Penetration depth studies of unconventional superconductors

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PENETRATION DEPTH STUDIES OF UNCONVENTIONAL SUPERCONDUCTORS

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Abstract

We have setup a tunnel-diode oscillator based self-resonating technique operating at 26 MHz to probe the temperature-dependence of the magnetic penetration depth λ . Using this high resolution setup with a noise level of 2 parts-per-billion (ppb), we have measured and present in this thesis penetration depth data down to ~ 0.4 K for the following superconducting samples — the Pd-Bi based structurally isomeric single crystalline superconductors α -PdBi₂ and β -PdBi₂, the Chevrel phase-based single crystalline superconductor CsMo₁₂S₁₄, single crystals of the quasi-one-dimensional superconductor Tl₂Mo₆Se₆, and polycrystalline samples of the filled skutterudite superconductor Pr_{1-x}Ce_xPt₄Ge₁₂ for $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 .

For both α -PdBi₂ and β -PdBi₂, analysis of the penetration depth as well as the superfluid density data points towards a conventional single-gap moderate-coupling symmetry of the superconducting order parameter, suggesting similar pairing mechanism in this class of materials. For the superconductor CsMo₁₂S₁₄, our data show strong signatures of multi-gap superconductivity. We attribute weak-interband coupling between the band-specific superconducting gaps to be responsible for two separate critical transition temperatures, clearly visible in the overall penetration depth and superfluid density data. Our claim for multi-band superconductivity is supported by thermodynamic critical field data, and also by electronic band structure calculations. Our penetration depth measurements on Tl₂Mo₆Se₆

show an exciting two-step superconducting transition, originating from the dimensional crossover from a longitudinally coherent one-dimensional superconducting phase to a globally coherent three-dimensional superconducting ground state. We show that electrical transport measurements on the same sample show a similar two-step transition as well. Finally, for the skutterudite superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$, our data suggest multi-gap superconductivity with one unconventional gap with point node and one nodeless conventional gap. Preliminary analysis of the superfluid density show that as the Ce doping concentration increases from the optimal value of $x = 0$, the contribution of the nodal gap decreases monotonically.

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Chapter 1

Introduction

In this chapter, the motivation of my thesis work will be introduced. The organization and contents of each chapter will be presented at the end of this chapter.

1.1 Motivation

Superconductivity was first observed in pure solid mercury by Kamerlingh Onnes more than 100 years back [1], and since then has remained one of the most active areas of research in the field of condensed matter physics. It is a novel phenomenon in which a material when cooled below a certain *critical* temperature T_c , offers no electrical resistance. Soon afterwards, while studying the magnetic field distribution outside a superconductor, it was discovered that these materials have the unique ability to expel externally applied magnetic fields from the bulk. This elegant feature of superconductors is called the Meissner effect [2]. Qualitatively, this phenomenon can be explained as follows. In response to the external magnetic field, circular non-dissipative eddy currents are generated in the superconductor near the surface. The magnetic moment induced by this current loop cancels out the externally applied field. However, a certain amount of energy is

required to generate these eddy currents in the first place, suggesting that the field can penetrate a finite distance and this distance is called the magnetic penetration depth λ .

Ginzburg and Landau in their microscopic model, showed that the superconducting phase can be characterized by a unique non-zero order parameter (OP) [3]. The concept of an OP was further validated by the microscopic theory proposed by BCS (Bardeen, Cooper, and Schrieffer) in 1957, which attributed superconductivity to the formation of electron-electron pairs called Cooper pairs [4]. According to their model, a Cooper pair formed via electron-phonon interaction is a Boson-like entity, and analogous to Bose-Einstein condensation, these Cooper pairs can form a condensate which corresponds to the globally coherent superconducting ground state. This condensate which exists only below T_c corresponds to the superconducting OP, and constitutes the superfluid density ρ_s . The magnetic penetration depth λ is directly related to the density of the superconducting electrons, and can be used to extract ρ_s . Probing the temperature dependence of both λ and ρ_s can thus provide vital information about the pairing symmetry of the superconducting OP.

Till 1980s, the highest T_c exhibited by any superconducting specimen was between 20–23 K, with the BCS theory being successful in explaining the phenomenon. However, a stir was created amongst the science community with the discovery of LaBaCuO in 1986 [5], due to the *apparent* failure of the conventional BCS theory to explain the pairing mechanism. With the discovery of YBCO ($T_c \approx 93$ K) [6] the following year, the era of high T_c cuprate superconductors began. Strictly speaking, the term “unconventional” superconductivity refers to the scenario where the pairing symmetry is lower than the symmetry of the crystal lattice, and therefore should not be solely associated with superconductors having a high T_c [7, 8]. The pioneering work of Hardy and co-workers demonstrated that high resolution

measurements of the magnetic penetration depth could directly discern the nodal features found in the unconventional d -wave pairing state in cuprates [9]. Since then, a large number of new superconductors belonging to different classes of chemical compounds have been discovered, many of which exhibit nontrivial departures from the conventional BCS behavior.

1.2 Outline of the thesis

In this thesis, I shall be presenting magnetic penetration depth measurements on a number of unconventional superconductors, namely the potential topological superconductor β -PdBi₂ and its structural isomer α -PdBi₂, the Chevrel phase-based superconductor CsMo₁₂S₁₄, the Chevrel phase-based quasi-one-dimensional superconductor Tl₂Mo₆Se₆, and the filled skutterudite superconductor Pr_{1-x}Ce_xPt₄Ge₁₂. In addition to penetration depth, measurements of other superconducting properties such as magnetization and electrical transport, that corroborate and aid our data analysis have been presented in relevant chapters. The thesis is organized as follows:

- **Chapter 2:** Fundamental theoretical ideas regarding magnetic penetration depth are introduced. The temperature dependent expressions for λ and ρ_s are derived, and their utility in distinguishing a conventional superconductor from an unconventional one is highlighted. The chapter also contains brief discussion on some novel superconducting properties such as multi-band and topological superconductivity.

- **Chapter 3:** The tunnel-diode-oscillator (TDO) based self-resonating technique, that we use to probe the magnetic penetration depth is introduced. Methodology of measurement, and key experimental features such as cooling down the sample to ~ 300 mK, maximization of the signal-to-noise ratio of this setup etc. are discussed in detail. The data analysis procedure is discussed briefly, and its implementation in the conventional BCS superconductor Al that we use to calibrate the system is presented.

- **Chapter 4:** Penetration depth and superfluid density data of the structurally related superconductors α -PdBi₂ and β -PdBi₂ are presented. We did not detect any signature of unconventional superconductivity that can possibly arise from the topologically protected surface states that have been observed in β -PdBi₂ [10]. Rather, our analysis suggests a similar conventional BCS-like pairing symmetry for both these compounds.

- **Chapter 5:** Measurement and data analysis of penetration depth and superfluid density, along with magnetization and thermodynamic critical fields on the superconductor CsMo₁₂S₁₄ are shown – all of which suggest multi-band superconductivity.

- **Chapter 6:** The quasi-one-dimensional superconductor Tl₂Mo₆Se₆ is studied by penetration depth and electrical transport measurements, both of which exhibit signatures for a dimensional crossover from one-dimensional to three-dimensional superconductivity, similar to the related superconductor Na₂Mo₆Se₆ [11]. A comprehensive analysis of the dimensional crossover is presented.

- **Chapter 7:** Penetration depth studies of the superconductor Pr_{1-x}Ce_xPt₄Ge₁₂ for the doping concentrations $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 are presented. Preliminary analysis suggests multi-band superconductivity in this compound with gradual reduction of the unconventional nodal gap contribution relative to the conventional gap with increase in x . This is in line with specific heat data reported elsewhere [12].

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Chapter 2

Magnetic Penetration Depth

In this chapter, some fundamental ideas regarding magnetic penetration depth and its usefulness as a powerful tool to probe the pairing symmetry of the superconducting order parameter have been discussed. The chapter contains the following sections: (1) some general ideas about superconductivity, (2) basic theory of penetration depth, (3) derivation of superfluid density and penetration depth from quasiparticle density of states (QDOS), (4) temperature-dependence of the superconducting gap, and (5) novel superconducting phases: multi-band superconductivity and topological superconductivity.

