5 to 3 [12].

The symmetry of energy gap in momentum space depends on the pairing mechanism, symmetry of the crystal lattice, and the shape of Fermi surface. Electrons have a spin of $1/2$ and hence the total spin (S) of a Cooper pair can be 0 (singlet) or 1 (triplet) depending on the spins of paired electrons. Since electrons are fermions, the full wavefunction of the Cooper pair should be anti-symmetric in terms of interchange of electrons. Therefore, for spin singlet pairing ($S = 0$), the spatial part of the wave function should be even ($l = 0, 2, \dots$) and for spin triplet pairing ($S = 1$), the spatial part should be odd ($l = 1, 3, \dots$).

The symmetry of the gap is the symmetry of spatial part of the superconducting state. For a conventional superconductor, the cooper pair is formed by electrons with opposite spins, which means the spin state of the cooper pair is singlet. The corresponding spatial wave function has the familiar form of s -wave ($l = 0$) of spherical harmonics. An isotropic s -wave gap around the Fermi surface in a conventional superconductor is shown in Figure 1.9(a). The blue shaded portion represents the Fermi surface and the

FIGURE 1.9: Different gap symmetries. Blue shaded region represents the Fermi surface. Red and green regions represents the gap with different phases. (a) an isotropic s -wave gap, (b) p -wave gap, and (c) d -wave gap.

red portion represents the gap with a single phase. Depending on the crystal lattice and Fermi surface, the gap can be slightly anisotropic as well.

It is understood that in conventional superconductors, the electron coupling is mediated by phonons, but in unconventional superconductors, there is no common theory on the origins of the interaction that causes electron pairing. Various theories are proposed such as spin fluctuations [13], Resonating valence bond theory [14], interlayer coupling [15], etc. This gives rise to diverse gap scenarios.

An example of a d -wave gap ($l = 2, S = 0$) is shown in Figure 1.9(c). One immediately notices that the gap goes to zero at some points in the Fermi surface and that the phase of the wave function changes sign at these points. They are called *nodes*. The nodes in the d -wave gap are called line nodes as the typical Fermi surface for such superconductors are cylindrical and extends in z -direction, the nodes extend on lines in z -direction. A 3D visualization of d -wave gap with line nodes on a cylindrical Fermi surface is shown in Figure 1.10. Figure 1.9(b) shows a p -wave gap. As we discussed earlier, this happens in spin-triplet systems ($S = 1, l = 1$). As seen in the figure, there are two line nodes in a p -wave system with a cylindrical Fermi surface.

FIGURE 1.10: A d -wave gap with line nodes on a cylindrical Fermi surface.

1.4 Normalized superfluid density

John Bardeen introduced the **two-fluid model** of superconductivity in 1958 [16]. He explained that the behavior of a superconductor is analogous to that of superfluid helium that flows without viscosity below certain critical temperature. Similar to the mechanism of superconductivity, the formation of a Bose-Einstein condensate (of helium atoms as helium-4 atoms are bosons) is the underlying mechanism behind superfluidity.

In his two-fluid model of superconductivity, John Bardeen showed that the two-fluid model by Landau [17] that explains the superfluidity can be used as a phenomenological basis for superconductivity too. According this model, in a fluid below its transition temperature, a fraction of the fluid behaves as a superfluid (zero viscosity) and the rest behave as a normal fluid. Similarly, in a superconductor below its transition temperature, a part of the conducting electrons behave as superconducting electrons and the

rest behaves as normal electrons. The fraction of superconducting electrons increases as the temperature is decreased and reaches unity at $T = 0$ K. The fractional density of superconducting electrons is called the normalized superfluid density (ρ_s) and is given by,

$$\rho_s = \frac{n_s}{n_s + n_e} \quad (1.10)$$

where n_s is the density of superconducting electrons, n_e is the density of normal electrons, and $n_s + n_e = n$ is the total density of electrons.

Please note that the London theory and the two-fluid model are phenomenological theories for superconductivity and the concept of a Bose-Einstein condensate is absent in them, which is why we define superfluid density (n_s) as the number density of superconducting electrons. The equations (see section 1.2.1) however contain the terms – superfluid charge density ($e^*n_s^*$) and charge to mass ratio (e^*/m^*), which are more consistent physical quantities when relating the phenomenological models to the microscopic theory of Bose-Einstein condensation (e^* , m^* , and n_s^* are respectively the effective charge, effective mass, and effective number density of quasiparticles [1]). For Cooper pairs, $e^* = 2e$, $m^* = 2m$, and $n_s^* = n_s/2$, but the London penetration depth (Eqn. 1.4) remains unchanged [1]. The quantity $e^*n_s^*$ will be the same, be it the charge density of electrons, Cooper pairs, or the condensate as a whole, and is sometimes used as an alternate definition for superfluid density. Note that the normalized superfluid density defined above will be same in both cases.

Normalized superfluid density will have a maximum value of one at $T = 0$ K and go to zero at T_c . The normalized superfluid density can be calculated from the energy gap (Δ) as [1],

$$\rho_s = 1 + 2 \int_0^{4\pi} \frac{d\Omega}{4\pi} \int_0^\infty \frac{\partial f}{\partial E} d\epsilon \quad (1.11)$$

where ϵ is the normal-state quasiparticle energy relative to the chemical potential, $E = \sqrt{\epsilon^2 + \Delta^2}$ is the superconducting state quasiparticle energy, and f is the Fermi function given by $f = (\exp(E/k_B T) + 1)^{-1}$. The integral over solid angle $d\Omega$ on the Fermi surface is to account for anisotropies in the gap.

The temperature dependence of the normalized superfluid densities for a superconductor with a BCS s -wave gap (blue line) and for one with d -wave gap (red line) is shown in Figure 1.11. The s -wave gap is calculated using Equation 1.9 with BCS weak coupling parameters ($\delta_{sc} = 1.76$ and $\Delta C/C = 1.43$) and the d -wave gap has a functional form $\Delta'(T) = \Delta(T) \cos(4\theta)$, where $\Delta(T)$ is the isotropic gap given by Equation 1.9. The parameters used for weak coupling d -wave are $\delta_{sc} = 2.14$ and $\Delta C/C = 0.95$ [18].

FIGURE 1.11: Temperature dependence of normalized superfluid densities for a BCS s -wave gap and a d -wave gap.

At $T = 0$ K, all the conducting electrons are in the superconducting state and hence $\rho_s = 1$. As temperature increases, electrons are excited from the condensate and hence the superfluid density decreases. At $T = T_c$, the superconducting gaps closes, all the electrons are at the normal state and therefore the superfluid density goes to zero.

As seen from the figure, $\rho_s(T)$ is dependent on the symmetry of the gap. For an s -wave gap, the gap is isotropic around the Fermi surface and the number of excited quasiparticles is very low at low temperatures. Therefore, ρ_s stays close to unity at these low temperatures. As the gap begins to shrink and more electrons gets excited, $\rho_s(T)$ decreases and eventually goes to zero at $T = T_c$. For a d -wave gap, since there are nodes, quasiparticles can be excited near the nodes even at low temperatures. This is reflected in the normalized superfluid density curve as ρ_s for the d -wave superconductor stays under that of the s -wave superconductor. Even at very low temperatures, there is significant decrease in ρ_s for a gap with nodes.

Normalized superfluid density from penetration depth:- From Eqn. 1.5, the superfluid density can be obtained from penetration depth as,

$$n_s(T) = \left(\frac{mc^2}{4\pi e^2} \right) \frac{1}{\lambda^2(T)} \quad (1.12)$$

Dividing by $N = n_s + n_e$ on both sides to convert to normalized superfluid density and noting that $n_s = N$ at $T=0$ K, we obtain,

$$\rho_s(T) = \frac{\lambda^2(0)}{\lambda^2(T)} \quad (1.13)$$

where $\lambda(T)$ is the temperature dependent penetration depth and $\lambda(0)$ is the penetration depth at $T = 0$ K. We use this expression to calculate ρ_s from penetration depth measurements. This will be explained in section 2.3.3.

1.5 2D superconductivity

According to the Mermin-Wagner theorem [19], a continuous symmetry-breaking phase transition is not possible at finite temperatures in systems with dimensions $D \leq 2$. This was rigorous proof to the concepts introduced by Bloch and Peierls in 1930s [20, 21], where they showed that long range (magnetic) order is not possible in two dimensions by energetic and entropic arguments. This is because long range fluctuations can be created with little energy cost in such systems and this is preferred as it increases the entropy. As a consequence of this theorem, superconductivity is forbidden in 2D.

However, it was shown that under certain circumstances, a quasi-long range order can occur in 2D which is called the Berezinskii-Kosterlitz-Thoules (BKT) transition [22]. This was first shown in the 2D XY model of spins. They showed that the spins can form vortices and anti-vortices which behave as quasiparticles. Above the BKT transition temperature (T_{BKT}), these vortices and anti-vortices are free, while below T_{BKT} , vortices and anti-vortices bind together to form vortex-anti-vortex pairs (see Figure 1.12). It was shown that a 2D system can also become superconducting through a similar process.

FIGURE 1.12: Schematic of a vortex-anti-vortex pair in the 2D XY model. Adapted from [23].

In 2D superconductors, the order parameter appears at a transition temperature (T_{c0}), but there is no phase coherence. At the BKT transition temperature T_{BKT} , phase coherence is achieved and the system becomes superconducting. These two transition temperatures follow $T_{c0} > T_{BKT}$.

A superconductor is considered 2D when the thickness of the film $d \ll \xi$, where ξ is the Ginzburg-Landau coherence length. As the typical values for ξ can be hundreds of nanometers for conventional type-I superconductors, the film thickness of 2D superconductors can be much larger than a single-atomic layer. For unconventional superconductors however, ξ can only be a few nanometers and is therefore much harder to realize a 2D superconducting system. Another challenge in experimental realization is that 2D superconductivity is fragile and a superconductor-insulator transition occurs in presence of disorder. This is in contrast to conventional 3D superconductors which are robust against disorder.

1.6 Penetration depth

1.6.1 Temperature dependence

We know from equations 1.5 and 1.13 that the penetration depth is inversely proportional to the square root of superfluid density and that the penetration depth diverges at transition temperature. The typical temperature dependence of penetration depth for a BCS superconductor is shown in Figure 1.13. As seen in the figure, at $T = 0$ K,

FIGURE 1.13: Temperature dependence of penetration depth for a BCS s -wave gap.

the penetration depth is $\lambda(0)$ and it increases slowly with temperature. As the temperature approaches T_c , λ increases rapidly and diverges at $T = T_c$. After this, the system becomes a normal metal with a finite skin-depth and susceptibility. For a BCS superconductor at low temperatures ($T < 0.3 T_c$), the temperature dependence of penetration depth can be approximated as an exponential behavior given by [1],

$$\lambda(T) = \lambda(0) \left(1 + \sqrt{\frac{\pi \Delta(0)}{2k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \right) \quad (1.14)$$

For unconventional superconductors with nodes, the low-temperature ($T \ll T_c$) penetration depth has a power-law dependence with temperature given by,

$$\lambda(T) - \lambda(0) \propto T^p \quad (1.15)$$

p is the power-law exponent which depends on the nature of nodes. For 3D line nodes such as the d -wave gap, $p = 1$ and the temperature dependence of penetration depth is linear. For 3D point nodes, $p = 2$. For anisotropic gaps without nodes, the temperature dependence will be exponential. More details can be found in references [24–26]. This will be explained more in the future chapters when our experimental data is analyzed.

1.6.2 Non-local corrections

Although London theory 1.2.1 was successful in describing the electrodynamics of superconductors, it was found that the penetration depth measured for conventional superconductors is larger than predicted by the London equations. This was because London equations (Eqn. 1.2 and 1.3) only consider local effects, which means the current density ($\vec{J}_s$) at a point is related to the vector potential ($\vec{A}$) at that point only, i.e.,

$$\vec{J}_s = -\frac{\vec{A}}{\Lambda} \quad (1.16)$$

In 1950, Pippard introduced a generalization of London equations by considering non-local effects [27]. He argued that the current density at a point depends on the average of vector potential over a volume of radius ξ_0 around the point. Eqn. 1.16 is therefore replaced by,

$$\vec{J}_s = -\frac{3}{4\pi\Lambda\xi_0} \int \frac{\vec{A}(r') \cdot \vec{R}}{R^4} e^{R/\xi} d^3r' \quad (1.17)$$

where ξ_0 is called the Pippard coherence length and is closely related to the Ginzburg-Landau coherence length introduced in section 1.2.3. ξ_0 is given by,

$$\xi_0 = a \frac{\hbar v_F}{k_B T_c} \quad (1.18)$$

where a is a numerical constant and v_F is the Fermi velocity. Now there are two important length scales; the London penetration depth, λ_L given by Eqn. 1.5, over which the magnetic field varies inside a superconductor and ξ_0 is the characteristic length over which superfluid density (n_s) varies in a superconductor.

In conventional type-I superconductors, $\xi_0 \gg \lambda_L$, and non-local effects are therefore important. The average value of $\vec{A}$ for a point near the surface is less than the value of $\vec{A}$ at the point, which means the screening current is less, and hence the magnetic field penetrates deeper than predicted by London theory. In this non-local limit or the Pippard limit, the actual penetration depth is given by,

$$\lambda_p \approx \left(\frac{\sqrt{3}}{2\pi} \lambda_L^2 \xi_0 \right)^{1/3} \quad (1.19)$$

In the local limit or the London limit, $\lambda_L \gg \xi_0$, London theory is valid because $\vec{A}$ can be considered a constant at distances ξ_0 around a point, and the penetration depth is $\lambda_p = \lambda_L$. No conventional superconductors are usually in this limit, but the local limit is achieved in some unconventional superconductors like the cuprates.

Our discussion was based on the assumption that the superconductors are pure and there is no impurity scattering. However, in reality, this is not always the case. In presence of scattering, according to Pippard, the coherence length (ξ) is given by the relation,

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{l} \quad (1.20)$$

where ξ_0 is the coherence length for the pure material and l is the electron mean free path. If there is negligible scattering ($l \gg \xi_0$), the material is said to be in the clean limit and the coherence length $\xi \approx \xi_0$. In the dirty limit ($l \ll \xi_0$), scattering dominates, which means $\xi \approx l$. In the dirty limit, penetration depth is given by,

$$\lambda_{dirty} \approx \lambda_L \sqrt{1 + \frac{\xi_0}{l}} \quad (1.21)$$

We can see that the penetration depth is dependent on the presence of impurities, which is one of the significant results of Pippard's theory.

1.6.3 Measuring penetration depth

As seen in previous sections, probing the penetration depth as a function of temperature can give information about the superfluid density (eq.1.5), the nature of energy gap, the phase transition, etc. When the penetration depth of a sample decreases, the susceptibility decreases causing the sample to expel magnetic field. This causes the local magnetic flux around the sample to increase. Similarly, the local flux around the sample decreases when the penetration depth increases. Most of the experimental techniques measure this change in magnetic flux around the sample to determine the penetration depth. Some of the common methods used to measure penetration depth are the following;

- Muon-spin resonance (μ SR) [28]: A beam of spin polarized muons directed at the samples evolves in the local magnetic moment, decaying to emit a positron in the direction of their spin. Magnetic field around the sample can be found by detection of these emitted positrons.
- SQUID magnetometry [11]: Superconducting quantum interference device (SQUID) measures the change of magnetic flux around the superconductor. The change in inductance of a coil on SQUID head indicates the change of magnetic flux.
- Torque magnetometry [29]: The magnetization of the sample is measured by a torque magnetometer, which is a cantilever with sample at the end. The deflection of the cantilever in a magnetic field is measured with high precision, which gives a measure of the penetration depth of the sample.
- Resonant oscillator technique [30]: Sample is placed inside the inductor of a resonant LC circuit. Changes in magnetic flux around the sample changes the inductance of the coil and thus the resonant frequency.

Different techniques has advantages and disadvantages. While other techniques mentioned above are sensitive to the sample surface and shape, μ SR measures the bulk behavior and is insensitive to the surface properties. The main advantage of the SQUID technique is that the magnetic fields and currents are DC, and therefore avoids any frequency dependence in penetration depth measurements. Resonant oscillator-based techniques can only measure the change in penetration depth of the sample as a function of temperature, while μ SR can measure the absolute value of penetration depth at different temperatures. However, data from μ SR can be noisy and comes with rather big error bars which make them not ideal for fitting to various models. μ SR can only be used to measure type-II superconductors in the vortex phase or type-I superconductors with domain separation, and it requires modeling of the spatial distribution of vortex

lattice, which may introduce errors as the results may depend on the assumptions in models used [31]. μ SR also requires a particle accelerator beam line (source of muons), which are not available in many places. Resonant oscillator technique on the other hand can be very sensitive to changes in penetration depth and can yield data with very low noise levels. Moreover, they can be relatively inexpensive to run as well.

We use the resonant oscillator technique with a tunnel diode based oscillator to measure the penetration depth. The major advantages of our technique is it's low noise levels and surface sensitivity. The experimental setup and procedure is explained in detail in chapter 2.

1.7 Motivation for the study

As explained in this chapter, unconventional superconductors show interesting physics that are still not completely understood. The understanding of symmetry of superconducting gap and the strength of coupling is not only important from a theoretical perspective, but also required for many practical applications. Understanding the quasiparticle density of states and the nature of energy gap is important in the making and study of superconductor interfaces with metals, semiconductors, or other superconductors. High temperature superconductors that can be used for various practical applications such as for power transmission, transport system using levitation, high-field magnets, etc belong to the category of unconventional superconductors, generating practical interest for the study of underlying physics.

Penetration depth measurements give direct information on the superfluid density and the energy gap. The nature of the gap such as the presence of nodes, the pairing mechanism and the coupling strength can be obtained from penetration depth. Measurements can be done with a high degree of accuracy with very low noise using our technique (described in next chapter), making this method an important tool in the study of superconductivity. Combined with other physical measurements using tools such as the MPMS (Magnetic Property Measurement System for critical field measurements and magnetization measurements), PPMS (Physical Property Measurement System for measuring electrical resistivity and specific heat), etc., a good understanding of the physics of a superconductor can be achieved.