2.1 General Ideas about Superconductivity

The original theory of superconductivity by Bardeen-Cooper-Schrieffer (BCS) attributed the phenomenon to electron-phonon interaction. According to this theory, as a superconducting system is cooled down (in its normal phase) to ultra-low temperatures, phonon mediated interaction can cause electrons to pair up, and each such pair is called a *Cooper pair*. As the system is cooled below the superconducting transition temperature T_c , Cooper pair formation starts. Each such Cooper pair behaving like a Boson (instead of a Fermion) settles in a new ground state, and thus builds up a Bose-Einstein

condensate. At $T = 0$, all the charge carriers have formed Cooper pairs, and thus the superfluid condensate formation is complete. The condensate is separated from the excited states in the normal phase by an energy gap $2\Delta(T)$, where $\Delta(T)$ is the binding energy of each *quasiparticle* forming a single Cooper pair. To clarify, the term quasiparticle refers to each charge carrier forming the Cooper pair, in accordance to the terminology of the Fermi-liquid theory. The phase transition from the normal to superconducting phase is characterized by lowering of the Gibbs free energy as well as the entropy of the system i.e. $S_N > S_{SC}$, with S_N and S_{SC} being the entropy in the normal and the superconducting phase respectively. To thermally activate each Cooper pair from the condensate, the thermal energy $k_B T$ has to be at least equal to $2\Delta(T)$. If the thermal energy is greater than the gap energy, then one would expect on average each Cooper pair to break up into two quasiparticle excitations with each quasiparticle settling into a single particle energy state. The energy of each such state for a singlet superconducting system is given as,

$$E_k = \sqrt{\xi_k^2 + \Delta_k^2}, \quad (2.1)$$

where ξ_k represents the normal-phase single quasiparticle energy measured relative to the chemical potential (μ) and Δ_k is the gap function which serves as the order parameter (OP) of the superconducting phase. The original BCS theory was for a gap that is isotropic and is only a temperature dependent function. However the crystalline anisotropy needs to be taken into account and that is why the gap becomes a $\mathbf{k}$ -dependent function as illustrated in Eq. 2.1. So in the $\mathbf{k}$ -space scenario, for a system with a high density of states (DOS) at the Fermi surface (FS) a superconducting gap opens up on the FS when cooled below T_c . If the gap is anisotropic in nature, then the threshold energy to break a single Cooper pair into two quasiparticles is the minimum value of $2|\Delta(\mathbf{k})|$ on the Fermi Surface (FS), given as $2\Delta_{min}$. Please note that

the notation $\Delta(\mathbf{k})$ represents the *gap function* while Δ_{min} is the magnitude of the gap.

Any superconductor can be characterized by two primary parameters – (i) the magnetic penetration depth λ which is the characteristic length scale for magnetic field penetration and (ii) the coherence length ξ which gives the spatial extent of variation of the OP describing the superconducting phase. This OP which is basically a quantum mechanical wavefunction describing the superconducting state, consists of a spin (S) part and an orbital (L) part. Usually we shall be dealing with singlet superconductors, by which we mean the two electrons in each Cooper pair have opposite spins, with zero net spin ($S = 0$). Thus the spin part of the total wavefunction is odd under particle exchange. Since the total wavefunction has to be antisymmetric under particle exchange, the orbital part has to be even, i.e. the allowed values are $L = 0$ (s -wave), $L = 2$ (d -wave) and so on. Additionally, we have investigated the possibility of spin-triplet superconductivity in the putative topological superconductor α -PdBi₂, and for such systems allowed values of L are 1 (p -wave), 3 and so on.

The materials that conform to the BCS kind of non-zero isotropic gaps are usually referred to as *conventional* superconductors having an s -wave symmetry of the superconducting OP. Microscopic calculations have shown that, for such materials the normalized superfluid density $\rho_s(T)$ (ratio of the number density of charge carriers that form Cooper pairs to the total number density of charge carriers) at low temperature ($\leq 0.3T_c$) is given as follows [1],

$$\rho_s(T) \approx 1 - \sqrt{\frac{2\pi\Delta}{k_B T}} e^{-\frac{\Delta}{k_B T}}. \quad (2.2)$$

Note that Eqn. 2.2 is derived from the exponential expression for penetration depth $\lambda(T)$ for conventional superconductors with an isotropic gap (derived later in the thesis). For conventional s -wave materials, the superconducting gap function $\Delta(T)$ remains constant at the lowest temperatures from $T =$

0 till about $0.3T_c$. This is a necessary condition in the derivation of the low temperature exponential T -dependence for λ [1], thereby giving an upper limit $\sim 0.3T_c$ for the applicability of the exponential expression for $\lambda(T)$ and hence Eqn. 2.2.

The energy gap for conventional superconductors can be anisotropic as well. Then Δ in the above equation needs to be replaced by the minimum value of the gap Δ_{min} , suggesting that low temperature $\rho_s(T)$ would have a dominant contribution from quasiparticle excitations along the direction of the gap minima. Since the inception of the BCS theory, there has been discovery of different families of superconducting materials that do not conform to the BCS theory in one way or the other. They are referred to as *unconventional* superconductors. The most widely accepted signature of unconventional superconductivity is that for such materials magnitude of the gap becomes zero at certain points on the FS. For such materials $\Delta_{min} = 0$, and these points are referred to as *nodes*. Nature of the nodes viz. point nodes, line nodes etc. are determined by the FS topography as well as the nature of the gap function [2]. In addition to such symmetry-protected nodes, there exists accidental nodes that can be removed by local perturbation such as increased disorder concentration [3].

A well-illustrated example of unconventional pairing mechanism is in YBCO which is a d -wave superconductor with a gap function $\Delta(\hat{\mathbf{p}}) = \Delta_0(\hat{p}_x^2 - \hat{p}_y^2)$.

The 3D gap function has a $d_{x^2-y^2}$ symmetry and a cross sectional view of the same has been shown in Fig. 2.1 . The thick solid line represents the outline of the gap projected on a 2-D FS and one can see four nodal points along the radial directions $p_x = \pm p_y$. One can quite clearly understand that, even at low temperature gapless thermal excitations are possible along the direction of these nodes, rendering the thermodynamic behavior different from that of the conventional BCS superconductors. If Δ_0 is the peak gap

Figure 2.1: Schematic showing the polar plot of the order parameter of a d -wave superconductor projected on a 2D Fermi Surface in momentum space. The shaded region is the completely filled Fermi Sea, while the circle with the dashed contour has a radius of $E_F + k_B T$ and represents the maximum energy of the thermally excited quasiparticles. The alternate signs on the four lobes are due to the ϕ -dependence of $\Delta_k(\phi)$.

value then in terms of the azimuthal angle ϕ , the gap function can be written as,

$$\Delta(\phi) = \Delta_0 \cos(2\phi). \quad (2.3)$$

Another way of understanding conventional and unconventional superconductivity is from the perspective of crystal symmetry. A conventional superconductor is one for which the symmetry of the underlying crystal structure determines the gap symmetry. For example, in case of an uniformly gapped s -wave superconductor, the isotropic symmetry of the crystal suggests that Δ_k possess an isotropic symmetry. While for an anisotropic s -wave material, the anisotropy in the crystal structure dictates the variation of the energy

gap Δ_k along different directions in $\mathbf{k}$ -space. On the other hand, an unconventional superconductor is one for which the symmetry of Δ_k will be usually lower than the crystal symmetry [4]. It is perhaps important to mention that, a vast majority of the condensed matter community describes the spin-singlet sign-changing $s^\pm$ -wave order parameter (commonly suggested for the pnictides) as unconventional as well. This multi-band $s^\pm$ -wave state is a very unique gap state and displays numerous unexpected novel superconducting properties, such as a strong reduction of the coherence peak, non-trivial impurity effects and nodal-gap-like nuclear magnetic resonance signals among others [5].

2.2 Basic Theory of Penetration Depth

Let us derive an expression for the magnetic penetration depth λ when an external field is applied. The following derivation closely resembles that done in [4]. According to Maxwell's third equation [in *SI* units], when a time dependent magnetic field $\mathbf{B}(t)$ is applied to a system, an electromotive field $\mathbf{E}$ would be induced as follows,

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}. \quad (2.4)$$

Using Newtons law of motion and taking into consideration the fact that there is no scattering, the equation of motion of a quasiparticle (Cooper pair) in this induced field $\mathbf{E}$ is given as follows,

$$m^* \frac{d\mathbf{v}}{dt} = -e\mathbf{E}, \quad (2.5)$$

where m^* is the effective mass, v is the drift velocity and e is the charge of an electron. If n_s represents the number density of the superconducting electrons, then the current density $\mathbf{J}_s$ in the superconducting phase is given

as,

$$\mathbf{J}_s = -en_s \mathbf{v}. \quad (2.6)$$

Taking time derivative of Eq. 2.6 and substituting from Eq. 2.5 we get,

$$\frac{d\mathbf{J}_s}{dt} = \frac{n_s e^2}{m^*} \mathbf{E}. \quad (2.7)$$

Now, taking curl on both sides of Eq. 2.7 and substituting from Eq. 2.4 (with the partial derivative being changed to total derivative) it can be shown that,

$$\frac{m^*}{n_s e^2} \left(\nabla \times \frac{d\mathbf{J}_s}{dt} \right) = -\frac{d\mathbf{B}}{dt}. \quad (2.8)$$

If we remove the time derivative on both LHS and RHS of Eq. 2.8 we get,

$$\nabla \times \mathbf{J}_s = -\frac{n_s e^2}{m^*} \mathbf{B}. \quad (2.9)$$

Next, we take the curl of the fourth Maxwell's equation $\nabla \times \mathbf{B} = \mu_0 \mathbf{J}_s$ with ($\mathbf{E} \neq \mathbf{E}(t)$) and substitute from Eq. 2.9. We get the following expression,

$$\lambda^2 (\nabla \times \nabla \times \mathbf{B}) + \mathbf{B} = 0, \quad (2.10)$$

where,

$$\lambda^2 = \left(\frac{m^*}{n_s e^2 \mu_0} \right)_{SI} = \left(\frac{m^* c^2}{4\pi n_s e^2} \right)_{CGS}. \quad (2.11)$$

Here, λ is defined as the London penetration depth. Using the vector identity $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$ and noting that $\nabla \cdot \mathbf{B} = 0$, we get from Eq. 2.10,

$$\nabla^2 \mathbf{B} = \frac{4\pi n_s e^2}{m^* c^2} \mathbf{B}, \quad (2.12)$$

where λ_{CGS} has been used.

For an external magnetic field applied along the x -axis parallel to the surface of a superconductor with penetration along the z -axis, Eq. 2.12

reduces to,

$$\frac{d^2}{dz^2}B_x = \frac{1}{\lambda^2}B_x. \quad (2.13)$$

Eq. 2.13 has a general solution of the form,

$$B_x(z) = B_0 \exp(-z/\lambda), \quad (2.14)$$

where B_0 is the magnitude of the field at the surface $z = 0$.

Thus, we can see that the externally applied field exponentially attenuates inside a superconducting sample. We have already qualitatively defined the normalized superfluid density ρ_s and will show in subsequent sections that it is directly proportional to n_s . One should also appreciate the fact that ρ_s too represents the superconducting OP because it has a finite non-zero value only in the superconducting phase. The Eq. 2.11 clearly shows that λ gives information about the ratio n_s/m^* and hence facilitates direct measurement of the OP. Since n_s is a function of temperature, λ would also vary with the same. This temperature dependence of λ is precisely the measurement we perform with our home-built experimental setup. Details of the setup and principle of measurement shall be described in Chap3.

2.3 Derivation of Superfluid Density and Penetration Depth from Quasiparticle Density of States (QDOS)

In this section we shall try to derive the expression for QDOS and use it to derive expressions for the normalized superfluid density $\rho_s(T)$ and the London penetration depth $\lambda(T)$ for both conventional and unconventional superconductors.

If n_s, n_n and n be the number density of superconducting electrons,

quasiparticle excitations and total charger carriers respectively, then based on the two-fluid model description we can write,

$$n = n_s + n_n. \quad (2.15)$$

The normalized superfluid density ρ_s is defined as,

$$\rho_s = \frac{n_s}{n_s + n_n} = \frac{n - n_n}{n} = 1 - \frac{n_n}{n}. \quad (2.16)$$

From [4] the normal fluid density in the superconducting phase at a finite temperature T is given as,

$$n_n = n \int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial E_k} \right) d\xi, \quad (2.17)$$

where E_k is the Bogoliubov quasiparticle energy and $f(E_k)$ is the Fermi function.

Using Eq. 2.17, ρ_s from Eq. 2.16 can be written as,

$$\rho_s = 1 + 2 \left\langle \int_0^{\infty} \left(\frac{\partial f}{\partial E_k} \right) d\xi \right\rangle_{FS}. \quad (2.18)$$

Here, $\langle \dots \rangle_{FS}$ represents the average over the FS. Writing Eq. 2.18 in terms of E it can be shown that [4],

$$\rho_s = 1 + 2 \left\langle \int_0^{\infty} \frac{N(E)}{N_0} \left(\frac{\partial f}{\partial E} \right) dE \right\rangle_{FS}, \quad (2.19)$$

where $N(E) = \sum_k \delta(E - E_k)$ denotes the single-quasiparticle density of states (DOS) and N_0 is the normal phase DOS measured at the Fermi level E_F .

Considering a continuous distribution of all possible states in the excitation spectrum and using the expression for quasiparticle energy from Eq. 2.1, we can use an approach similar to that done in [6] to derive an expression

for $N(E)/N_0$ as shown below,

$$N(E) = \int \delta(E - E_k) \frac{d^3k}{(2\pi)^3} = N_0 \int \frac{d\Omega}{4\pi} \int d\xi \delta(E - E_k). \quad (2.20)$$

Taking derivative of Eq. 2.1 and substituting $d\xi$ in Eq. 2.20 we get,

$$\frac{N(E)}{N_0} = \int \frac{d\Omega}{4\pi} \int d[\sqrt{E_k^2 - \Delta_k^2}] \delta(E - E_k) = \int \frac{d\Omega}{4\pi} \int \frac{E' dE'}{\sqrt{E'^2 - \Delta_k^2}} \delta(E - E'). \quad (2.21)$$

Here, the integration over the solid angle Ω (assuming spherical symmetry) is performed with the limits $\Delta_k^2 < E^2$. Integrating over the δ function, Eq. 2.21 can be simplified as follows,

$$\frac{N(E)}{N_0} = \int \frac{d\Omega}{4\pi} \frac{E}{\sqrt{E^2 - \Delta_k^2}}. \quad (2.22)$$

Finally, substituting $N(E)/N_0$ in Eq. 2.19 we get,

$$\rho_s = 1 + 2 \left\langle \int_0^\infty \frac{E dE}{\sqrt{E^2 - \Delta_k^2}} \frac{\partial f}{\partial E} \right\rangle_{\text{FS}}. \quad (2.23)$$

Here, the integration over the solid angle has been absorbed within the $\langle \dots \rangle_{FS}$ i.e. Eq. 2.23 represents the angled averaged superfluid density that has been normalized to its zero temperature value. We shall be using Eq. 2.22 and Eq. 2.23 to calculate the QDOS and ρ_s for any arbitrary gap function Δ_k . Please note that strictly speaking these equations are valid in the pure local limit i.e. $\xi \ll \lambda$ [4], with ξ being the superconducting coherence length.

Next, let us try to derive an expression for $\rho_s(T)$ for an s -wave superconductor. For such isotropic conventional superconductors the dominant term (in Eq. 2.23) causing the reduction of $\rho_s(T)$ with increase in temperature in the limit $T \ll T_c$ comes from $\partial f / \partial E$ and not from the temperature-dependence of the gap.

If the magnitude of the gap at $T = 0$ is given as $\Delta(0)$ then in the limit

$T \ll T_c$ it can be showed that (please refer to [1] for the detailed steps),

$$n_n(T) = n \sqrt{\frac{2\pi\Delta(0)}{k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right). \quad (2.24)$$

$$\therefore \rho_s(T) = 1 - \frac{n_n(T)}{n} = 1 - \sqrt{\frac{2\pi\Delta(0)}{k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right). \quad (2.25)$$

Using the expression for λ_{CGS} from Eq. 2.11 and taking into account the fact that $n = n_s(0)$ we can write,

$$\rho_s(T) = \frac{n_s(T)}{n_s(0)} = \frac{\lambda^2(0)}{\lambda^2(T)}. \quad (2.26)$$

Here, $\lambda(0)$ is the London penetration depth at $T = 0$.

Thus, substituting $\rho_s(T)$ from Eq. 2.25, we get the following expression for $\lambda(T)$ for an s -wave superconductor in the limit $T \ll T_c$,

$$\lambda(T) = \lambda(0) \left[1 - \sqrt{\frac{2\pi\Delta(0)}{k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \right]^{-1/2}. \quad (2.27)$$

$$\therefore \lambda(T) \approx \lambda(0) \left[1 + \sqrt{\frac{\pi\Delta(0)}{2k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \right] \quad (T \ll T_c). \quad (2.28)$$

This implies, for an s -wave superconductor, the low-temperature penetration depth data can be fit to an exponential function of the form shown above. To be more specific, it has been shown by Bernhard Mühlischlegel [1] that a necessary condition for the derivation of this exponential-dependence is that $T \leq 0.3T_c$ — above which the temperature dependence of the gap $\Delta(T)$ no longer remains constant.