Novel superconducting physics such as multi-band superconductivity [32, 33], topological superconductivity [34], etc has generated much interest in recent years. In a multi-band superconductor, multiple gaps with different properties (including gap ratio and transition temperature) coexist on distinct parts of the Fermi surface. Using the penetration

depth measurements, these multi gap scenarios can be identified and by using different multi-gap models to fit the superfluid density, the properties of these gaps can be found. Topological superconductors are characterized by full pairing gap in the bulk and gapless states at topological boundaries such as surfaces or defects. The existence of exotic particles such as Majorana fermions at these gapless states makes it an interesting field of research, not only for the study of fundamental particles, but also for potential applications in spintronics, quantum computation, etc.

The home-made penetration depth measurement system at our lab can make low-noise high resolution measurements (sensitivity less than 4 parts per 10^9). We believe that with this powerful tool, our studies contribute to the ever-expanding and intriguing field of superconductors and help in understanding the underlying physics of a wide variety of unconventional superconductors.

Chapter 2

Experimental Method - The Tunnel Diode Oscillator

A resonant oscillator technique is implemented to study the penetration depth. The idea is to place the superconducting sample inside the inductor of an oscillator tank circuit as shown in Figure 2.1. The resonant frequency (f) of a tank circuit with inductance L and capacitance C_0 is given by,

$$f = \frac{1}{2\pi\sqrt{LC_0}} \quad (2.1)$$

When the temperature is decreased and the sample becomes superconducting, it expels magnetic field as explained in 1.2.1. This will cause the inductance of the coil to change, which will be reflected in the resonant frequency of the tank circuit. Thus, by measuring the changes in resonant frequency of the circuit with temperature ($\Delta f(T) = f(T) - f(T_{min})$), we can obtain the change in penetration depth of the sample as a function of temperature.

FIGURE 2.1: Resonant Oscillator technique - sample inside the inductor of a tank circuit.

The change in penetration depth ($\Delta\lambda$) is related to the change in resonant frequency (Δf) of the circuit by the following relation;

$$\Delta\lambda(T) = G\Delta f(T) \quad (2.2)$$

G is a calibration factor which depends on sample and coil geometries. More details on this will be explained later in the chapter.

In this chapter, I explain the experimental setup in detail, which uses a tunnel diode based resonant oscillator and a helium-3 cryostat that can cool down to 300 mK. The system was developed by Sourav Mitra [25] and is inspired by the setup developed by Dr. Bryan Yanof [35].

2.1 Tunnel Diode Oscillator (TDO)

2.1.1 Tunnel Diode

Tunnel diodes are heavily doped semiconductor junctions which have a narrow depletion region that enables electron tunneling across the barrier. Discovered by Leo Esaki [36], these tunnel diodes can operate at high frequencies since the tunneling action is very fast.

FIGURE 2.2: (a) The unbiased band structure and (b) I-V characteristics of a tunnel diode.

The band structure at unbiased state and the forward bias I-V characteristics of a tunnel diode is shown in figure 2.2(a) and (b) respectively. Since it is heavily doped, the Fermi energy (E_F) falls in the valence band of the p-type and the conduction band of n-type semiconductors as shown. For a conventional diode, there is no current at low voltages in forward bias [green dotted line in Figure 2.2 (b)]. But for a tunnel diode, when a small

FIGURE 2.3: The band structure of a tunnel diode at different bias conditions.

positive bias is applied, electrons tunnel from n-type to p-type side causing a tunnel current, shown as the red dotted line in Figure 2.2(b).

The tunnel current depends on the alignment of available states in p-type to that of the filled states in n-type. The band structure at different bias conditions is shown in Figure 2.3. As seen in the figure, the tunneling current increases at low voltages in forward bias [Figure 2.3(b)], reaches a maximim [Figure 2.3(c)] and then decreases and reaches zero [Figure 2.3(d)] depending on the availability of states for electrons to tunnel to. After this point, at higher bias voltages, the tunnel diode acts like a normal diode in forward bias.

This combination of tunnel current and diffusion current results in the unique IV characteristics shown in Figure 2.2(b). The part of the curve with negative slope is called the negative differential resistance region or simply the negative resistance region. This property of I-V curve is exploited for applications of tunnel diodes in oscillators, fast switching, etc. We use this property to make a stable resonant oscillator for our experiment.

2.1.2 Tunnel diode oscillator (TDO)

A typical LC oscillator circuit and its output is shown in Figure 2.4(a). The oscillations produced by this tank circuit are damped because of the resistances present in the circuit. When a tunnel diode operating in the negative resistance region is added to the circuit as shown in Figure 2.4(b), it compensates for the dissipative losses in the tank circuit,

sustaining the oscillations. This is the basic principle of a TDO. In other words, the tunnel diode serves as the ac power source for driving the oscillations. The resistances R_1 and R_2 in the figure are used to keep the tunnel diode biased in the negative resistance region. In the following sections, I will explain how this is implemented in our setup to measure the penetration depth.

FIGURE 2.4: Typical LC oscillator circuits without(a) and with(b) a tunnel diode. Adapted from [37].

2.2 Experimental setup

Our home-made experimental setup consists of the following;

1. Low temperature circuit which consist of the TDO components.
2. Room temperature components for processing the signal.
3. Helium-3 cryostat.
4. Sample coldfinger and TDO cell

2.2.1 Low temperature circuit

The small size and low power requirements of the tunnel diode enables the TDO circuit to be placed inside the cryostat at low temperature (4 K). Maintaining the TDO circuit at a constant temperature is essential to provide a stable oscillation frequency and thus

achieve the high accuracy required for penetration depth measurement. The design of low temperature circuit is based on the design and analysis done by Van Degriift [38]. The schematic of the low temperature circuit is shown in Figure 2.5.

FIGURE 2.5: The low-temperature circuit. $C_0=47$ pF, $C_1=10$ nF, $C_C=22$ pF, $R_1=1500$ Ω , $R_2=330$ Ω , $R_p=270$ Ω .

The tank circuit: The primary coil ($L_{primary}$), tapping coil (L_{tap}), and the capacitor (C_0) make the tank circuit. The sample is placed inside the primary coil. The tapping coil is required for impedance matching with the tunnel diode and thus obtain a stable oscillation. The resistance R_p prevents any parasitic oscillations due to stray capacitances in the tunnel diode. The resonant frequency for our circuit is approximately 26 MHz.

Biasing the tunnel diode: A precision DC current is generated at room temperature and passed to the low temperature circuit using a co-axial cable. Resistances R_1 and R_2 make a voltage divider setup and bias the tunnel diode in the negative resistance region. Details of the DC current source is given in the next section.

Passing the oscillation signal to room temperature electronics: The radio frequency oscillations generated by the tank circuit are passed to the room temperature electronics through the same coaxial cable that provides the DC current. The capacitor C_1 is large and allows the oscillations to pass through from the ground line to the coaxial cable without allowing the DC bias to drain to the ground. The coupling capacitor C_C is small and allows a part of this signal to bypass the resistor R_1 and reach the room temperature electronics.

The temperature of these components are kept constant while the temperature of the sample is changed and the changes in resonant frequency of the tank circuit measured. More details on the signal processing and mechanical components are given in the subsequent sections.

2.2.2 Room temperature circuit

The room temperature circuit has two functions - (i) provide the DC current for biasing the tunnel diode and (ii) process the oscillation signal and measure its frequency. The schematic for the room temperature circuit is shown in Figure 2.6. The coaxial cable that carries the DC voltage to the low temperature circuit and the oscillation signal back is shown at the middle. The components to its left are to provide the DC bias and the components to its right are for signal processing and measurement.

FIGURE 2.6: The room-temperature circuit

DC Bias current: The DC current passed to the low temperature circuit should be extremely stable since the biasing of tunnel diode in the negative resistance region is of prime importance for getting sustained oscillations. A semiconductor reference (REF10) provides a stable 10 V output, which is buffered through a low-noise op-amp. This is then converted to a precision current source by a 5 k Ω resistor and a potentiometer that allows us to change the current. The voltage across the 5 k Ω resistor is monitored on a Keithley-2000 voltmeter to make sure that there are no fluctuations. The DC current is passed through a Butterworth filter which blocks any ac components and then passed to the low-temperature circuit through the coaxial cable. The Butterworth filter also blocks out the oscillation signal that comes back from the TDO.

Signal processing and measurement: The coaxial cable carries the oscillation signal back from the TDO. The capacitor to its right ($0.01 \mu\text{F}$) blocks the DC current and allows only the TDO oscillations to pass through. The signal is then amplified using a RF amplifier and is monitored on a spectrum analyzer to get a rough idea of the frequency, which will be used accordingly to set the reference frequencies of signal generator and lock-in amplifier (This will be explained in the next subsection). The amplified signal is fed into a mixer. The mixer compares this signal with a reference frequency synthesized from SRS DS 345 and outputs the difference of two frequencies, effectively converting the MHz signal to KHz. This is then fed to the bandpass filter of a lock-in amplifier that is centered at the reference frequency. This helps further reduce any unwanted frequencies present. The output from lock-in amplifier is passed to the frequency counter (HP 53131A) which measures the frequency. The stable timebase of the frequency counter is also used in the signal generators to ensure zero phase lag. All major instruments are interfaced to a PC using GPIB cables and controlled using NI LabVIEW software.

Signal Generator and Lock-in Reference: As explained, the amplified signal from oscillator (ω_s) and a reference signal generated (ω_{r1}) is passed to the mixer in the circuit. The mixer outputs the difference of the two frequencies ($|\omega_s - \omega_{r1}|$). This is to reduce the MHz signal to kHz for the bandpass filter using lock-in amplifier. This can be done because we are only interested in the frequency change and not the absolute frequency of the oscillator (Eqn 2.2). The choice of reference signal for mixer will depend upon the frequency range we want to measure. The bandpass filter of lockin will be set to be centered on the output of mixer.

The default lock-in reference frequency for bandpass is 10 kHz. This means that the reference frequency for mixer will be $\omega_{r1} = \omega_s + 10 \text{ kHz}$. The bandpass filter has a range of 1/5 of this reference around the reference frequency – in this case 2 kHz range. This is the overall frequency change that we can measure using this setting. The reference frequencies for the mixer and lock-in can be adjusted depending on the frequency range required for each sample.

2.2.3 Helium-3 cryostat

We use a Helium-3 based cryostat (Cryo Industries He3SV) to attain temperatures as low as 300 mK. Helium-3 (He-3) is an isotope of helium with a boiling point of 3.19 K, while the most abundant isotope of helium is Helium-4 (He-4) which has a boiling point of 4.23 K. The schematic of the cryostat and an enlarged view of its important parts is shown in Figure 2.7. The diagram is a simplified version by excluding vacuum pump

FIGURE 2.7: The cryostat schematic

ports, electrical contacts and connectors, needle valve controls, pressure release valves, etc.

The probe containing a He-3 chamber, charcoal sorb, and a vacuum chamber is inserted into the cryostat which will be filled in with liquid He-4 (LHe). The vacuum chamber (IVC in short for inner vacuum chamber) encloses a 1-K pot, a He-3 pot, and the mount stage on which the sample coldfinger and TDO cell are mounted prior to insertion. The probe is immersed in LHe (temperature ≈ 4.2 K), but the components inside the IVC and the charcoal sorb are thermally isolated from the LHe chamber and the He-3 chamber is outside the cryostat at room temperature as shown in the diagram. A tube connects the He-3 chamber, the charcoal sorb, and the He-3 pot as shown and allows for transfer of He-3 between these components.

Attaining 1 K at the 1-K pot: The 1-K pot is a small chamber thermally isolated from other components except for the tube that carries He-3. The pot is connected to a scroll pump. Liquid He-4 from the bath is allowed inside the pot through a needle valve which can be controlled from outside. Once the pot is filled, the needle valve is closed. The vacuum pump pumps out the vapor from the pot, decreasing the vapor pressure inside and thus cooling the liquid. This process is called *evaporative cooling*. Temperatures around 1 K can be achieved in this way. Once the pot runs out of LHe, the needle valve is opened again and the process repeats.

Condensing He-3: As mentioned earlier, a tube connects the He-3 chamber, the charcoal sorb and the He-3 pot. This tube is in thermal contact with the 1-K pot as well. High purity activated charcoal at the charcoal sorb adsorbs He-3 at low temperatures. The adsorption of gas by charcoal is highly dependent on its temperature - the lower the temperature, the higher the adsorption. When the sorb reaches 4.2 K, most of the gas in He-3 chamber is adsorbed. At this point, the 1-K pot is filled and pumped to achieve 1 K as explained above. Now, the charcoal sorb is heated using premounted heater coils upto 20 K, which releases the adsorbed He-3 gas. Due to the temperature gradient, the released gas flow towards the 1-K pot instead of the He-3 chamber, where it is condensed to liquid (Since the boiling point of He-3 is 3.19 K). The condensed helium drops into the He-3 pot.

Attaining 300 mK at the He-3 pot: The liquid He-3 should be pumped on to decrease the vapor pressure and attain temperatures down to 300 mK. When enough He-3 is condensed (a few minutes), the charcoal sorb is allowed to cool down to LHe bath temperature (4.2 K). Since the adsorption is high at low temperatures, the charcoal acts as a sorption pump on He-3 pot and temperatures down to 300 mK are achieved by evaporative cooling. The same temperature is achieved on the mount stage which is connected to the lower side of the He-3 pot.

The temperature of the charcoal sorb can be further decreased to increase the pumping if needed, as it is inside a chamber similar to the 1-K pot with a needle valve and a scroll pump connected. We found it useful when the bath LHe level is low.

2.2.4 Sample coldfinger and TDO cell

Figure 2.8(a) and (b) respectively shows the schematic and a photograph of the sample mount and TDO cell. A single crystal sapphire rod (diameter 0.15 cm) is fixed using thermally conductive silver epoxy on a machined single-piece gold-plated oxygen-free high-conductivity (OFHC) copper that attaches to the mount stage of the cryostat [see Figure 2.8(c)]. Sample is mounted on the sapphire rod using GE varnish. Sapphire is an electrical insulator and a good thermal conductor. Since Sapphire doesn't have noticeable susceptibility changes at low temperatures, it won't contribute much to the background data (shown later in Figure 2.12). Since it is electrically insulating, it doesn't produce heating due to eddy currents while inside the primary coil. A Cernox sensor sits at the bottom of the copper piece to measure temperature. A base temperature of 350 mK is achieved at the sapphire in this setup. The mount stage of the cryostat has inbuilt heaters that we use to control the sample temperature using a controller (Lakeshore LS-350).

FIGURE 2.8: (a) The schematic and (b) photograph of the sample mount and TDO cell. (c) The sample mount and coldfinger. (d) TDO cell.

Increasing the thermal load on the He-3 pot will limit the base temperature system can reach. Therefore, the TDO components are thermally isolated from the sample coldfinger and the mount stage. This is done by attaching them to the coldfinger using a thin highly-insulating tube made of Vespel as shown in Figure 2.8(a) and (b). The primary coil is on a copper stage and the other TDO components (tapping coil, resistors, capacitors) are inside a copper housing which can be opened from one side [see Figure 2.8(d)]. Since the resonant frequency is temperature dependent, the temperature of the TDO cell should be maintained at a constant value. The primary coil holder is thermally anchored to the 1-K pot using copper braids. Four G-10 spacers connect the copper housing to the primary coil holder which ensures that there is no thermal conduction between the two. The electronics stage is thermally anchored using copper braids to 4.2 K of the LHe bath and the primary coil stage is thermally anchored to the 1K pot. The primary coil is anchored to a lower temperature to minimize the thermal radiation from the sample coldfinger to it since they operate in close proximity. A heater coil and temperature sensor each are mounted on the primary coil stage and the electronic housing stage which allows for precise control of their temperatures using a Lakeshore LS-335 controller.

Primary and tapping coils: The coils are handmade using insulated copper wires as described in detail in [35, 39]. Two wires are wound side-by-side the required number of turns over a drill bit of desired diameter. Stycast glue is applied on top and one

of the wires is removed before the glue is fully cured, which leaves a uniformly spaced coil which can be removed once the stycast is cured. Thin mylar sheets are wound on the drill bit before winding the wires to prevent the glue from sticking on drill bit and thus facilitating easy removal of the coil. The primary coil should be long enough to attain uniform magnetic field at the center. The windings of the coils are uniformly spaced (spacing equal to the diameter of copper wire used) to minimize the shunting capacitance between adjacent turns. Our primary coil has 22 turns and a length of 0.53 cm and the secondary coil has 8 turns and a length of 0.20 cm. The inner diameter of the coils are 0.30 cm and the diameter of wires used is 0.010 cm.

FIGURE 2.9: Photographs of a handmade coil.

The length and diameter of the primary coil is chosen such that the magnetic field produced by the coil is uniform around the sample, which is typically a platelet with approximate base dimensions $1 \text{ mm} \times 1 \text{ mm}$ and thickness 0.1 mm . The magnetic field along the axis of a solenoid is given by [40],

$$B_z = \frac{\mu_0 n I}{2l} \left[\frac{(l/2 - z)}{\sqrt{r^2 + (l/2 - z)^2}} + \frac{(l/2 + z)}{\sqrt{r^2 + (l/2 + z)^2}} \right] \quad (2.3)$$

where n is the number of turns, I is the current through the coil, l is the length and r is the radius of the coil. This expression tends to a constant value of $B = \mu_0 n I / 2l$ in the limit $(l/2 - |z|) \gg r$, which means we should make quantity l/r as large as possible to achieve a uniform region of magnetic field at the center of the coil. This can be seen in Figure 2.10(a), which shows B_z calculated using eqn.2.3 for different values of r with a fixed value of l . Also, as seen in Figure 2.10(b), while the radial component of magnetic field is zero/negligible close to the centre, it is considerable close to the edges or sides of the coil. Another consideration in making the coil is that the signal to noise ratio will depend on the filling factor of the sample inside, which is the ratio of volume of sample to the volume inside coil (assuming uniform field inside). This means it is not ideal to have a small sample inside a very large coil as the change in resonant frequency due to the sample will be small in that case.

FIGURE 2.10: (a) Magnetic field along the axis for solenoid with fixed length ($l = 5.3$ mm) and different values of r calculated using eqn.2.3. (b) Visualization of magnetic field lines in a solenoid. Adapted from [41].

2.3 Measurement and data processing

2.3.1 Measurement procedure

The sample is mounted on the sapphire rod using GE varnish at room temperature. The GE varnish is allowed to cure and the coldfinger and TDO cell are assembled and mounted on the mount stage of the probe. The vacuum chamber (IVC) is sealed using vacuum grease and pumped for some time. The probe is then inserted into the cryostat. All the sensors and heater coils are checked and the IVC is pumped using a turbo-molecular pump overnight.

Liquid nitrogen is transferred to the cryostat bath to pre-cool the system to 77 K. Helium-4 exchange gas may be introduced in the IVC to facilitate faster cooling. After the system reaches 77 K, the liquid nitrogen is removed and liquid helium is transferred in. The IVC is pumped using the turbomolecular pump and the 1-K pot and outer chamber of the charcoal sorb are connected to scroll pumps. After all the components reach 4 K, the 1-K pot is filled by opening the needle valve and He-3 is condensed to reach the base temperature of 350 mK (see section 2.2.3 for more details).

All the instruments are interfaced to a PC using GPIB cables. Programs written in LabVIEW software are used for monitoring and controlling them. The TDO frequency is monitored at the spectrum analyzer and the signal references to the mixer and lock-in amplifier are set accordingly. The temperature of the TDO cell and primary coil are kept constant using temperature controllers. Now, the drift in frequency with time is measured at the base temperature for a few minutes. Then the temperature of the sample is increased at a constant rate till it passes the transition temperature and the

FIGURE 2.11: Snapshot of the setup.

oscillation frequency is measured as a function of temperature. At the transition, a huge jump in frequency can be seen as the sample goes from a perfectly diamagnetic superconductor that expels field to a normal metal.

2.3.2 Minimising noise

To ensure the noise in the measured data is minimal, we have to understand the sources that can cause errors and keep them in check. The most important of these is the temperature stability of TDO electronics cell and primary coil. As mentioned in section 2.2.4, the primary coil and the electronics stage are thermally anchored to the 1-K pot and liquid helium bath respectively using thick copper braids. There are heaters and temperature sensors on both the primary coil and the electronics stage that allows for precise control of their temperatures using a Lakeshore LS-335 temperature controller. The fluctuation of temperatures of these components are kept under 1 mK. The PID values for temperature control are set accordingly before each measurement.

Another important factor that can affect the stability of oscillations is the biasing of tunnel diode. Section 2.2.2 explains how a precision current source provides a very stable bias for the tunnel diode. The voltage across the 5 k Ω resistor (~ 3 V) is monitored on a Keithley-2000 voltmeter and the fluctuations are kept under 1 μ V. To achieve voltage this stable, one has to wait at least 12 hours after connecting the instruments and cooling

down the system to 4 K. Waiting for a long time after transferring liquid helium is also helpful in reducing vibrations induced due to vigorous boiling of the liquid.

The vacuum pumps are placed on vibration buffers and are connected to the cryostat via vibration dampers to minimize the mechanical vibrations. The cryostat is covered with a mu-metal shield that ensures no electromagnetic interference to the components inside. There are also systematic errors present such as the drift in data and the background signal. Tackling of these will be explained in the following section.

Ensuring accuracy of the sample temperature: It is important that the measured sample temperature is accurate so that we capture an accurate temperature dependence of the penetration depth. We saw in section 2.2.4 that the sample is mounted on a sapphire rod and the temperature is measured using a Cernox sensor mounted close to the other end of the sapphire (which is much closer to the sample than the inbuilt sensor on the cryostat mount stage) to get an accurate measurement of the sample temperature. To ensure good thermal contact between the sample and sapphire, we use a small amount of GE varnish to mount the sample. Once the GE varnish solidifies, sample is stuck to the sapphire rod and mechanical vibrations will not affect the contact between sample and sapphire. Similar TDO systems have previously been shown to have reliable sample temperatures down to low temperatures [35].

We use a slow temperature ramp rate at low temperatures (typically 30 mK per minute for $T < 1$ K). We wait for a few seconds (10 s) before taking measurements at each step for the temperature to ramp up and to ensure that the sample reaches the set temperature. Measurements of frequency is then taken for a few seconds and is averaged. For each sample, we do multiple runs to compare the temperature dependence. We also compare the major features such as the transition temperature with other measurements like resistivity. We have also measured standard samples like Aluminum and found that the temperature dependence is as expected (more details on this in the next section).

2.3.3 Data processing

We measure the resonant frequency of the oscillator circuit as a function of temperature of the sample – $f(T)$. We then subtract the systematic errors such as drift and background, estimate $f(T = 0)$ and subtract it from the data to obtain $\Delta f(T)$, then convert it to $\Delta\lambda(T)$ and then to ρ_s . In this section, I explain this process of obtaining penetration depth and normalized superfluid density from the measured data.

2.3.3.1 Drift and background in data

There is a drift in data even when the temperature of all the components and the sample is kept constant. This changes for every measurement and can be monotonically increasing or decreasing in most cases. We wait at base temperature for the drift to increase or decrease monotonically and measure the drift as a function of time for a few minutes before each experiment. We then measure the data assuming the drift stays the same for the duration of measurement. During the measurement, time is also noted at each data points. The drift is then fitted with a straight line and subtracted from the data. The usual drift during measurement is in the range 0.01-0.05 Hz per minute. This is very small compared to the temperature-dependent change in resonant frequency of the circuit caused by the sample, which is usually hundreds of Hz.

FIGURE 2.12: Background data and linear fit.

There is a small background data due to the sapphire rod and the GE varnish that is used to mount samples on it. We have measured this background data without any sample mounted as a function of temperature. This is fitted to a straight line or polynomial appropriately in different temperature ranges. This background signal is subtracted from the data measured. An example for the background data is shown in Figure 2.12. The data is a bit noisy because the change in frequency is very small. The change in frequency due to this background is less than 1 Hz when temperature changes from 0.4 K to 10 K and is even negligible at low temperatures. Most of the samples we measure have

T_c less than 10 K and have a frequency change of the order of kHz, so this background is very small compared to the actual signal. By eliminating even small systematic errors, we have made our data accurate to a high degree (noise levels less than 4 parts per 10^9).

2.3.3.2 Obtaining penetration depth

As we have seen in the start of this chapter (equation 2.2), the change in penetration depth, $\Delta\lambda(T) = \lambda(T) - \lambda(0)$, can be obtained by,

$$\Delta\lambda(T) = G\Delta f(T) \quad (2.4)$$

where $\Delta f(T) = f(T) - f(0)$ is the change in oscillator frequency with respect to the frequency at $T = 0$ K and G is a calibration factor. Details of derivation of this equation and other equations in this section can be found elsewhere [26, 35, 39].

Since we cannot measure $f(0)$, the next step in data processing after subtracting background and drift is the estimation of frequency at $T = 0$ K. We have already seen in section 1.6 that the low temperature behavior of the penetration depth can be exponential or power-law depending on the nature of pairing mechanism and symmetry. We fit the low temperature part ($T < 0.3T_c$) of the frequency data ($f(T)$) with an exponential or a power-law depending on its behavior with an additional intercept parameter. The y-intercept obtained from the fit is the estimated $f(0)$. This $f(0)$ is then subtracted from the data to obtain $\Delta f(T)$.

To convert $\Delta f(T)$ to $\Delta\lambda(T)$, we need to determine the calibration factor G . This depends on the sample and coil properties as [24],

$$G = \left(\frac{2R_{3D}(1-N)}{V_s} \right) \frac{V_c}{f_0} \quad (2.5)$$

V_c is the volume of primary coil and $f_0 = 1/(2\pi\sqrt{LC})$ is the resonant frequency of the TDO without sample. These two parameters are dependent only on the TDO setup and therefore do not change for different measurements. V_s is the volume of the sample and N is the demagnetization factor (explained below) for the sample. R_{3D} is an effective dimension of the sample. For a square sample with side $2w$ and thickness $2d$ with $d \ll w$, R_{3D} can be calculated as [42],

$$R_{3D} = \frac{w}{2 + \left[2 \left(1 + \frac{2d}{w} \right)^2 \tan^{-1} \left(\frac{w}{2d} \right) \right] - \frac{4d}{w}} \quad (2.6)$$

Demagnetization factor (N): When a magnetic sample is placed in an external magnetic field, an opposing field is developed inside the sample known as demagnetizing field. This effectively changes the strength of magnetic field in the material, causing erroneous measurements of magnetic properties. This situation can be overcome by correcting the magnetic field strength with a demagnetization factor that depends on the sample geometry. The demagnetization factor can be obtained from the magnetization vs field (M vs H) measurements using an MPMS (Magnetic Property Measurement System). The slope of M vs H curve in the Meissner state ($H < H_{c1}$) gives the demagnetization factor;

$$\frac{M}{H} = \frac{-1}{4\pi(1 - N)} \quad (2.7)$$

M is the magnetization per unit volume of the sample (in emu/cm³) and H is the applied field (in Oe). It should be noted that the obtained N is in SI units, i.e., $0 < N < 1$. This definition of N will be used subsequently in this thesis unless specified otherwise.

For samples with large aspect ratios, N can also be estimated approximately as [42],

$$\frac{1}{1 - N} \approx 1 + \frac{w}{2d} \quad (2.8)$$

System calibration: We first measure a high purity (99.9995%) aluminum sample with $d \ll w$ as a reference sample as superconducting parameters for aluminum is well known. The data obtained is converted to normalized superfluid density and then fit to known BCS standard curve in the pure non-local limit where superfluid density is given by [1],

$$\rho_s(T) = \left[\frac{\Delta(T)}{\Delta(0)} \tanh \left(\frac{\beta \Delta(T)}{2} \right) \right]^{-1/3} \quad (2.9)$$

A gap of the form eqn 1.9 and the weak-coupling parameters mentioned in section 1.3 was used for fitting. The data and fit is shown in Figure 2.13. The process of obtaining ρ_s and fitting will be explained in subsequent sections.

We obtain G for the reference aluminum sample (G_{Al}) from this fit ($G_{Al} = 10.7 \text{ } \text{\AA}/\text{Hz}$ for our case). Using equation 2.5, we can find G for any other sample with a similar geometry ($d \ll w$) as,

$$\frac{G}{G_{Al}} = \frac{2R_{3D}(1 - N)}{2R_{3D,Al}(1 - N_{Al})} \frac{V_{Al}}{V_s} \quad (2.10)$$

G , R_{3D} , N , and V_s are the values for the sample measured and G_{Al} , $R_{3D,Al}$, N_{Al} , and V_{Al} are the corresponding values for the aluminum reference sample.

The estimated G using these techniques might have up to 20% error [43]. But since it is a multiplicative factor, the functional dependence of penetration depth is not affected.

FIGURE 2.13: Normalized superfluid density data and non-local BCS fit of Al reference sample. Inset is a picture of the sample.

For all the parameters such as gap-ratio obtained from the superfluidity data, we find the standard error taking into account this error in estimating G .

2.3.3.3 Obtaining normalized superfluid density

As explained in section 1.4, the normalized superfluid density gives information about the energy gap, pairing symmetry, and coupling strength. The last step in data processing is to calculate the normalized superfluid density and then use the relation 1.11 to do a fitting and obtain the physics of energy gap. To obtain ρ_s from $\Delta\lambda$, we rewrite equation 1.13 as,

$$\rho_s(T) = \left(\frac{\Delta\lambda(T)}{\lambda(0)} + 1 \right)^{-2} \quad (2.11)$$

$\lambda(0)$ is the penetration depth at $T = 0$ K. This can be determined by methods such as muon-spin resonance (μ SR) [28]. If this is not available, we keep this as a variable and determine it by fitting ρ_s using equation 1.11. From this fit, we obtain the value of $\lambda(0)$ (if it is a fitting parameter) along with other parameters such as the gap ratio (δ_{sc}) and specific heat jump ($\Delta C/C$). Different gap models (s -wave, d -wave, anisotropic s -wave, etc) will be used to identify the best fit for data. Usually, T_c is identified from

the measured data as the temperature at which a huge jump that corresponds to the superconducting transition occurs (see Figure 1.13).

We do not fit the penetration depth directly, because the penetration depth diverges at T_c and is hence impractical to fit it using different models for the whole temperature range. Penetration depth for typical BCS superconductors follows [1]

$$\lambda(T) = \frac{\lambda(0)}{\sqrt{1 - (T/T_c)^4}} \quad (2.12)$$

As we have seen in chapter 1, it is at low temperatures ($T < 0.3T_c$) that the difference between nodal and nodeless gap is most pronounced. Therefore, we analyze the penetration depth data at low temperature and then convert it to normalized superfluid density to analyze the data over the whole temperature range. In some nodal superconductors, low-temperature penetration depth can have a false quadratic behaviour even when superfluid density is linear at low temperatures. It is important to analyze ρ_s in such cases. By converting to ρ_s , we can also ensure that the whole data gets significant contribution in the fit and it enables us to see features in intermediate temperatures better.

Error in ρ_s : Let's now try to figure how uncertainty in measuring penetration depth translate to uncertainty in the calculated normalized superfluid density. Using σ_x to denote the standard deviation in measurement of the variable x , from equation 1.13, the uncertainty in ρ_s can be expressed as

$$\sigma_{\rho_s}^2 = 2 \left[\sigma_{\lambda(0)}^2 + \sigma_{\lambda(T)}^2 \right] \quad (2.13)$$

Since $\lambda(T) = \lambda(0) + \Delta\lambda(T)$, where $\Delta\lambda(T) = G \Delta f(T)$, this becomes

$$\sigma_{\rho_s}^2 = 2 \left[2\sigma_{\lambda(0)}^2 + \sigma_G^2 + \sigma_{\Delta f(T)}^2 \right] \quad (2.14)$$

The uncertainties in measuring the resonant frequency are quite low since the random fluctuations in frequency measurement is only around 0.05 Hz (see Figure 2.12). For example, let's say $\Delta f = 1$ Hz at the base temperature. Assuming typical values of $G = 10 \text{ \AA/Hz}$ and $\lambda(0) = 2000 \text{ \AA}$, we calculate ρ_s to be 0.99007. Calculating the error bar considering a fluctuation of 0.05 Hz in measurement, we obtain $\rho_s = 0.9901 \pm 0.0005$. Do note that as the temperature increases, the value of Δf increases while the fluctuations staying the same, and hence the error contribution from frequency measurement will decrease. For example, at $\Delta f = 1000$ Hz, the error contribution due to frequency measurement is 2×10^{-6} while $\rho_s = 0.278$. Let's look at the normalized superfluid

FIGURE 2.14: (a) Random error (green shaded region) due to frequency measurement in normalized superfluid density. Inset shows the low-temperature region. (b) Change in normalized superfluid densities due to 10% change in G . Inset shows the corresponding change in fitting parameters. (c) Change in normalized superfluid densities due to 10% change in $\lambda(0)$. Inset shows the corresponding change in fitting parameters.

density for PdTe_2 (which will be discussed in Chapter 3) as an example. The error calculated in the normalized superfluid density due to the fluctuations in frequency measurement is shown as the green shaded region in Figure 2.14(a). It is almost too small to see in the figure as even the error bars at low temperatures are only about the size as line-width for the plot. The low-temperature region of the data is shown in the inset and it can be seen that the error decreases with increasing temperature as expected.

The major contribution of error in ρ_s is from the calibration factor G and $\lambda(0)$, as they can have up to 10% error. To visualize this, the normalized superfluid densities for PdTe_2 calculated with three different values of G and $\lambda(0)$ are shown in Figure 2.14 (b) and (c) respectively. While it doesn't affect our conclusions from fitting the data (isotropic gap with moderate coupling in this case), it does affect the fitting parameters as shown in the table in the inset. The gap ratio doesn't change much in both cases, but the estimated specific heat jump does have a considerable spread.

From the above exercise, we see that the error in ρ_s from random fluctuations in frequency measurements is negligible and the main contributors are G and $\lambda(0)$. G is calculated from sample dimensions and $\lambda(0)$ is determined experimentally using other methods such as magnetization or μSR , or used as a fitting parameter. Care should be

taken to determine these quantities with reasonable accuracies to minimize the error in normalized superfluid density.

2.4 Fitting ρ_s

2.4.1 Implementation in MATLAB

As discussed earlier, to obtain parameters such as gap ratio, specific heat jump, and the nature of superconducting energy gap, we have to fit the obtained data to various models and determine the best fit. I used MATLAB to write a code that will fit the data using a theoretical model and determine the best fit. The code will then give the parameters for best fit as output.

FIGURE 2.15: Logic flow for fitting code.

The simplified algorithm for fitting is shown in Figure 2.15. The experimental data of normalized superfluid density is given as input. The user then chooses what parameters to vary and which ones to keep constant. Generally, T_c , which can be determined from the penetration depth data is kept constant. The gap ratio (δ_{sc}) and specific heat jump ($\Delta C/C$) required to calculate the energy gap ($\Delta(T)$) are variables. After selecting the parameters to vary, the user then inputs the values of constant parameters and an initial guess value for the variables. These inputs are then used to calculate the energy gap and then ρ_s . This simulated superfluid density is then compared with the input data and the MSE (Mean Square Error) between the fit and data is calculated. A minimization function is used to minimize the MSE by varying parameters and repeating the process

to find the best fit. After the function is minimized, the code outputs the best fit and the parameters used for best fit.

There are various inbuilt functions for optimization in MATLAB such as *fminsearch*, *lsqnonlin*, etc that can be used for minimization and fitting problems [44]. We found it effective to use the *fminsearch* function for our purpose. It uses an algorithm based on Nelder-Mead simplex algorithm [45]. It varies the fitting variables following the algorithm to minimize the MSE and thus obtain the best fit. The Jacobian matrix returned by the function is used to find the errors in the obtained fitting parameters.