Next, let us consider the example of a gap function with nodes. Lets take the simplest case of a d -wave superconductor, for which (as mentioned in Section 2.1) $\Delta_k = \Delta_0 \cos(2\phi)$. Substituting Δ_k in Eq. 2.22, the normalized

QDOS for a d -wave scenario is given as,

$$\frac{N(E)}{N_0} = \int_0^{2\pi} \frac{E}{\sqrt{E^2 - \Delta_0^2 \cos^2(2\phi)}} \frac{d\phi}{2\pi}. \quad (2.29)$$

Using an approach as described in [7], in the limit $E \ll \Delta_0$ it can be shown that Eq. 2.29 can be simplified as follows,

$$\frac{N(E)}{N_0} \approx \frac{E}{\Delta_0} \quad (E \ll \Delta_0). \quad (2.30)$$

Now, we can write Eq. 2.17 in terms of ϕ to get,

$$n_n = n \int_0^{2\pi} \frac{d\phi}{2\pi} \int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial E_k} \right) d\xi = 2n \int_0^{\infty} \left(-\frac{\partial f}{\partial E} \frac{N(E)}{N_0} \right) dE. \quad (2.31)$$

Substituting $N(E)/N_0$ from Eq. 2.30 and performing the integration we finally get the following expression for $n_n(T)$,

$$n_n \approx 2n \ln 2 \frac{T}{\Delta_0} \quad (T \ll T_c). \quad (2.32)$$

Finally, following a procedure similar to that done for the s -wave case in the preceding paragraphs, it can be shown that the low- T ($T \ll T_c$) penetration depth $\lambda(T)$ for a d -wave material has the following form,

$$\lambda(T) \approx \lambda(0) \left(1 + \ln 2 \frac{T}{\Delta_0} \right) \quad (T \ll T_c). \quad (2.33)$$

That is, the low- T penetration depth data for d -wave superconductors varies linearly with temperature.

In our experimental setup, we can directly measure the change in penetration depth: $\Delta\lambda(T) = \lambda(T) - \lambda(T_{min})$, with T_{min} being the base temperature of our cryostat. Let us consider $T_{min} \rightarrow 0$ and try to find an expression for $\Delta\lambda(T)$ for both s -wave and d -wave superconductors.

For *s*-wave: Using Eq. 2.28 we can write,

$$\Delta\lambda(T) = \lambda(T) - \lambda(0) = \lambda(0) \sqrt{\frac{\pi\Delta(0)}{2k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \quad (T \ll T_c). \quad (2.34)$$

For *d*-wave: Using Eq. 2.33 we can write,

$$\Delta\lambda(T) = \lambda(T) - \lambda(0) = \lambda(0) \left[\ln 2 \frac{T}{\Delta_0} \right] \quad (T \ll T_c). \quad (2.35)$$

Do note that, for unconventional superconductors having either symmetry protected nodes or accidental nodes, the low-temperature penetration depth has a power-law dependence of the form $\Delta\lambda(T) \propto T^n$, where n is a power law exponent and depends on the dimensionality of the nodes [8]. Table 2.1 summarizes the T -dependencies of the key experimental parameters for different techniques, while probing nodal superconductors with linear dispersion. The enhanced thermal excitation of the quasiparticles in the vicinity of the nodes is responsible for changing the temperature-dependence from an exponential one to a power-law. On the other hand if there is no nodal feature, then even for an anisotropic gap the low-temperature behavior of $\Delta\lambda(T)$ will be exponential in nature, determined by the smallest gap magnitude [4].

Table 2.1: Signature for nodal superconductivity [8,9]

	3D point node	3D line node
Penetration depth λ	T^2	T
Specific heat C_{el}	T^3	T^2
NMR relaxation $1/T_1$	T^5	T^3
Thermal conductivity κ	T^3	T^2

$\lambda(0)$ is a material-dependent constant that can be obtained from other experimental methods, for example muon spin rotation (μSR) which can also probe $\lambda(T)$ albeit with a higher error bar. Using that value, we can *fit our low- T data directly* to Eq. 2.34 and Eq. 2.35 to check for the better fitting result. That is our experimental setup provides a direct approach to estimate

the likelihood of a newly-discovered superconducting sample to either have a BCS like conventional pairing symmetry or an unconventional one. We should mention here that the T_{min} of our cryostat is ~ 350 milliKelvin (mK), and the data value obtained at this temperature cannot be taken as the $T = 0$ data point, especially for samples with a low critical transition temperature T_c . Since $\lambda(0)$ from μSR is not available in literature for all the samples measured, we have our own method to estimate the $T = 0$ K data point from our *raw* data. How we do so shall be discussed later while analyzing the data.

In the previous paragraph we have used the word estimate on purpose. Because fitting the low- T $\Delta\lambda(T)$ data to one of the two gap functions might be helpful in predicting whether the superconducting gap has nodes or not, but it is not a sufficient condition to conclude with absolute certainty the nature of the pairing symmetry. We will briefly elaborate on this point using the argument provided in [7].

It has been shown that for the d -wave superconductor, normalized superfluid density $\rho_s(T)$ varies linearly with temperature in the form $\rho_s(T) = 1 - \alpha \frac{T}{T_c}$, where $\alpha = \text{const} \frac{d\phi}{d\Delta}|_{node}$ gives the inverse of the angular slope of the gap function near the nodes [10]. On the other hand penetration depth $\lambda(T)$ can be expanded in a Taylor series of the form,

$$\lambda(T) = \lambda(0) \left[1 + \frac{1}{2} \left(\frac{\alpha T}{T_c} \right) + \frac{3}{8} \left(\frac{\alpha T}{T_c} \right)^2 + \dots \right]. \quad (2.36)$$

If α is small i.e. the gap function drops very fast to zero near the nodes, only then can we neglect the higher order terms in Eq. 2.36. Thus, we see that even though $\rho_s(T)$ varies linearly with temperature that is not strictly the case for $\lambda(T)$. In this thesis we shall always convert $\lambda(T)$ data to $\rho_s(T)$ and then subsequently fit to different models to analyze data.

2.4 Temperature-dependence of the Superconducting Gap

From Eq. 2.23 we can see that, to fit superfluid density $\rho_s(T)$ data to different theoretical models over the full temperature range up till T_c , it is imperative to have knowledge about the nature of the gap function Δ_k . To remind the readers, Δ_k simply represents the $\mathbf{k}$ -dependent gap function which also has an explicit dependence on temperature for both conventional and unconventional superconductors. We would like to briefly talk about $\Delta(T)$, the temperature dependence of the gap with focus on the different models we have used and how they affect the overall $\rho_s(T)$ data.

Based on the original BCS theory, an expression for Δ_k can be determined by treating it as a variational parameter and by minimizing the free energy of the superconducting phase with respect to variations in this Δ_k . The detailed derivation based on this approach can be found elsewhere and the end result is a self-consistent gap equation of the following form [4],

$$\int_0^\infty \left[\frac{\tanh\left(\frac{\sqrt{E^2 + \Delta^2}}{2T}\right)}{\sqrt{E^2 + \Delta^2}} - \frac{1}{E} \tanh\left(\frac{E}{2T_c}\right) \right] dE = 0. \quad (2.37)$$

Over the years, several semi-empirical expressions for $\Delta(T)$ have been derived based on theoretical predictions in conjugation with fits to real experimental data. For example, Gross *et al.* in their work [2] used the following expression for $\Delta(T)$ to obtain $\rho_s(T)$ curves and fit to experimental data for both isotropic as well as nodal superconductors,

$$\Delta(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\}. \quad (2.38)$$

Here, $\delta_{sc} = \Delta(0)/k_B T_c$ with $\Delta(0)$ being the gap magnitude at $T = 0$, a is a constant dependent on pairing mechanism and $\Delta C/C$ is the jump in

electronic component of the specific heat at the transition point. For BCS weak-coupling superconductors, the parameters have the following values: $\delta_{sc} = 1.76$, $a = 2/3$ and $\Delta C/C = 1.43$.

If the low- T experimental $\Delta\lambda(T)$ data of any new sample does not fit to a power-law, our first intuition is usually to try to fit the extracted $\rho_s(T)$ data to that for a conventional BCS-like superconductor. In that scenario, using Eq. 2.38 often poses a problem since both the parameters a and $\Delta C/C$ are usually unknown for newly discovered samples. Here we would also like to mention that; $\Delta(0)$ is used as the fitting parameter in the data analysis and the obtained value of δ_{sc} is then compared to the BCS value of 1.76. We can thus qualitatively classify the sample as one of the following categories of conventional superconductors – weak-coupling, moderately weak-coupling ($\delta_{sc} \sim 1.76$ to 2.00), strong-coupling ($\delta_{sc} > 2.00$) etc with coupling referring to electron-phonon coupling.

To avoid the necessity of knowing $\Delta C/C$ and a , we tried using an interpolation formula for the gap by Carrington *et al.* [11]. The expression for this $\Delta(T)$ (which we shall call the Carrington gap) has been shown below,

$$\Delta(T) = \frac{\Delta(0)}{k_B T_c} k_B T_c \tanh \left\{ 1.82 \left[1.018 \left(\frac{T_c}{T} - 1 \right) \right]^{0.51} \right\}. \quad (2.39)$$

As one can see, for a sample with known T_c the only variable in this expression is $\Delta(0)$, which as we have already mentioned is used as the fitting parameter. This is a phenomenological model that essentially assumes that the temperature variation of the gap, given by $\Delta(T)/\Delta(0)$ follows the BCS theory, but the ratio $\Delta(0)/k_B T_c$ can still be used as an adjustable parameter. This approach is based on the famous α -model (with $\alpha = \Delta(0)/k_B T_c$) by Padamsee *et al.*, whose work introduced a semi-empirical expression that found an excellent agreement between numerical and experimental values of $\Delta(0)/k_B T_c$ for both weak-coupling as well as strong-coupling superconductors. [12]

Figure 2.2: Comparison of the temperature dependencies of the superconducting gap $\Delta(T)$ obtained from the solution to the BCS self-consistent integral (Eq. 2.37), to the interpolation formulae by Carrington *et al.* (Eq. 2.39) and Gross *et al.* (Eq. 2.38) [Using the same $T_c = 2$ K].

To do an effective comparison between these models, we have used MATHCAD to plot (Fig. 2.2) Eq. 2.37, Eq. 2.38 and Eq. 2.39 on the same graph for an arbitrary $T_c = 2$ K, considering weak-coupling BCS values. From Fig. 2.2 one can see that the three curves nearly overlap. To fit our experimental data, we have primarily used the Gross gap and resorted to using the Carrington gap only in particular instances.

2.5 Novel Superconducting Phases: Multi-band Superconductivity and Topological Superconductivity

In this section, we would like to qualitatively introduce some novel superconducting physics that we have used to explain some of the more *unorthodox* data, obtained from our penetration depth measurements.

(I) Multi-band Superconductivity: For conventional superconductors with weak electron-phonon coupling, there is usually a single gap on the Fermi surface with the normalized gap magnitude $\Delta(0)/k_B T_c = 1.76$, and the BCS theory shows robust numerical agreement with experimental data. However, for samples with multiple Fermi pockets in their band structure as well as for samples with a strong anisotropy in their gap-structure or belonging to the so called strong-coupling limit ($\Delta(0)/k_B T_c > 2.00$), a significant deviation of the experimental data from the theory has been observed. Even though the original BCS theory predicted that the gap ratio higher than 2.00 and lower than 1.76 has no physical meaning, superconductors violating both the upper and lower bounds have been discovered over the years. It had been suggested that for superconductors with strong electron-phonon coupling [$\Delta(0)/k_B T_c \sim 2.5$] the quasiparticle excitations should have energy comparable to principal phonon energies resulting in short quasiparticle lifetime and hence the “quasiparticle picture” of the BCS theory breaks down [12]. On the other hand, observed values of $\Delta(0)/k_B T_c$ lower than 1.76 has been attributed to gap anisotropy [15].

Multi-band superconductivity has been predicted to occur in materials having multiple energy bands crossing the Fermi level E_F , with the number of superconducting gaps and nature of the gap symmetry being dictated by inter and intraband scattering. A well-known example is MgB_2 (Fig. 2.3) having three distinct bands crossing E_F , and for which fits to superfluid

Figure 2.3: Multi-band superconductivity in MgB₂ from previous experiments. (Top) Electronic band structure of MgB₂. Quasi-2D σ -band as well as 3D π -bands have been indicated by arrows. Figure reprinted with permission from [13]. Copyright 2001 by the American Physical Society. (Bottom) Two components of the superfluid density $\rho_s(T)$ in single crystalline MgB₂, extracted from penetration depth measurements. Solid lines are the fits to the α -model (please refer to Chapter 5). Long-dashed line are the separate contributions from the σ and π bands, respectively. The short-dashed line is the weak-coupling BCS. Inset shows temperature dependencies of the two gaps used for the fits. Figure reprinted with permission from [14]. Copyright 2005 by the American Physical Society.

density $\rho_s(T)$ from penetration depth measurements found two distinct superconducting gaps – a smaller gap with $\Delta(0)/k_B T_c \approx 0.75$ on the π -bands and a larger gap with $\Delta(0)/k_B T_c \approx 2.00$ on the σ -bands [16]. The two-gap α -model that has been used to fit $\rho_s(T)$ for MgB_2 , is based on an original model developed by Suhl *et al.* [17].

Figure 2.4: Schematic representation of the multi-gap model by Suhl *et al.* [17] for a particular set of parameters. Normalized superconducting gap $\Delta(0)/k_B T_c$ as a function of normalized temperature T/T_c for a superconductor with two gaps (two solid curves), on two distinct energy bands. The two BCS-like gaps have intrinsic transition temperatures T_{c1} and T_{c2} . For the situation where interaction energy due to interband coupling is absent i.e. $V_{sd} = 0$, the two transition temperatures are observed separately. On the other hand, when V_{sd} is finite but weaker than interaction energy for intraband interaction $V_{ss} V_{dd}$, T_{c1} is not observed and instead both the gaps close at T_{c2} — a single effective gap as shown by the dotted curve is obtained.

In their work, Suhl *et al.* extended the standard BCS formalism to the case of possible multi-band superconductors, by taking into account electron-phonon and electron-electron interactions for both intraband and interband scenarios. They considered interaction between itinerant electrons of the s and d orbitals, with density of states N_s and N_d respectively. This interaction

energy is the average phonon emission and absorption energies from these two orbitals after subtracting the Columb repulsive terms. Accordingly, they used three possible interaction energies – (i) V_{sd} which is the interband interaction and (ii) V_{ss} and V_{dd} which correspond to the intraband interactions. Similar to the coupled Eliashberg equations, these interaction terms can be obtained by numerically solving a set of coupled equations which depend on the number of interacting energy bands. For two superconducting gaps that open on bands s and d , with respective normalized gap magnitudes A and B , the *coupled* equations are given as follows,

$$A = V_{ss}N_sAF(A) + V_{sd}N_dBF(B) \quad (2.40)$$

$$B = V_{ds}N_sAF(A) + V_{dd}N_dBF(B), \quad (2.41)$$

where,

$$F(A) = \int_0^{\hbar\omega} \frac{\tanh\left[\frac{(\varepsilon^2 + A^2)^{1/2}}{2k_BT}\right]}{(\varepsilon^2 + A^2)^{1/2}} d\varepsilon, \quad (2.42)$$

and similarly for $F(B)$. Here, ε is the electron kinetic energy relative to E_F . When there is no interaction between the two energy bands i.e. $V_{sd} = 0$, the two band-specific gaps manifest independently and two distinctive superconducting transitions are observed. However, when there is a weak but finite interband coupling, the transition temperature T_{c1} of the smaller gap is raised to T_{c2} of the bigger gap and an effective single gap (with a distinctive kink between T_{c1} and T_{c2}) is observed.

The curves in Fig. 2.4 have been plotted by solving Eqns. 2.40, 2.41 and 2.42 for a particular set of parameters. The solid curves represent the individual BCS-like Gap 1 and Gap 2, while the dotted curve is the effective gap when a finite interband coupling is introduced. In the context of our penetration depth measurements, this concave/convex nature of the effective gap should be observed in the superfluid density — similar to the

bottom graph in Fig. 2.3. We have observed similar multi-band like features in our experimentally obtained $\rho_s(T)$ data for the samples $\text{CsMo}_{12}\text{S}_{14}$ and $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$, as shall be discussed in later chapters.