2.4.2 Various gap models and calculation of ρ_s

To calculate normalized superfluid density, equation 1.11 is used. In terms of E , it can be written as,

$$\rho_s(T) = 1 + 2 \int_0^{4\pi} \frac{d\Omega}{4\pi} \int_0^\infty \frac{\partial f}{\partial E} \frac{EdE}{\sqrt{E^2 - \Delta^2(T)}} \quad (2.15)$$

The Fermi function (f) and energy gap ($\Delta(T)$) are functions of temperature. As we have seen in section 1.6, the low temperature behavior of penetration depth can be used to identify the symmetry and number of nodes of the energy gap. This narrows down what energy gap to be used for this calculation. If the low temperature behavior of penetration depth is exponential as described in equation 1.14, then we use the gap equation 1.9;

$$\Delta(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\} \quad (2.16)$$

Anisotropic gaps without nodes can also give an exponential behavior at low temperatures. So, if the isotropic s -wave doesn't fit the data very well, or if the values obtained from fit are unphysical, then we try and use anisotropic gaps to obtain the best fit. In this case, Δ depends on polar coordinates θ and ϕ on the Fermi surface and the integration over solid angle $d\Omega/4\pi$ in equation 2.15 will account for the anisotropy.

For unconventional superconductors with nodes in the energy gap, the low temperature behavior of penetration depth is a power-law as described in equation 1.15. We use the exponent to determine the symmetry of the system as explained in section 1.6. Then we use appropriate gap functions to calculate the ρ_s . Similar to the anisotropic case, energy gap will depend on θ and ϕ . A d -wave gap with line nodes has a functional form as,

$$\Delta'(T) = \Delta(T) \cos(2\theta) \quad (2.17)$$

where $\Delta(T)$ is the isotropic gap described in equation 2.16. More details on different gap symmetries and their functional forms can be found in [24].

FIGURE 2.16: Calculated normalized superfluid densities for various gaps: (a) s -wave gap (Equation 2.16 with weak coupling parameters), (b) d -wave gap (Equation 2.17 with weak coupling parameters), and (c) two s -wave gaps (Equation 2.18 with $r=0.5$).

Another class is the multiple gaps that contribute to superfluid density in multi-gap superconductors. The normalized superfluid density in this case is calculated as

$$\rho_s = r\rho_{s1} + (1 - r)\rho_{s2} \quad (2.18)$$

where ρ_{s1} and ρ_{s2} are normalized superfluid densities calculated using two different gaps. r can range from 0 to 1 and is the weight factor that determines the contribution of each gap to superfluid density. The two gaps may or may not have the same symmetry and can have different transition temperatures as well. This means that the gaps can close at two different temperatures.

Figure 2.16 shows calculated normalized superfluid densities for an isotropic s -wave gap, a d -wave gap, and a multi-gap with two isotropic s -wave gaps. BCS weak coupling parameters (see section 1.3) were used for calculations and r for the multi-gap model was set to be 0.5. Details on fittings for specific samples and changes will be explained later as needed.

2.5 Comparison with other techniques

As we have seen so far, TDO-based penetration depth measurement technique can be used to get information on the superconducting energy gap, including the pairing symmetry and the presence of nodes. Common techniques that are used to measure penetration depth were introduced and compared in section 1.6.3. Penetration depth is not the only measurement that can be done to study the symmetry of superconducting order parameter. In this section, I briefly introduce some of the common experimental techniques and compare them with our TDO-based system and talk about the pros and cons of each.

Specific heat measurements [46]: The specific heat has a discontinuity at the superconducting transition temperature and the specific heat jump at T_c is considered an indicator of the coupling strength as explained in section 1.3. Different calorimetry techniques are used to measure the specific heat. The temperature dependence of electronic specific heat at low temperatures can be used to identify the presence of nodes in the energy gap. This is similar to the case for penetration depth as the temperature dependence of low temperature data is indicative of the presence of excited quasiparticles. An exponential behaviour is expected for isotropic gaps and a power-law behaviour is an indicator of the presence of nodes. Information about the energy gap can be further obtained by fitting the specific heat data to various gap models. The major difference of this technique compared to TDO is that specific heat is a bulk measurement while TDO is a surface sensitive measurement. Extracting electronic specific heat requires subtraction of the phonon contribution, which is tricky and can introduce errors [47]. The TDO technique has a much higher resolution and is much more sensitive to impurities too.

Tunneling measurements [48]: STM (Scanning Tunneling Microscopy)-based spectroscopic techniques are used to measure the quasiparticle spectrum in the superconducting state. In its simplest form, the tunneling current between a normal metal and a superconductor sample is measured at different voltage levels, which can then be converted to quasiparticle density of states. For an isotropic gap, the conductance at low voltages (energies less than the gap magnitude) is zero, while for a gap with nodes, it is linear. The obtained spectrum can be fit using various gap models. Using point contacts and directional studies, anisotropies in the energy gap can also be studied. Tunneling spectroscopy is a surface sensitive technique and requires crystals with a clean and atomically smooth surface plane. This technique also relies on the quality of contacts, and there are uncertainties due to the tunneling cone and surface stress/distortion.

Photoemission studies [49]: A photon of sufficient energy can cause the ejection of electrons from the surface of a material due to the photoelectric effect. By measuring the angles and kinetic energies of emitted electrons, the electronic band structure in the energy-momentum space can be mapped. Angle-resolved photoemission spectroscopy (ARPES) is used to measure the superconducting energy gap around the Fermi surface directly. The symmetry and magnitude of the gap can thus be obtained. ARPES measurements are extremely sensitive to the sample surface.

The TDO method is a surface sensitive measurement, but is not extremely surface sensitive as ARPES or STM (few Å). Typical penetration depths of superconductors range from 10-1000 nm at 0 K and increase with increasing temperature. TDO probes the region inwards starting at the base temperature. While we need samples to be clean, we do

not require the extreme surface cleanliness and ultra high vacuum environment required for surface measurements like ARPES. Normalized superfluid density can be calculated and fitted to different gap models with relative ease, but TDO measurement and the subsequent fitting are an average over the Fermi surface. Therefore, we cannot distinguish gaps that are similar when averaged over the Fermi surface, while techniques like ARPES can probe the angular dependence of the gap directly. The main advantage of using TDO is it's high resolution with noise levels less than 4 parts in 10^9 , which enables us to identify the temperature dependence robustly, especially at low temperatures.

TABLE 2.1: Summary of some common measurement techniques.

Technique	Pros	Cons
Specific Heat	<ul style="list-style-type: none"> • Bulk measurement. • Parameters such as Sommerfeld coefficient, Debye temperature, and entropy are obtained. • Can identify gap symmetry from fitting. 	<ul style="list-style-type: none"> • Cannot directly probe gap symmetry. • Requires subtraction of phonon contribution, which can cause errors.
ARPES	<ul style="list-style-type: none"> • Measures the gap in k-space directly. • Can also be used to study pseudo-gap and other features in the band structure. 	<ul style="list-style-type: none"> • Extremely sensitive to the surface. • Requires ultra high vacuum environment from sample growth to measurement.
STS	<ul style="list-style-type: none"> • Measures the density of states at surface. • Can be fitted to identify gap symmetry. • Anisotropies in gap can be studied by modifying the technique. 	<ul style="list-style-type: none"> • Extremely surface sensitive. • Requires ultra high vacuum environment. • Depends on quality of tips/contacts. • Uncertainties due to surface stress and tunneling cone.
μ SR	<ul style="list-style-type: none"> • Bulk measurement. • Insensitive to shape and surface properties. • Measures absolute value of penetration depth. • Identifies gap symmetry from fitting. 	<ul style="list-style-type: none"> • Noisy data - large error bars. • Requires access to particle accelerator. • Can only measure type-II SC or type-I SC with domain separation. • Requires modeling of vortex lattice which may introduce errors.
TDO	<ul style="list-style-type: none"> • Surface sensitive. • High resolution. • Identify gap symmetry from fitting. 	<ul style="list-style-type: none"> • Only able to measure the change in penetration depth. • Cannot probe the gap symmetry directly.

Chapter 3

PdTe₂ - A Topological Superconductor ?

3.1 Introduction

Transition metal dichalcogenides (TMDs) are extensively studied in recent years for physical phenomena such as superconductivity [51, 52] and charge density waves [53], and as two dimensional materials [54]. TMDs have a general formula of MX₂ where M is a transition metal and X is a chalcogen (S, Se, Te). They have a layered structure crystallizing in an octahedral or trigonal prism structure as shown in Figure 3.1.

Topological superconductors (TSC) have a bulk superconducting gap and topologically protected gapless surface states [55–57]. These surface states can host Majorana fermions, which are zero-energy excitations of quasiparticles. They are of high research interest due to its intriguing physics and potential applications such as in quantum computing [58]. The search for topological superconductors is thus of high interest in the recent years. Topological band structure in the normal state may be an indication of topological superconductivity. One method is to induce superconductivity in a topological insulator by doping or by proximity effect by stacking it with a regular fully-gapped superconductor [55].

FIGURE 3.1: Structure of TMDs. Adapted from [50].

Weyl semimetals are another candidate [57]. They are materials with conduction band and valence band touching at Weyl points in the Brillouin zone [59, 60]. These Weyl points are protected against gap formation by time reversal symmetry or crystalline symmetry. Dirac semimetals are a closely related class which are a 3D analog of graphene with a cone shaped linear dispersion called Dirac cones around Dirac points [59, 60]. They have a double degeneracy. Time reversal symmetry breaking or inversion symmetry breaking can lead to breaking of the degeneracy and formation of a pair of Weyl cones [61]. This can be achieved by external fields, magnetic order, etc.

$PdTe_2$ was recently found to be a type-II Dirac semimetal [62, 63]. In type-II Dirac semimetals, Lorentz invariance is broken, whereas in type-I, it is obeyed [64, 65]. Unlike the case for high-energy physics, Lorentz symmetry (which requires physical laws to be independent of the frame of reference) can be broken in low-energy condensed matter systems. In Dirac semimetals, this is realized as having tilted Dirac cones. In this case, the Fermi energy plane cuts the cone in a line, compared to a point in type-I, making the topology different. This can lead to type-II Weyl semimetals [66]. Majorana modes predicted to be found in topological superconductors are more stable in type-II Dirac semimetals [55].

FIGURE 3.2: (a) Breaking degenerate Dirac cone to form a pair of Weyl cones.
(b) Type-I and Type-II Weyl cones. Adapted from [67, 68]

Although superconductivity in PdTe_2 with a T_c of 1.7 K was discovered in 1961 [69] and single crystals were prepared in 1974 [70], it is only in the recent years that PdTe_2 (and other TMDs) gained a lot of research interest as a candidate for topological superconductivity. PdTe_2 is the first compound discovered having both superconductivity and Dirac fermions. Similar band structures were also observed in other TMDs such as PtSe_2 , WSe_2 , etc [71]. In 2015 Y. Liu et.al. discovered topological surface states which are well separated from bulk states in PdTe_2 superconductor by ARPES measurements [72]. They found helical spin texture similar to that in a 3D topological insulator, but the Dirac cone was found to be well below the Fermi level as opposed to being near the Fermi level in a topological insulator. A later study in TMDs (mainly 1T- PdTe_2) showed formation of tilted type-II bulk Dirac cones which are caused by the band inversions of the p -orbitals of chalcogenides, and hence are resilient to changes in crystal structure or orbital mixing [71]. Later studies found more evidence for type-II Dirac fermions and identified more topological surface states including ones that intersect the Fermi level [62, 63].

The study of superconducting properties of PdTe_2 gained a newfound interest with these discoveries. Conventional superconductivity or a fully gapped superconductivity was the conclusion from majority of these studies including scanning tunneling microscopy (STM) [63, 73], heat capacity [74], scanning tunneling spectroscopy (STS) [75], penetration depth [76], point contact spectroscopy [77], etc. However, these studies don't seem to agree on the coupling strength. The most surprising and controversial observation was however the nature of superconductivity itself with magnetic and transport measurements showing type-I superconductivity in PdTe_2 [78]. Binary compounds like this are usually type-II with only a small number of exceptions. This observation was confirmed in STM, penetration depth, and μSR studies too [73, 76, 79], until evidence for type-II superconductivity was observed at the surface from ARPES studies [63]. Further studies have revealed a mixture of type-I and type-II superconductivity in the material with the bulk having type-I superconductivity and type-II superconducting regions existing on the surface [77, 80].

It is therefore interesting to measure this sample and find out the superconducting gap, and more importantly the coupling strength as the literature doesn't agree on this matter. In this chapter, I present the penetration depth data of PdTe_2 single crystals measured using our TDO setup. The change in penetration depth shows an exponential behavior at low temperature implying a nodeless gap, which is in agreement with studies mentioned above. The fit to superfluid density confirms this and the fit parameters indicate that PdTe_2 is a moderately coupled superconductor. We also figure out whether it is a type-I or type-II superconductor by comparing the penetration depth and coherence length. Our results confirm type-I superconductivity in the bulk. We

also discuss what these results mean for the compound to be a potential topological superconductor.

3.2 Data and Observations

PdTe_2 has a layered CdI_2 -type structure with octahedral coordination as shown in Figure 3.3(a) and belongs to the space group $P\bar{3}ml$. There is one palladium and two tellurium atoms in the unit cell. The lattice constants are $a = b = 4.03 \text{ \AA}$ and $c = 5.13 \text{ \AA}$. The c/a ratio of 1.27 is smaller than that of an ideal octahedron (1.63). The Brillouin zone is a hexagonal prism and is shown in figure 3.3(b).

FIGURE 3.3: (a) Tetragonal structure of 1T-PdTe₂. (b) The corresponding Brillouin zone. (c) Resistivity vs temperature for various applied fields

High-quality single crystals samples grown by chemical vapour transport were obtained from Sasagawa group at the Tokyo Institute of Technology, Japan [81]. These were cleaved *in situ* and have a platelet shape that is ideal for penetration depth measurements with our system. Figure 3.3(c) shows the resistivity vs temperature data for various

applied fields. The applied fields are parallel to the c -axis. When the external field is 0, the onset of transition occurs around 1.7 K and zero resistivity is attained at 1.5 K.

A rectangular platelet sample with base area 0.72 mm^2 and thickness 0.03 mm was used for penetration depth measurement. This gives a G value of $10.7 \text{ \AA/Hz}$. The sample was mounted such that magnetic field is parallel to the c -axis. The penetration depth data ($\Delta\lambda(T)$) for $PdTe_2$ is shown in Figure 3.4. As seen in the figure, the superconducting transition starts around 1.6 K and is quite sharp with a T_c of 1.7 K. The inset shows low-temperature portion ($T < 0.35T_c$) of the data. As discussed in section 1.6, we try to fit it with an exponential of the form 1.14 with δ_{sc} and $\lambda(0)$ as fitting parameters and T_c fixed. Red line shows the fit and is pretty good, which is an indication of nodeless superconductivity. The value for parameters obtained are: gap ratio, $\delta_{sc} = 2.14 \pm 0.05$ and penetration depth at absolute zero temperature, $\lambda(0) = 3100 \pm 500 \text{ \AA}$. This value of gap ratio is higher than the BCS weak coupling limit of 1.76, suggesting that $PdTe_2$ is a moderately-coupled superconductor.

FIGURE 3.4: Penetration depth data for $PdTe_2$. Inset shows the low temperature data and fit to an exponential.

We cannot draw any conclusions from the low temperature data only. So, now we proceed to calculate the normalized superfluid density as described in section 2.3.3.3 using the equation $\rho_s(T) = \left(\frac{\Delta\lambda(T)}{\lambda(0)} - 1 \right)^{-2}$. This is then fit using the procedure described in section 2.4. $\rho_s(T)$ and best fit is shown in Figure 3.5. Since the low temperature fit of

FIGURE 3.5: Normalized superfluid density for PdTe_2 . Blue circles are the data, red line is the best fit using an isotropic s -wave gap model, and green dashed line is the superfluid density for BCS weak coupling limit. Inset is an optical image of the sample.

$\Delta\lambda(T)$ suggested a nodeless gap, we used equation 2.16 as the gap model.

$$\Delta(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\} \quad (3.1)$$

For the fitting, we allowed δ_{SC} , $\Delta C/C$, and $\lambda(0)$ to be variables and kept the T_c constant at 1.61 K. This T_c was chosen because we noticed that the superfluid density goes to zero at this temperature for reasonable values of $\lambda(0)$. The best fit shown as red line in the figure was achieved for parameters $\delta_{sc} = 2.14 \pm 0.02$, $\Delta C/C = 2.25 \pm 0.04$, and $\lambda(0) = 2000 \pm 50 \text{ \AA}$. The curve for BCS weak coupling limit ($\delta_{sc} = 1.76$, $\Delta C/C = 1.43$, and $\lambda(0) = 2000 \text{ \AA}$) is shown as dotted green line for comparison. The value of gap ratio agrees perfectly with the one obtained from exponential fit of the low temperature penetration depth. The values for gap ratio and specific heat jump are higher than the BCS weak coupling values, implying that the coupling strength is moderate.

We chose to keep $\lambda(0)$ a fitting parameter and not to go with the value obtained from the low temperature fit. Generally, the value of $\lambda(0)$ from the low temperature fit of penetration depth is a rough estimate and is not regarded accurate. As we see, the estimate from superfluid density fit agrees with other similar studies [76] and is hence more accurate. This value of $\lambda(0) = 200 \text{ nm}$ however differs from the 39 nm obtained

in Ref.[78]. An explanation for this is given in Ref.[76] as the low value in obtained in Ref.[78] might be from overestimating the carrier density in calculations.

With this and taking the coherence length $\xi = 439$ nm from Ref.[78] and [76], we obtain a Ginzburg-Landau parameter $\kappa = \lambda(0)/\xi = 0.46$. As explained in sections 1.2.3 and 1.2.4.1, if $\kappa < 1/\sqrt{2}$, system prefers type-I superconductivity and if $\kappa > 1/\sqrt{2}$, type-II superconductivity is favoured. In our case, clearly, $\kappa = 0.46 < 1/\sqrt{2} \approx 0.7$. Therefore, we can confirm that the superconductivity of bulk $PdTe_2$ is indeed type-I.

FIGURE 3.6: (a) Penetration depth data for sample #2. Inset is an optical image of the sample. (b) Low temperature data and exponential fit. (c) Comparison of superfluid densities from both samples (d) Superfluid density and best fit for sample #2.