Table 2.2: Experimental values of $\Delta(0)/k_B T_c$ for some multi-gap superconductors

Sample	Experimental technique	Gap 1	$\Delta_1(0)/k_B T_c$	Gap 2	$\Delta_2(0)/k_B T_c$
MgB_2 [16]	TDO penetration depth	nodeless	1.97	nodeless	0.75
SnMo_6S_8 [18]	specific heat, STS	nodeless	2.43	nodeless	0.81
FeS [19]	specific heat	nodeless	1.60	line nodes	1.34
ThFeAsN [20]	specific heat, μSR	nodeless	2.14	line nodes	0.15
$\text{PrPt}_4\text{Ge}_{12}$ [21]	specific heat	nodeless	2.44	point nodes	1.58

To give an idea to the readers, we have listed down the experimentally obtained values of $\Delta_i(0)/k_B T_c$ ($i = 1, 2$ for Gaps 1 and 2 respectively) for some potential two-gap superconductors in Table 2.2, as obtained using different experimental techniques such as penetration depth, electronic specific heat and scanning tunneling spectroscopy (STS) measurements. In addition to MgB_2 , the list contains members from other superconducting families such as pnictides, skutterudites and chevrel phase materials as well. One common trend that becomes immediately visible is that for one of the gaps, $\Delta(0)/k_B T_c$ is usually $\geq$ the BCS weak-coupling value of 1.76, while it is significantly smaller for the other gap.

(II) Topological Superconductivity: The search for topological superconductors (TSCs) is one of the most urgent problems in modern condensed matter physics. The root for this immense interest in this exotic class of superconductors lies in the discovery of topological insulators (TIs). A topological insulator like Bi_2Se_3 has an insulating bulk, while strong spin-orbit coupling leads to presence of gapless surface states populated by Dirac Fermions [22]. Such topologically non-trivial *systems* are characterized by a topological number called a Chern number that is closely related to the conserved symmetries of the system. A three dimensional TSC should have a finite non-zero topological number with a fully-gapped bulk and possess zero-energy localized modes in its quasiparticle excitation spectrum called

Andreev bound states which can be localized either at the surface or at topological defects such as vortex boundaries. These edge states are expected to consist of Majorana fermions and are topologically protected i.e. they cannot be removed by the application of any local perturbation [23].

The realization of TSCs has proved to be quite challenging and the primary approach adopted thus far has been to dope TIs with conventional *s*-wave superconductors and use proximity effect to induce superconductivity. A successful example of this approach is Nb-intercalated Bi_2Se_3 which has been found to be a chiral *p*-type superconductor by penetration depth measurements [24]. The low-temperature penetration depth in this sample was shown to have a T^2 dependence suggestive of point nodes [Table 2.1], contrary to an exponential dependence as expected for nodeless BCS superconductors. For compounds in which Rashba-type [25] strong spin-orbit coupling is allowed, a mixed phase consisting of both spin-singlet and spin-triplet type order parameter can be found. It has been suggested that topologically non-trivial states if present, should be exclusive to the spin-triplet component of the mix [23]. Based on this reasoning, another approach to realize TSCs has been to investigate stoichiometric compounds that might exhibit spin-triplet superconductivity in the bulk. This sort of a spin-triplet pairing amongst the Cooper pairs is a rare occurrence and till date has been proposed in very few compounds such as Sr_2RuO_4 [26].

One of the key signatures to identify potential TSCs is to discern the pairing symmetry of the superconducting OP. As already mentioned, the surface-bound edge states should contribute to zero-energy excitations and hence the superfluid density should significantly deviate from a conventional BCS-like scenario. Smidman *et al.* has suggested that if the superconducting order parameter has a mixed nature having both spin-singlet and spin-triplet components, the Majorana modes should be exclusive to the spin-triplet component, i.e. the zero-energy gapless excitations should be

associated with p -type pairing symmetry [23]. These edge states have a very small spatial extent from the surface, necessitating the use of ultra-surface sensitive measurements to extract some significant information regarding the superconducting phase. As already pointed out in Section 1.3, low- T London penetration depth $\lambda(T)$ shows a clear change to power-law behavior from an exponential one for unconventional superconductors. Coupled with the fact that our $\Delta\lambda(T)$ measurement has sub-Angstrom resolution at low- T , we have used our setup to probe the pairing symmetry of the putative TSCs α -PdBi₂ and β -PdBi₂ as shall be discussed in later chapters.

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Chapter 3

Experimental Method

In my PhD project, we have developed a high precision technique, for the temperature dependent measurement of magnetic susceptibility χ in a superconductor, which is proportional to it's magnetic penetration depth λ . The overall design of our apparatus was motivated by an original system developed by Dr. Ismardo Bonalde and Dr. Brian Yanoff [1]. The utilization of a tunnel-diode as a self-resonating oscillator [we shall use the acronym TDO in subsequent sections] was originally suggested by Craig Van Degriфт, who illustrated in his paper [2] how to achieve a stability of 0.001 part-per-million (ppm) at low temperatures. This chapter contains the following sections: (1) impedance matching and self-resonant oscillation of a LC tank circuit, (2) methodology of measurement, (3) mechanical design, (4) operation of the Helium-3 cryostat, (5) system performance: drift, noise and background signal, (6) relation between inductance and susceptibility, (7) relation between susceptibility and magnetic penetration depth, (8) system calibration, and (9) extracting pure in-plane and inter-plane penetration depths.

3.1 Impedance Matching and Self-resonant Oscillation of a LC Tank Circuit

A parallel LC circuit comprises of an inductor (L) and a capacitor (C) in parallel and has an impedance $Z = -i\omega L/(\omega^2 LC - 1)$. Here $\omega = 1/\sqrt{LC}$

is the resonant frequency of the LC -tank circuit. Ideally, at resonance the circuit has infinite impedance; however in reality dissipative components are always present (resistance due to wire leads, poor winding of the coils etc.). Thus, the dissipative corrections have to be taken into calculation, and the schematic of a *real* LC circuit should include these resistive components as shown in Fig. 3.1. All the figures have been drawn using an electronic circuit simulation software.

Figure 3.1: (Left) Schematic of a real LC circuit (with dissipative components connected in series with L and C), and (right) a LC circuit with the tunnel-diode negative differential resistance coupled.

In the Fig. 3.1(right), $-R_n$ represents the negative differential resistance of the tunnel-diode. So, if the LC circuit is at resonance and $Z = R_n$, we would expect a self resonating oscillation that will be sustained (because $-R_n$ acts as an alternating current (ac) power source). Therefore, for impedance matching two conditions have to be satisfied – (a) The signs of Z and $-R_n$ have to be same that is Z has to be a real and positive number and (b) The magnitude of Z and $-R_n$ has to be same.

Z being a complex number, condition (a) can never be satisfied. Satisfying (b) is easy by tuning the value of L using a second coil, which we call the tapping/tap coil. The following part closely follows the analysis done by myself, Dr. Xian Yang Tee and final year project student Tam Qian Xin. Let us try to derive the requirement to satisfy condition (b). The problem

Figure 3.2: A resonant circuit with dissipative resistances.

can be solved by extracting the effective impedance of a RLC circuit that includes dissipative resistive components r_1 and r_2 in series as shown in Fig. 3.2.

If we assume, $Z_1 = iZ$ and $Z_2 = -iZ$ [Z being a real positive quantity], then the effective impedance Z_{eff} is a parallel combination Z_1 and Z_2 as shown below,

$$\frac{1}{Z_{eff}} = \frac{1}{r_1 + iZ} + \frac{1}{r_1 - iZ}, \quad (3.1)$$

which upon series expansion gives,

$$\frac{1}{Z_{eff}} = \frac{1}{iZ} \left[-\frac{r_1}{iZ} - \frac{r_2}{iZ} + \text{higher order terms} \right]. \quad (3.2)$$

Assuming $r_1 \ll Z$ (i.e. dissipative components *much smaller* than the impedance), we get,

$$\frac{1}{Z_{eff}} = \frac{1}{(iZ)^2} [r_1 + r_2] \implies Z_{eff} = \frac{Z^2}{r_1 + r_2}. \quad (3.3)$$

This is a real and positive number. As mentioned before, we need to tune the L value by using an additional tapping coil to satisfy condition (b).

In Fig. 3.3, x is the tapping fraction (can vary from 0 to 1), and we have $Z = x\omega_0 L$. That is, the effective impedance becomes,

$$Z_{eff} = \frac{x^2 \omega_0^2 L^2}{r_1 + r_2}. \quad (3.4)$$

Figure 3.3: The tank circuit with the tapping and primary coils shown separately.

It is not possible to calculate Z_{eff} precisely, hence we had to tune the number of turns of the tap coil to obtain the best oscillation in the necessary temperature range.

The most essential component of the TDO setup is a tunnel-diode. It is a very heavily doped p-n junction diode, in which (when forward biased) one can have tunneling phenomenon giving a very unique feature to the I-V curve. The I-V curve for the tunnel-diode (Model: Aeroflex Hermetic MBD1057-H20) used in our setup has been shown in Fig 3.4. Resistances R_1 , R_2 and R_p in this figure are used to DC bias the tunnel-diode in its *negative differential resistance* ($-dV/dI$). The value of R_n is expected to be very similar at 77 K and 4 K [3]. We must mention that even though it is possible to get TDO oscillation at 77 K, eventually we tuned the ratio between N_p (number of turns of the primary coil) and N_{tap} (number of turns

of the tapping coil) such that sustained oscillation only appears below 50 K. This greatly enhanced the signal to noise ratio at 4.2 K, which enhanced the measurement precision of our superconducting samples with critical transition temperatures T_c 's ≤ 10 K.

Figure 3.4: (Left) Comparison of the measured I-V curves of our tunnel-diode at 300 K and 77 K. (Right) I-V curve at 77 K showing the negative slope only. The red line is the region for most efficient impedance matching.

3.2 Methodology of Measurement

We report measurement of the magnetic penetration depth for different superconducting samples from their respective T_c 's down to the temperature as low as 350 mK, which can be achieved using our Helium-3 Cryostat Cryogenics Institute of America. The low-temperature component of the system consists of different resistive components in its electronic circuit, with distinct stages that need to be controlled at specific temperatures while being thermally insulated from each other. Clearly, careful mechanical design of the cold finger is essential to ensure we can reach the lowest base temperatures. In the later phase of setup, to shield the cryostat from stray signals (e.g. the earth's magnetic field) the dewar was surrounded by a mu-metal shield that can prevent fields as small as 1 mT from interfering with the measurement. This is extremely useful especially for samples with low $H_{c1}(T)$, as it ensures no vortices are trapped inside when the sample is cooled

below T_c .

The low-temperature circuit (used to bias the tunnel-diode and generate the sustained oscillation) has been shown in Fig. 3.5. All the values of the capacitors and resistors have been estimated using an original set of formula from Van DeGrifts paper [2]. The direct current (dc) bias for the tunnel-diode circuit is generated at room temperature by a semiconductor reference voltage source Burr-Brown model REF10, which provides a very stable 10 V output. The schematic of the room- T circuit has been shown in Fig.3.6.

Figure 3.5: Schematic of the low-temperature circuit showing values of the components used. The circuit components are based on an original design by Dr. Brian Yanoff [1].

Figure 3.6: Schematic of the room-temperature circuit showing values of the components used. The circuit components are based on an original design by Dr. Brian Yanoff [1].

This voltage is buffered with a low noise op-amp. The op-amp output is fed to a $5\text{ k}\Omega$ resistor which is connected to a $10\text{ k}\Omega$ potentiometer. Thus, a very stable V_{bias} can be maintained across the $5\text{ k}\Omega$, which in turn acts like a high precision current source. The bias current is filtered with a low-pass Butterworth filter before being passed down using a semi-rigid coaxial cable. The generated TDO RF oscillation signal (20-30 MHz) is carried back via this same coax cable. The low-pass filter ensures that the TDO signal does not interfere with the dc bias source. We found that using a semi-rigid cable instead of a flexible one, makes shielding to electromagnetic interference much better.

The ac component is coupled through a capacitor to an RF amplifier Trontech, Inc. model W50ATC and then to a balanced mixer Hewlett-Packard model 10514A. The frequency output from the mixer is the difference between the signal frequency and the frequency of the local oscillator (LO) signal from a synthesizer Stanford Research Systems model DS345. The LO frequency is adjusted to set the mixer output frequency to a convenient value, usually 15-20 kHz. The mixer output is then fed to a Lock-In Amplifier Stanford Research Systems model SR530. The audio amplifier of the Lock-In amplifies the mixer output. The reference signal (f_{LI}) of the lock in is provided by another function generator. The lock in has a fixed bandwidth of $f_{LI}/5$ (internal bandpass filter). The value of f_{LI} is decided based on the width of the frequency change at T_c . The preamplified filtered signal from the Lock in is observed on an oscilloscope Lecroy Wavejet Model 354 500 MHz Oscilloscope to verify the sinusoidal nature of the waveform. It is also fed to a universal frequency counter (Hewlett-Packard model 53131A). The frequency counter is equipped with an optional high stability time base (10 MHz from the internal crystal oscillator), which can provide up to a stability of 1 ppb. This 10 MHz time base signal is also used to generate the synthesized local oscillator signal and the lock-in reference signal. This

ensures that there is no phase lag between the outputs from the two function generators. The frequency counter also has a custom built oven inside, which makes sure that there is no thermal drift of the 10 MHz signal from the crystal oscillator.

3.3 Mechanical Design

As stated before, mechanical design of the low-temperature part is extremely pivotal, and has gone through numerous modifications before we could achieve the most optimum design which gave the best possible result in terms of sample base temperature (T_{base}) and stability of data. The low-temperature component primarily comprises of 3 parts — (i) the cold finger which should be able to cool down the sample to the lowest possible temperatures and then warm up smoothly up to more than the respective T_c 's, (ii) the electronics can housing the low-temperature electronic components viz. the resistors, capacitors, the tapping coil and the tunnel-diode and (iii) a separate stage that is thermally anchored to the primary coil. All the 3 stages are thermally insulated from each other. Stages (ii) and (iii) need to be maintained at fixed temperatures during measurement to ensure minimum drift and noise in data. We keep the primary coil and the tapping coil in separate stages on purpose; this allows us to keep the primary coil N_p fixed, while changing N_{tap} of the tapping coil to achieve the TDO oscillation at desired frequencies. We will briefly talk about the three stages below.

The cold finger comprises of two pieces – a gold plated 99.999% pure oxygen-free-high-conductive (OFHC) copper piece that is screwed (using stainless steel screws) to the sample mount of our Helium-3 cryostat and a 1.25 mm diameter single crystal sapphire rod that is glued inside the OFHC piece using thermally conductive Silver epoxy. Sapphire is an excellent choice because it is an electrical insulator and does not introduce significant magnetic susceptibility of its own within our desired temperature range. The

Figure 3.7: Photographs of (left) the electronics can and the primary coil holder, and (right) the cold finger.

sample is placed on top of the Sapphire rod using GE varnish. At the base of the sapphire rod inside a covered groove on the OFHC piece, there is a calibrated Lakeshore CX-1030 temperature sensor to measure the sample temperature. There is an additional RuO_2 sensor placed inside the cryostat sample mount. At T_{base} , I found that the thermal offset between the CX-1030 and the RuO_2 is only around 20 mK. This offset can be minimized by waiting for a longer duration to achieve thermal equilibrium. The hold time at T_{base} is constrained by the Liquid Helium-4 level in the dewar and the 1.5 K pot of the cryostat. I was able to bring down the T_{base} from 400 mK to 350 mK by spreading a minuscule drop of Apiezon-N Grease in between the cryostat sample mount and the cold finger base. The warming up of the sample is achieved using a $25\ \Omega$ heater, by carefully controlling the PID settings of the output of a Lakeshore-350 temperature controller.

The oscillator electronics is housed inside a copper can made of OFHC copper, which enables effective thermal control. The main component of the can is just a single piece of OFHC copper cut into three segments — two circular pieces with a thin rectangular flat segment in between. The electronics are all mounted on both sides of the rectangular piece with wires

passing through holes to each side. All the wires are thermally anchored to the copper plate using Stycast 2850. The copper piece acts both as the thermal anchor as well as the ground for the low-temperature circuit. To prevent short circuit between the electronics and this plate, the resistors and capacitors were mounted on a piece of tobacco paper. The grounding connections are achieved by soldering the wires to the Copper plate using Sn-Ag solder (97% Sn, 3% Ag, Kester Lead-Free solder) which has a lower T_c (3.7 K) than ordinary Pb-Sn solder (7.3 K). To prevent any sort of electromagnetic interference from effecting the TDO signal generation, the electronics mount is enclosed on both sides by two semi-circular pieces of OFHC copper, thus making the whole electronics can behave like an excellent Faraday cage. A small piece of semi-rigid coax cable (with stainless steel outer conductor) passes through a hole in one of the semi-circular copper pieces. The exposed core conductor inside this coax is soldered to the low-temperature circuit, while the other end is connected to a piece of flexible SMA coaxial cable. This SMA cable in turn is connected to another piece of long stainless steel semi-rigid coaxial cable that goes all the way to the room-temperature electronics. Since, this coaxial cable can bring down heat, it is thermally anchored (hermetically sealed) to the 4.2 K head of the Helium-3 cryostat. To make sure there is no ground loop, the chassis ground from the room-temperature instruments needs to be used for the low-temperature components as well. This is achieved by soldering the outer conductor of the small semi-rigid coax to the copper semi-circular shield.