To check the reproducibility of data and to confirm the findings, we took data on another $PdTe_2$ sample (Sample #2). Figure 3.6(a) shows the penetration depth data and 3.6(b) shows the low temperature data and exponential fit. As expected, the fit is good with the fitting parameters $\delta_{sc} = 1.87 \pm 0.03$ and $\lambda(0) = 2200 \pm 200$. A comparison of the calculated superfluid densities of the two samples are shown in Figure 3.6(c). As seen they are very similar within the margin of error. As mentioned earlier, the estimation of calibration factor for the sample is not accurate and there can be errors upto 20% in the estimated G. We account for this error in our parameter estimates. The best

fit for normalized superfluid density data of sample #2 is shown in Figure 3.6(d). The parameters for best fit are $\delta_{sc} = 1.95 \pm 0.03$, $\Delta C/C = 2.30 \pm 0.08$, and $\lambda(0) = 1670 \pm 30$ Å. The $\Delta C/C$ value agrees very well with the value for sample #1, and the values for δ_{sc} and $\lambda(0)$ also agree within reasonable margins. This confirms our findings that the coupling strength of PdTe_2 is moderate and the energy gap is an isotropic s -wave.

To confirm self consistency of the obtained parameters, we use the strong coupling correction equations [82],

$$\eta_\delta = 1 + 5.3 \left(\frac{T_c}{\omega} \right)^2 \ln \left(\frac{\omega}{T_c} \right) \quad (3.2)$$

$$\eta_c = 1 + 1.8 \left(\frac{\pi T_c}{\omega} \right)^2 \left(\ln \left(\frac{\omega}{T_c} \right) + 0.5 \right) \quad (3.3)$$

where ω is a characteristic frequency and η_δ and η_c are the correction factors for gap ratio and specific heat jump respectively, which is defined as the ratio of obtained value and BCS weak coupling value. We use $\eta_\delta = 2/1.76 = 1.14$ in equation 3.2, find ω and substitute it in equation 3.3 to find η_c . This gives $\Delta C/C = 2.35$ which is consistent with the obtained value from fits.

3.3 Discussion

This data is very similar to another compound our group had measured earlier: $\alpha\text{-PdBi}_2$ (See Ref.[83]). Much like PdTe_2 , $\alpha\text{-PdBi}_2$ is a topological superconductor candidate which was found to have nodeless s -wave like superconducting gap with moderate coupling by penetration depth measurements. It is therefore quite natural to compare these two compounds. A signature of the topological states which is predicted to host gapless excitations on the surface was notably absent in $\alpha\text{-PdBi}_2$. It was argued that this might be due to the limitation of penetration depth measurements to probe states that are less than $\lambda(0)$ away from the surface.

A visualization of this is shown in Figure 3.7. TDO probes states starting from $\lambda(0)$ inwards. The surface states in a topological superconductor are expected to be within a few coherence lengths from the sample surface. In a type-II superconductor, since $\xi \ll \lambda(0)$, TDO is unable to probe these surface states.

As we have already established that $\xi > \lambda(0)$ for PdTe_2 and is hence a type-I superconductor, this explanation doesn't hold for our case. An explanation can be found in Ref.[76] that has similar data and observations to ours from their penetration depth measurements. They find that the data is consistent with a fully gapped superconducting state with $\kappa < 1/\sqrt{2}$. They did not however find evidence for moderate coupling,

FIGURE 3.7: Limitation of TDO to probe surface states in a type-II superconductor. Adapted from [25].

probably because the gap ratio is not allowed to be a variable, but was fixed in the fitting to superfluid density.

Comparing this to detailed theoretical symmetry analysis, they find that the nodeless superconducting gap in PdTe_2 can have three possible pairing states, two of which can be topologically non-trivial. First possibility is the isotropic s -wave pairing, which is topologically trivial. The other two possibilities are odd-parity triplet states – a p -wave phase and another triplet order parameter, both of which can be topologically trivial or non-trivial, depending on the pairing mechanism.

This highlights another limitation of our penetration depth measurements. In our fitting of superfluid density using equation 1.11, we are averaging over the Fermi surface. Hence, we cannot distinguish between gaps that are similar when averaged over Fermi surface, even though their functional form might be different.

3.4 Conclusions

We have measured the penetration depth of single crystals of PdTe_2 superconductor to temperatures down to 350 mK using tunnel diode oscillator based setup. The transition temperature was found to be ~ 1.6 K and low temperature data was found to be exponential, indicating nodeless gap. From calculating the normalized superfluid density and fitting it, the superconductor was found to be fully gapped with moderate coupling strength. The gap ratio, specific heat jump and penetration depth at absolute zero were estimated from fitting as $\delta_{sc} = 2.0 \pm 0.1$, $\Delta C/C = 2.2 \pm 0.1$, and $\lambda(0) = 2000 \pm 400$

Å. The estimated $\lambda(0)$ is smaller than the coherence length, and the Ginzburg-Landau parameter $\kappa < 1/\sqrt{2}$, confirming that PdTe_2 is a type-I superconductor.

We do not see an evidence for topological superconductivity, possibly due to the limitations of our study. Further measurements using surface sensitive techniques have to be performed to confirm the presence of topological surface states in the superconducting phase.

Chapter 4

FeS - A Simple Iron-Based Superconductor

4.1 Introduction

Iron-based superconductors (FeSC) has seen much interest, both in the experimental and theoretical aspects, since its discovery over a decade ago [84, 85]. Even though some Fe-based superconductors existed before this [86, 87], after these discoveries, research interest in the iron-based superconductors intensified and FeSC emerged as a major family of unconventional superconductors. Before this, the only major family of unconventional superconductors with high transition temperatures were cuprates [88], a family of copper oxide based superconductors. Although there existed other superconductors such as MgB_2 ($T_c = 39$ K)[89] with high transition temperatures from earlier days, they were mostly considered exceptions and not unconventional SC as they can be explained by extensions of the BCS theory. The discovery of FeSCs changed the experimental approach as well as theoretical outlook towards unconventional and high-temperature superconductivity.

FeSCs and cuprates share a lot of similarities. The discovery of FeSCs showed that unconventional superconductivity and high-temperature superconductivity are not unique to cuprates. They both have similar phase diagrams with strong magnetism in the parent state and superconductivity emerging with electron or hole doping (Figure 4.1). Both have layered crystal structure and two-dimensional or nearly two-dimensional Fermi surfaces. However, the family of FeSCs are different from cuprates in a lot of ways too. Cuprates have strong electron correlations and the parent compounds are insulators, while FeSCs have weak electron correlations and the parent compounds are metals. In FeSCs, charge doping is not necessary for the emergence of superconductivity. In

most cases, suppression of magnetism by any means (pressure, substitution of Fe with non-magnetic elements, etc) results in superconductivity. For more information and comparison, see References [90, 91].

FIGURE 4.1: (a) General crystal structure of FeSCs. (b) Generic phase diagram of cuprates. (c) Generic phase diagram of FeSCs. Adapted from [90].

The gap symmetry and pairing mechanism of these unconventional superconductors are among the most studied and controversial topics in superconductivity. It is widely agreed that electron-phonon interactions are not primarily responsible for the emergence of superconductivity in these materials. The most popular theory for cuprates and FeSCs is the magnetic spin fluctuations [90, 91]. The proximity and sometimes coexistence of magnetism and superconductivity as seen in the phase diagrams (Figure 4.1) is a major reason for this. In cuprates, it is known experimentally that this leads to *d*-wave gaps with line nodes [88].

Most of FeSCs are known to have two sets of Fermi surfaces [90]. This leads to the prediction of possible multi-gap scenarios. Considering spin-singlet pairing, theoretical models predict the possibility of three gap models: *d*-wave gap with nodes, *s*-wave gap without nodes, and a $s_{\pm}$ gap which is generally nodless, but can be nodal depending on the material. Most theoretical and experimental evidence points towards a $s_{\pm}$ gap, but it is not conclusive and universal because of the practical difficulties in distinguishing *s*-wave and $s_{\pm}$ gaps [90, 91].

The general layered crystal structure of FeSCs is shown in Figure 4.1(a). Red circles are Fe and blue circles are $X = \text{As, P, or a chalcogen}$. These layers generally have a tetragonal structure as seen with planes of FeX tetrahedra. There may be a filler layer in between which can contain alkali and alkaline earth atoms, O, and Fe. FeSCs are divided into two major categories: (i) iron pnictides, which includes FeAs-based and FeP-based superconductors and (ii) iron chalcogenides, which includes FeSe, FeTe, and FeS based systems.

4.1.1 Iron Chalcogenides

Superconductivity in iron chalcogenides (FeX , $\text{X} = \text{Se}, \text{Te}, \text{S}$) was discovered after the initial discovery in iron pnictides [92]. They share similarities with iron pnictides (especially Fe-As based systems) in structure and properties [93]. FeSe was a prime candidate of study due to its special properties such as the enhancement of superconducting transition temperature from 8 K to 36 K by applying pressure [94], up to 45 K by intercalation [95], and above 100 K by growing monolayers [96]. Although FeS has also been shown to have similar electronic structure to FeSe from bandstructure calculations and was predicted to have either a superconducting state or a competing spin density wave (SDW) phase [97], it was only recently that the challenges in preparing pure and stoichiometric samples were overcome, and superconductivity in FeS crystals was discovered [98]. It has since been viewed as a simple platform for the study of iron-based high temperature superconductors, mainly because unlike FeSe, no structural phase transitions are observed in FeS at low temperatures [99].

Multiple electron and hole bands that contribute to superconductivity in iron chalcogenide compounds were identified by early density functional theory (DFT) studies [97]. FeS is predicted to have unconventional superconductivity with similar gap structure as FeSe, but the gap structure of FeSe remains controversial. Initial specific heat and thermal conductivity studies on FeSe revealed a nodeless gap [105, 106], but later investigations by STM and penetration depth on single crystals reported the presence of line nodes [107, 108]. However, this was not reproducible and multiple nodeless gaps were observed in the experiments that followed including thermal conductivity [109], specific heat and STM [110], and microwave conductivity [111].

For FeS, the pairing mechanism, coupling strength, and symmetry of the superconducting gap function are not clearly understood, and is up for debate in the recent years. Initial muon spin resonance (μSR) studies on polycrystalline samples showed that the superfluid density fits best to a nodeless two gap s -wave model [100], but more recent μSR studies on single crystals favored nodal behavior with a $s + d$ -wave model [101]. Strong coupling superconductivity was revealed by scanning tunneling microscopy (STM) studies and the data was found to fit well with either an anisotropic s -wave gap or a $s + d$ -wave gap [102]. Existence of gap(s) with nodes was also suggested by specific heat data with a single or double d -wave gap [103], and by quasiparticle heat transport measurements which pointed to the presence of both nodal and nodeless gaps at the Fermi surface [104]. Recent electronic structure study of FeS using DFT and tight binding model showed small differences in the band structure than previously thought [112], whereby three bands cross the Fermi energy level (E_F), and the topology of Fermi surface is similar to LaOFeP and LaOFeAs. Taking into account the correlation effects,

they concluded that the gap in FeS is nodeless on the electron pockets and nodal on the hole pockets.

In this chapter, I present high-resolution penetration depth measurements of FeS using a tunnel diode based resonant oscillator technique, and magnetization measurements using a SQUID (superconducting quantum interference device) based system. Our results show that FeS is a type-II superconductor with $H_{c1} = 58$ Oe, $\lambda(0) = 255$ nm, and $\kappa = 10$. The superfluid density data fits best for a multi-gap model with a $s + d$ wave.

4.2 Experimental Methods

Single crystals of FeS were grown by extracting potassium from the $K_{0.8}Fe_{1.6}S_2$ precursor by hydrothermal method [113]. A low de-intercalation temperature around 100 °C is chosen to avoid the collapse of the metastable tetragonal structure of FeS. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advanced diffractometer with the Cu-K α radiation. Resistivity measurements were carried out on a freshly-cut rectangular sample using standard four-probe technique.

We obtained samples from Prof. Shiyang Li at Fudan University [114] and Dr. Xiaofang Lai at Guangdong University [115]. One of the major challenges in measuring these samples was that the samples were sensitive to air. Long exposure results in degradation of the samples. Extreme care was hence taken to avoid exposure. Sample was shipped in vacuum sealed tubes, opened and later stored inside a glove box. Mounting samples for various measurements were done inside the glove box as well.

Magnetization measurements were done using a Quantum Design SQUID based magnetic property measurement system (MPMS). The sample used was in the shape of a platelet with basal area of 2.76 mm² and thickness 0.30 mm. It was mounted in a capsule and sealed while inside a glove box to avoid exposure to air. Magnetization at various temperature and magnetic fields with the field oriented parallel to c -axis were measured.

The change in penetration depth ($\Delta\lambda$) as a function of temperature is measured using our home-made tunnel-diode-oscillator (TDO) based setup. The sample is mounted on a sapphire rod and covered with a thin layer of GE varnish while inside a glove box. The sample used was in the shape of a platelet with dimensions 0.96 mm $\times$ 0.67 mm $\times$ 0.02 mm. This is oriented inside the TDO coil such that $H \parallel c$ -axis to measure $\Delta\lambda_{ab}$ (referred to as $\Delta\lambda$ interchangeably).

4.3 Results and Discussions

Figure 4.2(a) shows the XRD of the cleaved surface of the sample. Only the (00l) diffractions can be observed, indicating the sample is *c*-axis oriented. The calculated lattice parameter is $c = 5.0301 \text{ \AA}$, which agrees well with the previous report [98]. As shown in the inset, the yielded single crystals preserve the same shape of its $\text{K}_{0.8}\text{Fe}_{1.6}\text{S}_2$ precursor. The resistivity data from room temperature down to 1.3 K is shown in Figure 4.2(b). The inset shows zoomed portion near the transition. The superconducting transition occurs at $\sim 4.5 \text{ K}$ as seen. The large $\text{RRR} = 40$, together with the relatively narrow superconducting transition region shown in the inset, indicate the high quality of the acquired single crystals.

FIGURE 4.2: (a) XRD of the FeS single crystal. Inset is a typical optical image of the same batch. (b) In-plane resistivity vs temperature at zero field. Inset is the enlargement of region near transition. Measured by Prof. Shiyang Li's group at Fudan University [114].

FIGURE 4.3: (a) Magnetic susceptibility $4\pi\chi$ vs temperature for field cooled (FC) and zero field cooled (ZFC) measurements. (b) H_{c1} vs temperature. Red and green lines are fits to the equation $H_c(T) = H_c(0)(1 - (\frac{T}{T_c})^n)$ with $n=1.15$ and 2 respectively. Corresponding $H_c(0)$ obtained are 42 ± 1 Oe and 58 ± 4 Oe.

The field-cooled (FC) and zero-field-cooled (ZFC) volume magnetic susceptibilities (χ) measured in a field of 1 Oe is shown in Figure 4.3(a). Since our sample is a rectangular platelet and the field is oriented perpendicular to the surface, the susceptibility was corrected for the demagnetization field as $\chi = \chi_{exp} - 4\pi N$, where N is the demagnetization factor. N was estimated using two different methods as explained in section 2.3.3: i) from the sample dimensions (assuming the sample is a platelet with dimensions $2w \times 2w \times 2d$) using equation 2.8, which yielded a value of 0.72 and ii) from the slope of M vs H curve in Meissner state using equation 2.7 which yielded a value of 0.68. We used the average value of 0.70 for our calculations. From the plot, it is seen that the transition onset temperature is 4.2 K and a superconducting volume fraction close to 1 achieved below 2 K. The transition is rather broad. This trend is similar to some of the earlier reports [98, 104, 116].

The lower critical magnetic field H_{c1} as a function of temperature is shown in Figure 4.3(b). H_{c1} for different temperatures was estimated from M vs H curves as the point where the curve deviates from linear behavior as expected from a Meissner state. An example of this is shown in the inset to Figure 4.3(a). Since the measured values of H_{c1} are low, this method comes with rather high error bars which is shown in the graph. The standard ellipsoidal correction for demagnetization factor $H_{c1}^{corrected} = H_{c1}/(1 - N)$ was used [117]. H_{c1} at 1.8 K was obtained to be 38 Oe, which is similar to the values reported earlier [116]. We fitted the curve to the equation $H_c(T) = H_c(0)(1 - (T/T_c)^n)$ with n as a variable (red line) and with the standard BCS expression with $n = 2$ (green line) [1]. It is clear that the red line with $n = 1.15 \pm 0.10$ is a better fit. $H_{c1}(0)$ obtained from this fit is (58 ± 4) Oe.

To extract normalized superfluid density from the measured penetration depth data, we need to know the penetration depth at absolute zero, $\lambda(0)$. This is obtained by solving the equations [1, 118],

$$H_{c2}(0) = \sqrt{2}\kappa H_{c1}(0) \quad (4.1)$$

$$H_{c1}(0) = \frac{H_c(0)}{\sqrt{2}\kappa} \ln \kappa \quad (4.2)$$

$$H_{c1}(0) = \frac{\phi_0}{4\pi \lambda^2(0)} \ln \kappa \quad (4.3)$$

$H_{c1}(0)$ and $H_{c2}(0)$ are the lower and upper critical magnetic fields, $\kappa = \lambda(0)/\xi(0)$ is the Ginzburg-Landau parameter, and $\phi_0 = 2.07 \times 10^{-7}$ Oe cm² is the magnetic flux quantum. Using $H_{c1}(0) = (58 \pm 4)$ Oe obtained from our magnetic measurements and $H_{c2}(0) = 5000$ Oe from previous reports [100, 104], we obtain $\lambda(0)$ to be (255 ± 20) nm and $\kappa = 10$, which puts FeS well in the type-II regime. This value of $\lambda(0)$ is similar to that reported earlier by μ SR measurements on polycrystalline [100] and single crystal [101] samples. For calculating superfluid density, we will use this value of $\lambda(0)$.

The change in penetration depth, $\Delta\lambda$, at low temperatures is shown in Figure 4.4 with the inset showing data over the whole range. The transition is quite broad starting at 3 K and saturating at 4.3 K. The low temperature part of the data fits quite well to a power-law $\Delta\lambda(T) = a + bT^n$ with an exponent $n = 2.3 \pm 0.1$, suggesting the presence of nodes in the superconducting gap. The fit to the standard s -wave BCS model exponential (green line) is not good. To check how good the fit is and to see if there is a significant difference between a quadratic fit ($n = 2$) and $n = 2.3$, we plot the low temperature data against $(T/T_c)^n$ in Figure 4.5. As seen, a power law with $n = 2.3$ fits well below $0.3T_c$ and the deviation for temperatures above that is small too. Quadratic fit however, doesn't fit well even till $0.3T_c$ and the deviation from fit is very high at higher temperatures.

FIGURE 4.4: Low temperature dependence of the in-plane penetration depth. Red and green lines are respectively fits to a power-law and an exponential. The inset shows penetration depth data for the whole range.

FIGURE 4.5: Low temperature power-law dependence of the in-plane penetration depth. Solid lines are linear fits at low temperatures.

As discussed in section 1.6, the power-law exponent is an indicator of the symmetry of superconducting gap. A fractional exponent may be an indicator of multiple gaps or impurity scattering. For example, in a 2D Fermi surface as FeS, $n = 1$ indicates *d*-wave gap with line nodes along the *z*-direction in the clean limit. But in presence of impurities, this can change to a quadratic behaviour as observed in many cuprates [119]. We

therefore tried fitting with a dirty d -wave expression of the form $\Delta\lambda(T) = \alpha T^2/(T+T^*)$. T^* is the crossover temperature dictating crossover from a linear to quadratic dependence and α is a measure of scattering strength. However, our data does not fit to this with a reasonable value of crossover temperature T^* and α (fits not shown here).

Another possibility for having such a power-law might be $s_{\pm}$ gap. In case of a fully gapped $s_{\pm}$, the low temperature behaviour of penetration depth is expected to change from exponential dependence in the clean limit to a power-law of 2 in the dirty limit [120, 121]. In the case of an extended s -wave with nodes, the opposite is expected: a change from quadratic power-law behaviour in the clean limit to exponential behavior in the dirty limit. These kind of changes have been observed in iron based superconductors before [120, 121].

We can now calculate the normalized superfluid density from the change in penetration depth as described in section 2.3.3.3 using the equation,

$$\rho_s(T) = \frac{\lambda^2(0)}{\lambda^2(T)} = \left(\frac{\Delta\lambda(T)}{\lambda(0)} + 1 \right)^{-2}. \quad (4.4)$$

$\lambda(0) = 255$ nm is used. This is then fitted to theoretically calculated superfluid densities using different gap models as explained in section 2.4. To calculate the theoretical ρ_s , we use the expression,

$$\rho_s = 1 + 2 \int_0^{2\pi} \frac{d\varphi}{2\pi} \int_0^{\infty} \frac{\partial f}{\partial E} d\epsilon \quad (4.5)$$

For an isotropic s -wave, we estimate the gap as [11],

$$\Delta_s(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\} \quad (4.6)$$

where $\delta_{sc} = \Delta(0)/k_B T_c$, $a = 2/3$ and $\Delta C/C \equiv \Delta C/\gamma T_c$. We use δ_{sc} , $\Delta C/C$, and T_c as fitting parameters. For a d -wave gap, this gap is modified with angular dependence as $\Delta_d(\varphi, T) = \Delta_s(T) \cos(2\varphi)$. We also use an anisotropic s -wave gap given by $\Delta_{as}(\varphi, T) = \Delta_s(T) (1 + \epsilon \cos(4\varphi))$, since it was concluded to be the best fit by an STM study [102].

The normalized superfluid density and fits to different gap models are shown in Figure 4.6 and the parameters for best fits for each gap is given in Table 4.1. We use mean square error (MSE) of the fit to judge the better fit. The inset of Figure 4.6 shows the low temperature region. A good fit in this part is important as it is in this region that the effect of nodal quasiparticles (if present) is most pronounced. The superfluid density goes to zero at a lower temperature than the T_c from penetration depth.

Looking at the fits and MSE, it is clear that a single isotropic s -wave and d -wave model doesn't fit the data very well, especially at low temperatures. An anisotropic s -wave gap

FIGURE 4.6: Normalized superfluid density as a function of temperature. Solid lines are fits using different single gap models. The inset shows the low temperature part.

TABLE 4.1: Parameters for best fit for different single gap models in Figure 4.6.

Gap model	T_c	δ_{sc}	$\Delta C/C$	ϵ	MSE
s wave	3.21 ± 0.06	0.77 ± 0.01	0.32 ± 0.04	—	0.0087
d wave	4.2 ± 0.4	2.0 ± 0.3	0.10 ± 0.03	—	0.0057
anis. s wave	3.58 ± 0.06	0.92 ± 0.04	0.10 ± 0.01	0.60 ± 0.03	0.0006

with $\epsilon = 0.6$ fits the data quite well. Note that this model is not very different from the d -wave away from the nodal region, and with ϵ being large, the gap becomes small at $\varphi = \pi/4, 3\pi/4, 5\pi/4$, and $7\pi/4$. The $\Delta C/C$ values obtained for the fits are very small compared to the BCS value of 1.46. The values we obtain are even smaller than the value of 0.65 reported in the specific heat study [103]. The values of $\Delta(0)/k_B T_c$ for the isotropic and anisotropic s -wave fits are also smaller than the BCS weak coupling value of 1.76. Only the d -wave fit gives a reasonable value of gap ratio.

Multi-gap superconductivity is observed in other FeSCs as we discussed in the introduction to chapter, and is predicted for FeS with some experimental evidence. The superfluid density has a convex shape near the T_c (long tail), which is generally an indication of multiple gaps. We will fit the superfluid density with some two-gap models as explained in section 2.4. The superfluid densities from each gap adds up as

$$\rho_s = r\rho_{s1} + (1 - r)\rho_{s2} \quad (4.7)$$

FIGURE 4.7: Normalized superfluid density and fits using different multi-gap models. The inset shows the low temperature part.

TABLE 4.2: Parameters for best fit for different multi-gap models in Figure 4.7.

Gap model	T_{c1}	δ_{sc1}	$\Delta C_1/C_1$	r	T_{c2}	δ_{sc2}	$\Delta C_2/C_2$	MSE
s + s	3.21 ± 0.03	1.1 ± 0.2	–	0.56 ± 0.06	2.12 ± 0.05	0.85 ± 0.06	–	0.0026
s + d	3.57 ± 0.05	0.77 ± 0.08	–	0.55 ± 0.03	2.93 ± 0.10	1.94 ± 0.15	0.42 ± 0.06	0.0002
d + d	3.56 ± 0.07	4.42 ± 0.40	0.37 ± 0.08	0.58 ± 0.06	1.90 ± 0.14	5.34 ± 0.40	0.43 ± 0.07	0.0011

where r is a weight factor that determines contribution from each gaps. To reduce the number of parameters in the fitting equation, we use an approximate form of equation 4.6 given by [122],

$$\Delta_s(T) = \delta_{sc} k_B T_c \tanh \left\{ 1.88 \sqrt{\left(\frac{T_c}{T} - 1 \right)} \right\} \quad (4.8)$$

We use δ_{sc} and T_c as fitting parameters and eliminated the need for $\Delta C/C$. We tried fitting with a single gap s -wave of this form and found that the fit and parameters obtained are same as that given in Table 4.1. That justifies the use of this equation for s -wave gap. For d -wave gap, we still use the equation with $\Delta C/C$ as before (eqn. 4.6). The two gap fits are shown in Figure 4.7 and the parameters for fit are given in Table 4.2.

From the fits and MSE, we see that the $s + d$ wave model fits our data best. It is also interesting to note that the gap ratios for s -wave and d -wave in the two-gap fit is similar

to the single gap values. $\Delta C/C$ value is close to the value of 0.65 reported in the specific heat study [103] as well.

From our single and two-gap fits, we find that anisotropic s -wave and $s + d$ wave models give the best fits. Similar observations of strong coupling with anisotropic s -wave and $s + d$ wave models giving the best fit was also observed by Yang *et al.* [102]. For a 2D Fermi surface as in FeS, the angular dependence of the anisotropic s -wave gap is very similar to that of the $s + d$ wave model. A simplified schematic of $s + d$ wave, d -wave, and anisotropic s -wave gaps is shown in Figure 4.8 for visualizing this. Amplitude on the plot is on scale with the gap magnitude we obtained from our fits. As seen in the Figure, all three have similar angular dependencies. d -wave gap in the $s + d$ fit and single d -wave fit are similar in amplitude too, while anisotropic s -wave gap has a smaller amplitude. The $s\tau_3$ model used by Tan *et al.* [101] has a similar angular dependence too. As our measurements (as is true for other techniques such as specific heat, μ SR, etc.) is an average over the Fermi surface, its hard to distinguish between such similar gap models. A multigap $s + d$ model is consistent with the theoretical study [112] and is similar to the observations made by majority of other experimental studies on gap structure as well [101, 102, 104]. The specific heat study which concluded $d + d$ wave as the best fit also acknowledges that the $s + d$ fit for their data is good too [103].

FIGURE 4.8: Simplified schematic showing angular dependence of different gap models in $k_x k_y$ plane.

4.4 Conclusions

We measured London penetration depth and magnetization in single crystal FeS superconductor samples with a transition temperature of ~ 4 K. The values of H_{c1} , $\lambda(0)$, and κ were estimated to be 58 ± 4 Oe, 255 ± 20 nm, and 10 respectively from the magnetization measurements. The low temperature penetration depth fits to a power-law with

exponent $n = 2.3$. For an FeSC, this power-law dependence is an indicator of multi-gap superconductivity with or without nodes, with $s_{\pm}$ being the preferred candidate.

The normalized superfluid density was calculated and fit to different single and two-gap scenarios. It was found that superfluid density fits best to a $s + d$ wave gap model, which is agreement with some of the theoretical and experimental studies in FeS. However, we note that due to the limitation of our study, we cannot distinguish between gaps with similar angular dependences. We cannot detect the phase of the gap, which is important in distinguishing some of the proposed gaps for FeSCs, for example $s_{\pm}$ and s_{++} .

More studies that can probe the angular dependence and phase of the gap might be required to fully understand the pairing symmetry of this family of iron-based superconductors. TDO penetration depth can be implemented with introduction of controlled defects on samples to detect the phase changes of gaps in iron-based superconductors as shown in Ref. [121].

Chapter 5

CeCoIn₅ - Heavy Fermion Superconductor

5.1 Introduction

Heavy fermion superconductors (HFSC) were among the first unconventional superconductors discovered. First discovered in 1979 [123], they sparked intense theoretical and experimental research because of its differences from BCS superconductors, such as the proximity to magnetism. Heavy fermion systems are compounds containing rare earth elements such as Ce, or actinides such as U and Pu, in which there is strong correlation of f -orbital and conduction electrons. Quasiparticles with enhanced effective mass (m^*) are produced when f electrons hybridize with normal conduction electrons, hence the name heavy fermion systems. This large effective mass causes the density of states to change and forms sharp energy bands with high density of states near the Fermi level.

The effective mass of these heavy fermions can be 10-1000 times more than the normal electron mass ($m^*/m_0 \approx 10 - 1000$) [124, 125]. This causes pronounced effects in the physical properties of the material. This was demonstrated by specific heat measurements which showed that the electronic specific heat coefficient (γ) is typically 10-1000 times higher in heavy fermion systems [125, 126]. The specific heat jump at T_c is also correspondingly higher, making $\Delta C/\gamma T_c$ stay close to the BCS value of 1.43. The penetration depth in equation 1.5 is also modified as,

$$\lambda = \sqrt{\frac{m^* c^2}{4\pi n_s e^2}} \quad (5.1)$$

which makes the the penetration depth larger (a few thousand angstroms).

$CeCoIn_5$ has a relatively high transition temperature ($T_c = 2.3$ K) [127] compared to most other heavy fermion superconductors. This made it comparatively easier to study its superconducting state and was hence a subject of much experimental study. $CeCoIn_5$ belongs to a family of HFSCs with the common formula $CeMIn_5$, where $M = Co, Ir, Rh$, which is also called the Ce-115 family. The crystal structure of Ce-115 compounds is shown in Figure 5.1(a). It consists of quasi-two-dimensional layers of alternating $CeIn_3$ and MIn_2 layers forming a tetragonal crystal structure [127].

The Ce-115 family of HFSCs shares a lot of similarities with the cuprates and iron-based superconductors (which was discussed in chapter 4). The unconventional pairing mechanism, quasi-two-dimensional structure and Fermi surface, proximity to magnetism, anisotropy, etc. shows the similarities between these family of superconductors. This has led many to believe that these are all governed by a common superconducting mechanism – magnetic spin fluctuations [124]. According to this theory, antiferromagnetic spin fluctuations lead to spin singlet pairing with anisotropic gaps (like the d -wave), and ferromagnetic interactions lead to triplet pairing (p -wave). Although there are some experimental evidence for p -wave pairing [11], most of the HFSCs show singlet pairing [128]. Even though this is the most popular theory, there are alternate theories such as the resonating valence bond model [14] and quantum critical fluctuations [129], and the mechanism of superconductivity in these materials remains an unsolved problem as of now.

In a BCS s -wave superconductor, according to the Anderson's theorem, non-magnetic impurities do not affect the transition temperature [132]. The phase diagram of $CeCoIn_5$ upon doping with Sn [$CeCo(In_{1-y}Sn_y)_5$] and Cd [$CeCo(In_{1-x}Cd_x)_5$] are shown in Figure 5.1(b). Sn and Cd respectively are electron and hole doping. It is clear from the

FIGURE 5.1: (a) Crystal structure of Ce-115 compounds. (b) Phase diagram of $CeCoIn_5$ with Cd and Sn doping. Adapted from [130, 131].

diagram that T_c is suppressed strongly upon doping. This kind of superconducting dome behaviour is found in other unconventional superconductors as well and is generally considered an indication of d -wave behaviour [133].

Upon doping with Cd, the emergence of an antiferromagnetic order with a critical temperature T_N (Néel temperature) can be seen along with suppression of superconducting T_c . There is a region where both superconductivity and antiferromagnetism coexists, after which T_c is completely suppressed and only an antiferromagnetic phase exist. In case of Sn doping, there is no magnetic phase and superconducting T_c decreases linearly. It is understood that Cd doping only affects the electronic states close to the vicinity of dopants and doesn't affect the overall hybridization much, while Sn doping affects the hybridization uniformly throughout the crystal [131].

In this chapter, I present the penetration depth data for pure $CeCoIn_5$, Cd-doped $CeCoIn_5$ with the concentration $x = 0.6\%$ and 1.2% , and Sn-doped samples with concentrations $y = 0.6\%$ and 1.2% . All samples were grown using the standard In-flux method and were obtained from Prof. Tuson Park at Sungkyunkwan University [134].

5.2 Pure $CeCoIn_5$

$CeCoIn_5$ is the most studied compound in the Ce-115 family, mainly due to the comparatively high T_c of 2.3 K. Most of the experiments show evidence for d -wave superconductivity with line nodes [135–138]. Despite this, conclusive evidence for sign change in the superconducting order parameter is still lacking. Existence of quantum critical point [139], pseudo-gap like feature similar to cuprates [138], spin resonance modes [140], pressure dependence of superconductivity [141], etc are still under study. Even after two decades of studies, a complete picture of the superconducting properties has not emerged.

Most penetration depth studies show a $T^{1.5}$ dependence at low temperatures [135, 142], not the expected linear dependence for a d -wave superconductor. This has led to many possible theories. As we have seen in the last chapter, non-magnetic impurities can cause deviation from the linear dependence in a clean superconductor to quadratic behaviour in dirty superconductors [119]. However, considering the impurity fraction, the crossover temperature obtained from fitting were much higher [135, 142], leading many to consider alternate possibilities. The possibility of non-local effects that could cause a crossover from linear to quadratic behaviour below a crossover temperature predicted by Kostin and Leggett's (KL) theory [143] was explored in Ref.[135, 142]. While the crossover temperature calculated by KL theory is much higher than that of impurity scattering,

it was found to still be lower than experimental values [142]. However, the penetration depth measured in two directions ($H \parallel ab$, $H \parallel c$) were found to be different as predicted by KL theory [135].

A different interpretation was provided a few years later in Ref.[144]. They found that the penetration depth data for the whole range can be described by the expression $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$. This was explained to be caused by strong pair breaking scattering in the d -wave superconductor, making it gapless. Various other possibilities such as a Bose-Einstein condensate theory, non-Fermi liquid renormalization in the superconducting state, etc was also explored by some studies [142]. Some recent penetration depth studies have however shown a power-law exponent closer to 1 as expected in a d -wave superconductor with line nodes [145, 146].

We measured penetration depth using our TDO setup and find that low temperature data shows a $T^{1.5}$ dependence. By calculating the normalized superfluid density, we find that the data fits reasonably well to a d -wave gap. We compare our results with literature and various theories mentioned above and use it as a base for comparison of the Cd and Sn-doped samples.

5.2.1 Results and discussions

A rectangular platelet sample with base area 0.7 mm^2 and thickness 0.07 mm was used for penetration depth measurement. The in-plane penetration depth data is shown in Figure 5.2. The inset shows data over whole range. A sharp superconducting transition is observed at 2.3 K . The low temperature data ($T < 0.3T_c$) looks linear and no significant curvature is seen. However, when fitted to a power law of the form $a + b T^n$ (red solid line) as seen in the figure, the power law fits our data very well with an exponent of $n = 1.50 \pm 0.02$. This value of exponent agrees well with the $T^{3/2}$ dependence observed by other penetration depth measurements [135, 142].

As discussed earlier, non-magnetic impurities can change the penetration depth from $n = 1$ in clean d -wave superconductors to $n = 2$ in dirty d -wave superconductors [119, 121]. We therefore try fitting with the dirty d -wave expression for low-temperature penetration depth,

$$\Delta\lambda(T) = \alpha \frac{T^2}{(T + T^*)} \quad (5.2)$$

The fit is very good as shown by the green solid line. The crossover temperature (T^*) dictating the crossover from an impurity dominated quadratic region to linear region is obtained from the fit to be 0.5 K , which is slightly higher than the value reported in Ref.[135, 142, 147]. As explained in Ref.[135], a fit to low temperature superfluid density

FIGURE 5.2: Low temperature ($T < 0.3T_c$) penetration depth data and fits for pure $CeCoIn_5$. Inset shows the data over the whole range.

(ρ_s) might be a better measurement of non-linear behaviour. This is because, for a d -wave superconductor, there can be non-linear component(s) in penetration depth even when the superfluid density is linear, depending on the angular dependence of energy gap [148].

Therefore, we now proceed to calculate the normalized superfluid density using $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$. Since the value of $\lambda(0)$ in the literature varies from 190 nm to 500 nm, we decide to keep it a fitting parameter and fit the superfluid density to a d -wave gap model, as described in sections 2.3.3.3 and 2.4. For a d -wave gap, we use $\Delta_d(T) = \Delta(T)\cos(2\theta)$, where $\Delta(T)$ is the energy gap given by equation 1.9. We'll keep $\lambda(0)$, the transition temperature T_c , the gap ratio $\delta_{sc} \equiv \Delta(0)/k_B T_c$, and the specific heat jump $\Delta C/C$ as fitting parameters. The calculated superfluid density and best fit using the d -wave model is shown in Figure 5.3.

This model fits the data very well, except for $T < 0.5$ K (see inset). Superfluid density for BCS s -wave model (green dashes) is shown for comparison. The values of parameters for the best fit are $\lambda(0) = 356 \pm 8$ nm, $T_c = 2.24 \pm 0.01$ K, $\delta_{sc} = 2.48 \pm 0.03$, and $\Delta C/C = 2.22 \pm 0.08$. The fitted value of $\lambda(0) = 356$ nm agrees well with the values of 350 nm and 358 nm reported in the latest μ SR [149] and TDO [144] studies respectively. This value is also close to other earlier reports [135, 142, 147]. As shown in Ref.[149], some of the

FIGURE 5.3: Normalized superfluid density (blue circles) and d -wave fit (red line) for pure CeCoIn_5 . The green dashed line is isotropic BCS s -wave model. Inset shows the low temperature data and fits to a power-law and dirty d -wave

earlier reports underestimated or overestimated the values of penetration depth, and a value close to 350 nm is obtained after necessary corrections. The values of δ_{sc} and $\Delta C/C$ indicate moderate to strong coupling, which is generally agreed upon, even as there is some variation in the values obtained by different measurements [135, 137, 147, 150].

The low temperature portion ($T < 0.3 T_c$) of the superfluid density is shown in the inset to Figure 5.3. We fit it to power-law and dirty d -wave expressions in terms of superfluid density, which are respectively [43, 149],

$$\rho_s(T) = 1 - \left(\frac{T}{T_c} \right)^n \quad (5.3)$$

$$\rho_s(T) = 1 - \frac{\alpha T^2}{T_c(T + T^*)} \quad (5.4)$$

Both fits are good as seen in the Figure. The power law exponent from fit is $n = 1.41$. The crossover temperature from dirty d -wave fit is $T^* = 0.3$ K. This is lower than 0.5 K obtained from fitting penetration depth and agrees well with Ref.[135, 142]. The low value of T^* means that our data is limited by the base temperature of our system (0.38 K in this case). The T^* predicted by impurity scattering was calculated to be less than 0.065 K in earlier samples used for penetration depth measurements [135, 142].

The value obtained from experiments is clearly much higher than this value. Moreover, $CeCoIn_5$ is generally considered to be in the clean limit as the mean free path is several orders of magnitude higher than the coherence length [151].

Besides impurity scattering, an alternate explanation for this crossover behaviour was given by KL theory [143], according to which non-local effects can change the linear behaviour of pure d -wave superconductors to a quadratic below a crossover temperature given by $T^* = 2T_c \xi(0)/\lambda(0)$. Using $\xi(0) = 8.2$ nm from Ref.[152], the estimated crossover temperature is 0.1 K. While this is much closer to the experimental value, it is still considerably lower. More recent estimates of coherence length is lower [138], which will make the predicted crossover temperature even lower.

We also tried to fit the penetration depth data to $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$ as suggested in [144]. The fit is good from 0.5 K to 2 K with $T_c = 2.2$ K and $\lambda(0) = 373$ nm. This was explained to be a gapless d -wave gap, formed by strong pair breaking due to combined effects of magnetic and non-magnetic scattering in a d -wave superconductor. However, large values of $\Delta(0)/k_B T_c$ ($\approx 4\pi$) are predicted by this interpretation, which is not true in our case.

FIGURE 5.4: Penetration depth and fit to $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$.

5.3 $CeCo(In_{1-y}Sn_y)_5$

We have briefly discussed the effect of Sn-doping in the phase diagram of $CeCoIn_5$ [Figure 5.1(b)] and the suppression of superconducting T_c . Doping with Sn causes an increase of hybridization between the f electrons and conduction electrons, while simultaneously increasing the disorder in the system as Sn occupies an In site in the $CeIn_3$ layer shown in Figure 5.1(a) [131]. These effects combine to affect the T_c and other superconducting properties of the material. Previous studies have shown decrease in specific heat jump, an increase in the crossover temperature (T^*) and penetration depth, and significant deviation from the linear temperature dependence of penetration depth at low temperatures with increasing Sn substitution [147].

5.3.1 Results and discussions

Two concentrations of $CeCo(In_{1-y}Sn_y)_5$ were measured : $y=0.6\%$ and $y=1.2\%$. Dimensions of the samples respectively were $0.63 \text{ mm}^2 \times 0.05 \text{ mm}$ and $0.6 \text{ mm}^2 \times 0.009 \text{ mm}$. The penetration depth data of these samples are shown in Figure 5.5.

FIGURE 5.5: Penetration depth data for Sn-doped $CeCoIn_5$. Inset shows low temperature data and power-law fit for $y=0.6\%$.

As seen in the figure, the T_c is 1.9 K for $y=0.6\%$ and 1.4 K for $y=1.2\%$. The overall change in penetration depth for $y=0.6\%$ is much larger, which is strange. The inset of

Figure 5.5 shows the low temperature data and power law fit for both samples. For $y=0.6\%$ sample, the power-law exponent for the fit is $n = 2.7$. As we discussed before, impurity scattering in a d -wave superconductor changes the exponent from $n = 1$ in a clean d -wave to $n = 2$ in a dirty d -wave. This exponent of 2.7 doesn't fit to this impurity scattering model. To confirm this, we tried fitting a dirty d -wave (equation 5.2) and find that the low temperature data doesn't fit to a dirty d -wave model with reasonable values. This is in contrast with previous penetration depth studies, in which they were able to fit the low-temperature data of Sn-doped samples to a dirty d -wave model to find that the crossover temperature is directly proportional to the square root of doping concentration [147].

For $y=1.2\%$, as the T_c is lower, we don't have enough data below $0.3T_c$ as the base temperature for our TDO setup is 0.35 K. Therefore, the fits for this might be prone to error. The power-law fit below $0.3T_c$ is however good even when extended to higher temperatures as seen in the inset of Figure 5.5. The power-law exponent for this fit is $n = 2.2$. Similar to the case of $y=0.6\%$ sample, this data doesn't fit to a dirty d -wave model with reasonable values of T^* .

We now try to fit the penetration depth data to the expression $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$ which is thought to suggest gapless d -wave behaviour [144]. To do this, we need absolute value of penetration depth. We use the value of $\lambda(0) = 332$ nm and 485 nm from literature [147] for $y=0.6\%$ and $y=1.2\%$ samples respectively to convert our $\Delta\lambda(T)$ data to $\lambda(T)$. We note that even though these values are similar to the 350 nm we obtained for pure $CeCoIn_5$, variations in actual value might lead to some errors in the fitting, but

FIGURE 5.6: Penetration depth and fit to $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$ for Sn-doped $CeCoIn_5$.

is unlikely to cause change of behaviour. The fit to $\lambda = \lambda(0)/\sqrt{1 - (T/T_c)^2}$ for both samples is shown in Figure 5.6. Unlike the pure CeCoIn_5 sample, we find that this fit is not good for Sn-doped samples.

FIGURE 5.7: Normalized superfluid density and d -wave fits for Sn-doped CeCoIn_5 . Inset shows optical images of the samples.

Normalized superfluid density is calculated using $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$ and fit to a d -wave model of the form $\Delta_d(T) = \Delta(T)\cos(2\theta)$, where $\Delta(T)$ is the energy gap given by

TABLE 5.1: Parameters for best fit d-wave gap in Figure 5.7.

Sample	T_c	δ_{sc}	$\Delta C/C$	$\lambda(0)$ (fixed)
$y=0.6\%$	1.85 ± 0.03	4.12 ± 0.60	0.40 ± 0.03	332 nm
$y=1.2\%$	1.32 ± 0.01	4.36 ± 0.20	2.56 ± 0.12	485 nm

equation 1.9. We use $\lambda(0)$ from literature as mentioned above for calculating superfluid density (We tried keeping $\lambda(0)$ as a fitting parameter, but couldn't obtain reliable and consistent fits with reasonable values. Therefore, $\lambda(0)$ was kept as a fixed parameter for the fit.). The calculated superfluid density and fits for both samples are shown in Figure 5.7. This fit is reasonably good except at low temperatures. The parameters for the fit are given in Table 5.1.

FIGURE 5.8: Low temperature fits to normalized superfluid density for Sn-doped samples.

The low temperature portion of normalized superfluid density and fits to a power-law (eqn. 5.3) and a dirty d -wave (eqn. 5.4) for both samples are shown in Figure 5.8. Power-law exponents obtained from the fit are $n = 1.74$ and 1.71 respectively for $y = 0.6\%$ and 1.2% samples. Unlike what we saw in low-temperature penetration depth, the fits of superfluid density to a dirty d -wave is good. The crossover temperature from these fits are $T^* = 1.34$ K and 0.99 K for $y = 0.6\%$ and 1.2% samples respectively. The value of T^*/T_c of the order of unity is similar to the observation in a previous report [147]. But, the dependence of doping concentration and crossover temperature ($T^* \propto \sqrt{y}$) seen in their report is absent in our case. Lack of enough data at low temperatures might be the reason for this.

As mentioned before, in a d -wave superconductor, even if normalized superfluid density is linear [$\rho_s(T) = 1 - \alpha(T/T_c)$], the penetration depth can have non-linear components

[148]:

$$\lambda(T) = \lambda(0) \left[1 + \frac{1}{2} \left(\alpha \frac{T}{T_c} \right) + \frac{3}{8} \left(\alpha \frac{T}{T_c} \right)^2 + \dots \right] \quad (5.5)$$

which means there are higher order components in penetration depth depending on α , which in turn depends on the angular slope of energy gap at the nodes. Therefore, in d -wave superconductors, $\lambda(T)$ can sometimes give a false quadratic behavior even when $\rho_s(T)$ is linear. This difference in ρ_s and λ might be the reason why we see a difference in the low-temperature fitting parameters in the corresponding data.

5.4 CeCo(In_{1-x}Cd_x)₅

Cd doping in CeCoIn₅ suppresses superconductivity and paves way for emergence of antiferromagnetic phase as seen in Figure 5.1(b). This material is therefore very interesting to study as this emergence and coexistence of magnetism along with superconductivity might hold the clues to unfolding the relation between magnetism and superconductivity, and in extension the mechanism of unconventional superconductivity. However, this is the least studied material in CeCoIn₅ family. Even though studies have been made to understand the effect of Cd doping in the ground state and magnetism [131, 153], superconducting properties like the energy gap of Cd-doped CeCoIn₅ is not well understood.

5.4.1 Results and discussions

Cd-doped samples of two concentrations were measured: $x = 0.6\%$ and $x = 1.2\%$. We look at the data from these in this section.

5.4.1.1 $x = 0.6\%$

The sample was in the shape of a rectangular platelet with dimensions $0.63 \text{ mm}^2 \times 0.029 \text{ mm}$. The penetration depth data and low-temperature fits are shown in Figure 5.9. The superconducting transition temperature is $\sim 2.1 \text{ K}$ as seen in the inset. The low temperature data fits well to a power-law with exponent $n = 1.46 \pm 0.04$ and a dirty d -wave model (eqn. 5.2) with $T^* = 0.74 \pm 0.10 \text{ K}$. This is very similar to that of pure CeCoIn₅ in which a $T^{3/2}$ dependence and a T^* of 0.5 K was observed.

Normalized superfluid density is calculated using $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$. Since there are no reports of $\lambda(0)$ for Cd-doped CeCoIn₅ samples, we use the value of 356 nm that we obtained for pure CeCoIn₅ for this calculation. As we have seen in Sn-doped samples, $\lambda(0)$ for lightly doped samples is expected to be not too dissimilar from this value. The

FIGURE 5.9: Low-temperature penetration depth data and fits for Cd(0.6%)-doped $CeCoIn_5$. Inset shows the data for whole temperature range.

FIGURE 5.10: Normalized superfluid density for Cd(0.6%)-doped $CeCoIn_5$. Dashed green line is the calculated superfluid density for pure $CeCoIn_5$ for comparison. Inset shows an optical image of the sample.

calculated superfluid density is shown in Figure 5.10. Superfluid density calculated for pure $CeCoIn_5$ is also shown for comparison.

As seen in the figure, normalized superfluid density of Cd 0.6% doped sample greatly varies from that of the pure compound. The values of parameters for the best fit are $T_c = 2.05 \pm 0.01$ K, $\delta_{sc} = 4.9 \pm 0.3$, and $\Delta C/C = 5.5 \pm 0.4$. The low-temperature fits to superfluid density is shown in Figure 5.11. The power-law exponent from fit is $n = 1.40$ and the crossover temperature from the dirty d -wave fit is $T^* = 0.32$ K. This is very similar to that of the pure compound even though the data for the whole range is clearly different.

FIGURE 5.11: Low temperature fits to normalized superfluid density for Cd(0.6%) doped sample.

5.4.1.2 $x = 1.2\%$

Two samples with Cd concentration 1.2% from two different batches were measured. The samples were in the shape of a rectangular platelet with dimensions $0.23 \text{ mm}^2 \times 0.018 \text{ mm}$ and $0.66 \text{ mm}^2 \times 0.017 \text{ mm}$ and are labelled as B1s#1 and B2s#2 respectively. Samples from two different batches were studied to confirm some of the features observed in data, which will be discussed in this section. The penetration depth data for both samples are shown in Figure 5.12.

FIGURE 5.12: Penetration depth data for Cd (1.2%) doped $CeCoIn_5$. Inset shows the feature at ~ 1 K.

The superconducting transition is observed ~ 1.9 K as seen in the figure. The data continues to increase and at 3 K, we see another feature. This is identified as the antiferromagnetic to normal metal transition (T_N). Since TDO is sensitive to changes in the susceptibility of the sample, we are able to see the magnetic transition. The data becomes flat indicating normal state after 3 K. The superconducting transition temperature (T_c) and the Néel temperature (T_N) for antiferromagnetic transition agrees with the phase diagram [Figure 5.1(b)].

Apart from the two transitions, we observe another feature around 1 K. This is shown in the inset of Figure 5.14. The reason for this is unclear as of now. As it is seen in two samples grown in two different batches, chances are that it is something inherent to the compound. Impurities from the growth process is also a possibility.

Although the features and transition temperatures are similar for both the samples, the data from the two samples are different, especially the jump at superconducting transition. This might be due to the 10-20% error in the calibration factor G that we discussed in section 2.3.3. Since it is a multiplicative factor, the error is amplified for high values of $\Delta\lambda$.

FIGURE 5.13: Low temperature ($T < 0.3T_c$) penetration depth data for Cd(1.2%)-doped $CeCoIn_5$ and power law fits.

The low temperature data ($T < 0.3 T_c$) and power law fits ($a + b T^n$) for both samples are shown in Figure 5.13. The exponent for best fits are $n = 2.8 \pm 0.1$ and $n = 2.2 \pm 0.1$ respectively for s#1 and s#2. This is similar to our Sn-doped samples as $n > 2$ cannot be explained by a d -wave model with impurities. We try the dirty d -wave expression for penetration depth (equation 5.2) and it doesn't fit the data with reasonable values of T^* . Unlike the case of Sn-doped sample, this kind of behaviour is previously observed in a penetration depth study on Cd-doped $CeCoIn_5$ [154].

Normalized superfluid density is calculated for both samples using $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$. Similar to the 0.6% Cd-doped sample, we use the value of 356 nm that we obtained for pure $CeCoIn_5$ for this calculation as there are no reports of $\lambda(0)$ for Cd-doped $CeCoIn_5$ samples. The calculated superfluid density for both the samples is shown in Figure 5.14. Superfluid density calculated for pure $CeCoIn_5$ is also shown for comparison.

As seen in the figure, superfluid density greatly varied from the expected behaviour of a d -wave superconductor. There is a convex feature at ~ 1 K, corresponding to the feature observed in penetration depth data. It is clear that a single gap model cannot fit the data well. There is slight variation between the two samples as well. The low-temperature fits to the superfluid density is shown in Figure 5.15. The power-law exponent for the best fits are $n = 2.68$ and 2.01 respectively for B1s#1 and B2s#2 respectively. Unlike

FIGURE 5.14: Normalized superfluid density for Cd(1.2%)-doped CeCoIn_5 . Dashed green line is the calculated superfluid density for pure CeCoIn_5 . Inset shows the optical image of the samples.

FIGURE 5.15: Low temperature fits to normalized superfluid density for Cd(1.2%) doped samples.

the other samples, this data doesn't fit to a dirty d -wave model with reasonable values of T^* .

Lack of enough data below 0.35 K, and the question of sample quality are the major challenges presented by this sample. More samples should be studied to confirm these observations and more concentrations of samples could be measured to study the evolution of superfluid density from pure to doped $CeCoIn_5$.

5.5 Summary and Conclusions

TABLE 5.2: Summary of power-law and dirty d -wave fits at $T < 0.3T_c$ for $\Delta\lambda(T)$.

Sample	Power-law exponent (n)	Crossover temperature (T^*)
Pure	1.50	0.5 K
Sn 0.6%	2.7	doesn't fit
Sn 1.2%	2.2	doesn't fit
Cd 0.6%	1.46	0.74 K
Cd 1.2% B1s#1	2.8	doesn't fit
Cd 1.2% B2s#2	2.2	doesn't fit

TABLE 5.3: Summary of power-law and dirty d -wave fits at $T < 0.3T_c$ for $\rho_s(T)$.

Sample	Power-law exponent (n)	Crossover temperature (T^*)
Pure	1.41	0.3 K
Sn 0.6%	1.74	1.34 K
Sn 1.2%	1.71	0.99 K
Cd 0.6%	1.40	0.32 K
Cd 1.2% B1s#1	2.68	doesn't fit
Cd 1.2% B2s#2	2.01	doesn't fit

TABLE 5.4: Summary of d -wave fit for normalized superfluid density.

Sample	T_c	δ_{sc}	$\Delta C/C$	$\lambda(0)$
Pure	2.24 ± 0.01	2.48 ± 0.03	2.22 ± 0.08	356 nm
Sn 0.6%	1.85 ± 0.03	4.12 ± 0.60	0.40 ± 0.03	332 nm (fixed)
Sn 1.2%	1.32 ± 0.01	4.36 ± 0.20	2.56 ± 0.12	485 nm (fixed)
Cd 0.6%	2.05 ± 0.01	4.90 ± 0.30	5.50 ± 0.40	356 nm (fixed)
Cd 1.2%		— doesn't fit —		

We have measured penetration depth for a pure, two Sn-doped, and two Cd-doped samples of $CeCoIn_5$ superconductor. The summary of various fits for our data are given in Tables 5.2, 5.3, and 5.4.

We find that the penetration depth for pure sample shows a $T^{1.5}$ behaviour at low temperatures, which is consistent with previous studies. Based on fitting to dirty d -wave expression and the obtained crossover temperature value, we find that impurity

scattering and non-local effects cannot explain this dependence satisfactorily. A gapless d -wave scenario is also ruled out from the maximum magnitude of gap obtained from fitting superfluid density to a d -wave. $\lambda(0) = 356$ nm obtained from the fit is in agreement with literature, and the values for maximum gap magnitude and specific heat jump suggests moderate to strong coupling.

The penetration depth for Sn-doped samples show a power-law dependence with $n > 2$ at low temperatures and doesn't fit to dirty d -wave models with reasonable values. This is in contrast with previous studies [147]. However, the low temperature normalized superfluid density fits to a power-law with $n < 2$ and fits to dirty d -wave model with T^* close to 1 K. The superfluid density fits to a d -wave, but is different from pure CeCoIn₅.

The 0.6% Cd-doped sample shows trends very similar to pure CeCoIn₅. The low-temperature penetration depth data follows a power-law with exponent close to 1.5, and dirty d -wave model fits the data with a crossover temperature of 0.74 K. The superfluid density however, deviates from that of pure CeCoIn₅.

Similar to the Sn-doped samples, penetration depth for Cd 1.2% doped sample follows a power-law with $n > 2$ at low temperatures and doesn't fit to a dirty d -wave with reasonable values. This behaviour was observed in a previous study [154]. We also observe the antiferromagnetic transition at 3 K as expected. The superfluid density doesn't follow the expected behaviour of a d -wave superconductor. Unlike the Sn-doped samples, low temperature superconductivity doesn't fit to a dirty d -wave and has a power-law exponent $n > 2$.

There is an apparent change in the slope of superfluid density near the transition temperature for different doping concentrations. Sn 0.6% sample is convex near T_c while Sn 1.2% is concave, and Cd 0.6% sample is concave while 1.2% is convex near T_c . The convex shape near T_c might be an indication of the presence of multiple gaps and the change in concavity might be an indication of evolution of a second gap. However, more studies on more samples and doping concentrations are needed to confirm this.

More studies on these samples are required to confirm the observations and deviations from expected behaviour. As a future work, study of more doping concentrations could be performed to analyze the evolution of superfluid density and superconducting gaps from pure to doped samples. As the superconducting transition temperatures of these compounds are quite low, data at lower temperatures is needed to understand the behaviour accurately.

Chapter 6

Ionic Liquid Intercalated MoTe_2 - An Organic-Inorganic Hybrid Superconductor

6.1 Introduction

MoTe_2 is a transition metal dichalcogenide (TMD) that can crystallize in different forms such as $1T'$, $2H$, and T_d structures depending on the synthesis method and physical conditions (see Figure 6.1). The compound of our interest, T_d - MoTe_2 (will be referred as MoTe_2 unless specified) is a type-II Weyl semimetal in the bulk [155, 156] and a quantum spin hall insulator in the monolayer form [157]. ARPES measurements have shown the existence of topological Fermi arcs at the boundary between electron and hole pockets in MoTe_2 [156]. The existence of topologically non-trivial band states makes the study of superconductivity in MoTe_2 very interesting. Evidence has emerged recently for edge supercurrents in MoTe_2 from transport measurements in a magnetic field [158]. Topological superconductivity, Weyl and Dirac nodes, and more details on TMDs has been discussed in chapter 3.

Bulk MoTe_2 is superconducting only at a very low temperature of 0.1 K [160]. The superconductivity can be enhanced substantially by applying pressure with a maximum transition temperature (T_c) of 8.2 K achieved at a pressure of 11.7 GPa [160]. It was also discovered that sulphur (S) substitution of Te atoms can also enhance the transition temperature up to 1.3 K [161]. Another way of enhancing the superconductivity is by reducing the dimensionality. Monolayer and few-layer MoTe_2 samples were found to have critical temperatures as high as 8 K and 5.3 K respectively [162, 163]. However, they are not stable in air and require protective encapsulations. Ionic gating using

FIGURE 6.1: Crystal structure of MoTe₂. Adapted from [159].

KClO₄/polyethylene glycol was also shown to induce superconductivity on MoTe₂ based transistor-like devices with a T_c of 2.8 K [164].

The superconducting order parameter in MoTe₂ was determined to have two-gap *s*-wave symmetry from μ SR measurements [165]. Even though understanding the mechanism of superconductivity in MoTe₂ is of great interest, studies were limited due a variety of reasons such as the low transition temperature, unstable samples, complex fabrication process, etc. However, with the recently developed method of intercalating organic cations between the layers to enhance superconductivity, these challenges can be overcome. By intercalation using ionic liquids, stable samples with a bulk superconducting onset temperature upto 7.7 K was achieved in MoTe₂ [166].

Intercalation using organic cations creates a new class of organic-inorganic hybrid materials. These can be tailored to have enhanced superconductivity, topological properties and improved stability [166]. As explained before, reduced dimensionality enhances superconductivity in MoTe₂ – monolayer and few-layer MoTe₂ samples were found to have critical temperatures as high as 8 K and 5.3 K respectively [162, 163]. However, exfoliating bulk samples to create monolayers is difficult and the monolayer samples are unstable as it is extremely sensitive to air. Intercalation using large organic cations is an efficient strategy to control the interlayer coupling, thus enhancing superconductivity. By optimizing the growth process and using various cations, varying superconducting and topological properties can be achieved [166]. Furthermore, the samples are found to be stable and are hence easy to work with and more practical [166]. This allows us to study the properties of the sample and it is particularly interesting to look at how the superconducting properties including the energy gap evolve when the interlayer coupling in MoTe₂ is reduced.

In this chapter, I present high-resolution penetration depth measurements of ionic liquid (IL) intercalated MoTe₂ samples using our tunnel diode based resonant oscillator technique, and magnetization measurements using a SQUID (superconducting quantum interference device) based system.

6.2 Experimental methods

Pristine 1T'-MoTe₂ single crystals were grown by chemical vapor transport. This was then cooled to obtain T_d-MoTe₂ crystals. Large organic cations are then intercalated into MoTe₂ by electrochemical reaction method using ionic liquids [C_nMIm]⁺[TFSI]⁻¹ as the reacting agents. A gate voltage is applied between a counter electrode and the sample immersed in ionic liquid. Intercalated crystals can be obtained within a few hours. A schematic showing the intercalation and XRD data for pure and intercalated MoTe₂ samples are shown in Figure 6.2(a) and (b) respectively. The increase in interlayer spacing is evident from the shift in diffraction peaks in XRD to smaller angles. More details of the sample growth can be found in Ref.[166]. The samples were obtained from Prof. Shuyun Zhou at Tsinghua University [167].

FIGURE 6.2: (a) Schematic showing the intercalation of organic cation in MoTe₂. (b) XRD for pure and intercalated MoTe₂. Adapted from [166].

Transport measurements were performed using a Quantum Design physical property measurement system (PPMS). Four probe method was used to measure resistances. Magnetization measurements were done using a Quantum Design SQUID based magnetic property measurement system (MPMS). Sample used was in the shape of a rectangular platelet with dimensions $0.80 \text{ mm}^2 \times 0.03 \text{ mm}$. Magnetization at various temperatures and magnetic fields with the field oriented parallel to c -axis were measured.

¹1-Alkyl-3-Mehtylimidazolium-Bis (TriFluroMethylSulfonyl) Imide) ($n=1,2,\dots$)

The change in penetration depth ($\Delta\lambda$) as a function of temperature is measured using our home-made tunnel-diode-oscillator (TDO) based setup. A rectangular platelet shaped sample (same as the one used for magnetization measurements) is mounted on the sapphire rod using a small amount on GE varnish. This is then oriented inside the TDO coil such that $H \parallel c$ -axis to measure $\Delta\lambda_{ab}$ (referred to as $\Delta\lambda$ interchangeably).

6.3 Results and discussions

Figure 6.3 shows the resistance vs temperature for IL-intercalated MoTe₂. As seen in the data, the superconducting transition is broad with onset temperature ~ 4 K and zero resistance achieved at ~ 3 K. This is lower than the transition onset of 7 K reported in Ref.[166]. This is because, as explained in the paper, the sample growth produces samples with slightly varying inter-layer spacings which results in superconducting onset temperature ranging from 3.7 K to 7.0 K, and there is no way to control it presently.

FIGURE 6.3: Resistance vs temperature for IL-intercalated MoTe₂ sample. Measured by Prof. Shuyun's group at Tsinghua University [167].

The field-cooled (FC) and zero-field-cooled (ZFC) volume magnetic susceptibilities (χ) measured in a field of 5 Oe is shown in Figure 6.4(a). Since our sample is a rectangular platelet and the field is oriented perpendicular to the surface, the susceptibility was corrected for the demagnetization field as $\chi = \chi_{exp} - 4\pi N$, where N is the demagnetization factor. N was estimated from the slope of M vs H curve (shown in the inset) in Meissner state using equation 2.7 which yielded a value of 0.87. From the plot, it is seen that the transition onset temperature is 3.2 K and the transition is broad with a low superconducting volume fraction even at 1.8 K. This onset transition temperature is close to the zero resistivity temperature in Figure 6.3.

FIGURE 6.4: (a) Magnetic susceptibility $4\pi\chi$ vs temperature for field cooled (FC) and zero field cooled (ZFC) measurements. (b) H_{c1} vs temperature. Red line is the fit to the equation $H_c(T) = H_c(0)(1 - (T/T_c)^2)$.

The lower critical magnetic field H_{c1} as a function of temperature is shown in Figure 6.4(b). H_{c1} for different temperatures was estimated from M vs H curves as the point where the curve deviates from linear behavior as expected from a Meissner state. An example of this is shown in the inset to Figure 6.4(a). Since the measured values of H_{c1} are low, this method comes with rather high error bars. The standard ellipsoidal correction for demagnetization factor $H_{c1}^{corrected} = H_{c1}/4\pi N$ was used.[117] We fitted the curve to the standard equation[1] $H_c(T) = H_c(0)(1 - (T/T_c)^2)$ (red line). $H_{c1}(0)$ obtained from this fit is (31.5 ± 3.0) Oe.

Penetration depth and the coherence length at absolute zero ($\lambda(0)$ and $\xi(0)$ respectively) can be obtained by solving the equations,[1, 118]

$$H_{c2}(0) = \sqrt{2}\kappa H_c(0) \quad (6.1)$$

$$H_{c1}(0) = \frac{H_c(0)}{\sqrt{2}\kappa} \ln \kappa \quad (6.2)$$

$$H_{c1}(0) = \frac{\phi_0}{4\pi \lambda^2(0)} \ln \kappa \quad (6.3)$$

$H_{c1}(0)$ and $H_{c2}(0)$ are the lower and upper critical magnetic fields, $\kappa = \lambda(0)/\xi(0)$ is the Ginzburg-Landau parameter, and $\phi_0 = 2.07 \times 10^{-7}$ Oe.cm² is the magnetic flux quantum. Using $H_{c1}(0) = (31.5 \pm 3.0)$ Oe obtained and $H_{c2}(0) = 3.5$ T from previous reports,[166] we obtain $\lambda(0)$ to be (447 ± 90) nm and $\kappa = 46$, which puts this superconductor well in the type-II regime. This gives a $\xi(0)$ value of (9.7 ± 2.0) nm, which is consistent with 9.6 nm given in Ref.[166] and 9 nm for pure MoTe₂ under pressure [160]. The value of $\lambda(0)$ obtained is also similar to that of pure MoTe₂ under pressure [165].

FIGURE 6.5: Penetration depth data at low temperatures and fits for IL-intercalated MoTe₂. Inset shows the data over whole range.

The change in penetration depth, $\Delta\lambda$, at low temperatures is shown in Figure 6.5 with the inset showing data over the whole range. The transition is quite broad starting at ~ 3 K and saturating at ~ 4 K. This is similar to the transition seen in resistivity

(Figure 6.3). Similar observation was made in Cd doped CeCoIn₅ in chapter 5, where penetration depth data and resistivity has similar transition temperatures while other thermodynamic measurements like magnetization has a lower T_c . Penetration depth is a surface sensitive measurement, while magnetization is a bulk measurement.

The low temperature part of the data ($T < 0.3T_c$) fits quite well (red line) to a power-law $\Delta\lambda(T) = a + bT^n$ with an exponent $n = 1.57 \pm 0.01$, suggesting the presence of nodes in the superconducting gap. As we have seen in previous chapters, an exponent of $3/2$ can be an indicator of dirty d -wave behavior. Non-magnetic impurities can change the behaviour from $n = 1$ in a clean d -wave superconductor to $n = 2$ in dirty d -wave superconductor [119]. We therefore try to fit the data to a dirty d -wave expression of the form $\Delta\lambda(T) = \alpha T^2 / (T + T^*)$. This is shown as green line in the Figure and this fit is very good with a crossover temperature T^* of 1.20 ± 0.05 K.

We now proceed to calculate the normalized superfluid density (ρ_s) as described in section 2.3.3.3 using the equation,

$$\rho_s(T) = \frac{\lambda^2(0)}{\lambda^2(T)} = \left(\frac{\Delta\lambda(T)}{\lambda(0)} + 1 \right)^{-2}. \quad (6.4)$$

We use $\lambda(0) = 447$ nm obtained from magnetization measurements for this calculation. The superfluid density is shown in Figure 6.6.

As seen in the Figure 6.6, superfluid density goes to zero at 2 K even though the transition in penetration depth data (Figure 6.5) is at ~ 4 K. Even at the base temperature of 0.4 K, the value of superfluid density is very low. Ideally, the normalized superfluid density is expected to be close to unity at low temperatures, even for gaps with nodes. Such low value of superfluid density is unusual and might mean that the superconducting volume fraction of the sample is low even at low temperatures.

To confirm our findings, we measured another sample of IL-intercalated MoTe₂, labelled sample #2 with dimensions $0.69 \text{ mm}^2 \times 0.04 \text{ mm}$. The superfluid density and penetration depth (inset) data is shown in Figure 6.7. As seen in the figure, it is very similar to sample #1. The penetration depth shows a transition at ~ 4 K and the transition is broad. The low temperature penetration data ($T < 0.3T_c$) fits well to a power-law with $n = 1.51$ and to a dirty d -wave model with $T^* = 1.25$ (fits not shown here). The superfluid density goes to zero at ~ 2 K and the data is low even at the base temperature (0.36 K for sample #2).

The broadness of the transition and low value of superfluid density obtained poses some questions about the sample quality and data. The broad transition might be propagating to low temperatures and mimicking power-law dependence. We see from magnetization

FIGURE 6.6: Normalized superfluid density for IL-intercalated MoTe₂ (sample#1). Inset shows an optical image of the sample.

FIGURE 6.7: Normalized superfluid density for sample#2 of IL-intercalated MoTe₂. Inset shows the penetration depth data.

measurements [Figure 6.4(a)] that the superconducting volume fraction of the sample is low even at 1.8 K as perfect diamagnetism ($4\pi\chi = -1$) is not achieved. During the sample growth [166], samples with a range of T_c is obtained at random. Measuring the samples with the maximum T_c , which is more likely to be cleaner, might be one of the solutions for resolving this.

6.4 Conclusions

We have measured penetration depth of IL-intercalated MoTe₂ single crystals and found superconducting transition occurs at an onset of ~ 4 K. The low temperature penetration depth data fits to a power-law with exponent ~ 1.5 , which suggests the presence of nodes in the energy gap. Dirty d -wave fits the data well with a crossover temperature of ~ 1.2 K. The magnetization measurements show a lower T_c of ~ 3 K and the sample doesn't achieve superconducting volume fraction of 1 at 2 K. From M vs. H measurements, we calculate $\lambda(0) = 447$ nm and $\xi(0) = 9.7$ nm.

The superfluid density at base temperature is significantly low and goes to zero at 2 K. This might be due to some inherent physics or due to sample quality. More samples, especially with optimum 'doping' should be measured, which will hopefully bring more clarity to this. More studies that can go to even low temperatures will also help in understanding the physics better.

Appendix A

Common Symbols

Symbol	Meaning
T_c	Superconducting transition temperature
H_c	Critical magnetic field
λ	Penetration depth
ξ	Coherence length
κ	Ginzburg-Landau parameter ($\kappa = \lambda/\xi$)
Δ	Energy gap
k_B	Boltzmann constant
δ_{sc}	Gap ratio ($\delta_{sc} = \Delta(0)/k_B T_c$)
C	Specific heat
n_s	Superfluid density
ρ_s	Normalized superfluid density
f	Frequency of oscillator
G	Calibration factor
N	Demagnetization factor (SI units)
M	Magnetization per unit volume (emu/cc)
H	Applied magnetic field
χ	Susceptibility per unit volume
$2w$	Sample side dimension
$2d$	Sample thickness
T^*	Crossover temperature
T_N	Néel temperature

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