The primary and the tapping inductor coils are two of the most integral components of the low-temperature circuit, and (in conjugation with the capacitor C) are pertinent to getting a stable sustained TDO RF signal with observable amplitude. The coils are home-made and the fabrication process is similar to as described in [3]. A 3.06 mm diameter drill bit was taken, and several layers of Mylar sheet were wound on it. Two insulated copper wires

were wound together using a homemade coil winder over the Mylar sheets until the desired number of turns is achieved. Stycast 1266 A and 1266 B were mixed in the ratio 3:1, and carefully applied over the wound coil. A heat gun was used to treat the epoxy, when it settled partially one of the wires was carefully unwound, leaving behind a single uniformly spaced (spacing = diameter of the wire) coil. After the Stycast has settled completely the coil is removed, and the Mylar carefully peeled off. The advantage of this technique is that the shunting capacitance between adjacent turns is significantly reduced. The inductance (L) of the fabricated coils were calculated (as shown below) and eventually compared to the inductance value obtained from the resonant TDO signal (f_{TDO}).

Calculation of Inductance: The inductance of a single-layered, tightly wound, long, thin solenoidal coil where it is assumed that the current is uniformly distributed on the surface is given by [4],

$$L_0 = \frac{4\pi^2 N^2 r^2}{l} \times 10^{-9} \text{ Henries}, \quad (3.5)$$

where N = number of the turns with $N_p = 22$ (primary coil) and $N_{tap} = 8$ (tapping coil), l = length of the coil = 0.53 cm (primary coil) and 0.2 cm (tap coil), r = radius of the tap thread (in cm) = 0.153 cm.

However if the length of the coil is made shorter the field inside is no longer uniform and depends on the ratio of length and the radius of the coil. Also since the turns are spaced well apart uniformly, the current is concentrated over the wires primarily. These two factors require us to introduce two correction terms K_1 and K_2 respectively.

$$K_1 = \frac{1}{1 + 0.09 \left(\frac{r}{l}\right) - 0.029 \left(\frac{r}{l}\right)^2}, \quad (3.6)$$

$$K_2 = 1 - \frac{l(A + B)}{\pi N K_1}, \quad (3.7)$$

where $A = 2.3 \log \left(1.73 \frac{d}{c} \right)$ and $B = 0.336 \left(1 - \frac{2.5}{N} + \frac{3.8}{N^2} \right)$. Here d is the diameter (in cm) of the circular wire, and c is the winding pitch, i.e. the center-to-center distance between successive turns. Then the effective inductance of the LC circuit is,

$$L = L_0 \times K_1 \times K_2. \quad (3.8)$$

For our circuit we have the following parameters, $c = 2d = 0.02$ cm, where $d = 0.01$ cm. Calculating I got, $K_1 = 0.799$ (primary coil), $K_1 = 0.606$ (tapping coil) and $K_2 = 0.989$. These in turn gives, $L_{p0} = 0.789 \mu\text{H}$ and $L_{t0} = 0.276 \mu\text{H}$. Thus finally we get, $L_p = 0.624 \mu\text{H}$ and $L_{tap} = 0.165 \mu\text{H}$. So $L_{total} = L_p + L_{tap} = 0.789 \mu\text{H}$. Using $C = 47.1$ pF, we calculate a theoretical frequency, $f_{theory} = 26.12$ MHz. Experimentally, we obtain on a spectrum analyzer $f_{expt} = 26.52$ MHz. This implies $L = 0.765 \mu\text{H}$, which we can see does not vary much from the theoretical value of $0.789 \mu\text{H}$.

The low-temperature electronics can and the primary coil holder stage are thermally insulated using four G-10 spacers. The primary coil is epoxied inside a hollow tube made of solid Stycast 1266, and then this tube is pushed inside an OFHC copper hollow cylinder with more hardened Stycast holding the tube in place. Using Stycast (an excellent thermal conductor) is extremely crucial since the primary coil needs to be held at a fixed temperature (with minimum fluctuation) during the measurement. The tapping coil is held inside a small OFHC copper cylinder and screwed to the rectangular plate of the electronics can. The wires from the primary coil pass through a small hole at the top of the coil holder and enter the electronics can through another hole. A narrow PVC tubing prevents the coil wires from rubbing against the sharp edges of the holes.

The sample needs to be placed exactly at the center of the primary coil (as shown Fig. 3.8) so that it is in the most uniform part of the solenoidal coil magnetic field. The primary coil stage is aligned with respect to the cold finger using a hollow tube made of Vespel. The machined tube has a wall

thickness of only 1 mm. Vespel has an extremely low thermal conductivity at low temperatures, thus greatly minimizes the heat flow from the coil (which is maintained at 2-3 K) stage to the cold finger (that needs to reach 350 mK). The Vespel tube is connected to the coil stage and the cold finger using two drilled Brass flanges, which further mitigates the heat flow.

Figure 3.8: Schematic representation of the *ideal* sample position relative to the primary coil.

3.4 Operation of the Helium-3 Cryostat

We use a Helium-3 based cryostat, in which a fixed volume of high purity Helium-3 gas is circulated internally in a closed cycle to obtain base temperatures as low as 300 mK. As seen from the schematic diagram on the right panel of Fig. 3.9, the cryostat probe comprises of the following components – a cylinder of high purity Helium-3 gas, synthetic high purity charcoal necessary for adsorption of this gas, two capillary tubes to suck liquid Helium-4 using needle valves into the charcoal sorp and a 1.5 K pot, two pumping lines connected from the charcoal sorp and the 1.5 K pot to two dry scroll pumps (SP1 and SP2), and the inner vacuum can (IVC) which can be pumped on down to $\sim 10^{-5}$ mBar using a turbo pump. The schematic of the components mounted inside the IVC has been shown in the left panel

of Fig. 3.9.

Figure 3.9: (Left) Schematic showing the low-temperature components inside the IVC of the Helium-3 (He-3) cryostat. (Right) Overall schematic of the cryostat.

The Helium-3 gas cannister is kept at room temperature ~ 300 K, while the rest of the cryostat is immersed in liquid Helium-4 ~ 4.2 K. The basic principal of the cooling down process can be described as follows. As the temperature of the charcoal sorp is reduced and reaches 4.2 K, more and more Helium-3 gas is pulled down along the length of the probe due to temperature difference induced pressure gradient, and get adsorped in the synthetic charcoal. The 1.5 K pot is pre-filled with Liquid Helium-4 using the capillary tube 1, and when pumped on by SP2, the temperature inside drops from 4.2 K to 1.5 K. Now, when the charcoal is heated to ~ 40 K, all the adsorped gas gets released, and rush down to the even colder 1.5 K pot. As the Helium-3 gas is cooled down below it's boiling point ~ 3.2 K, liquid

Helium-3 starts collecting in the sample mount inside the IVC. This liquid Helium-3 conductively absorbs heat from the cold finger, and in effect a large volume of Helium-3 vapor gets regenerated. The charcoal sorp (maintained at 4.2 K or lower using SP1) acts as a cryo-pump and adsorbs this Helium-3 gas once again. This in turn keeps on lowering the temperature of the remaining liquid Helium-3, and in combination with the high vacuum generated inside the IVC; eventually helps to reach the desirable base temperature ~ 0.32 K (practically) at the sample mount location.

3.5 System Performance: Drift, Noise and Background Signal

As already mentioned in the previous chapter, in our experiment we measure probe change in the magnetic penetration depth $\Delta\lambda(T)$ by measuring the change in the frequency $\Delta f(T)$, while warming up the sample temperature from T_{base} to the sample specific T_c . Here $\Delta f(T) = \delta f(T) - \delta f(T_{base})$, where $\delta f(T) = f_{LO} - f_{TDO}$ with f_{LO} being the Local Oscillator input to the mixer from a DS 345 function generator. Since the low-temperature electronics comprises of heat dissipative components, thermal drift can significantly affect the quality of data. In addition, there is possibility of noise due to mechanical vibration of the three pumping stations [one of which is a turbo pumping station pumping on the Inner Vacuum Chamber (IVC) of the cryostat] and hoses, along with rubber tubings that carry Helium-4 gas back to our reliquefaction system. Since we get direct information about the pairing symmetry of the superconducting order parameter from our raw data itself, it is of utmost importance that we minimize the drift and noise to improve the data quality.

In order to minimize thermal drift and noise, the electronics can and the primary coil stage are controlled at fixed temperatures using two home-

made $25\ \Omega$ heaters. The temperatures are monitored using two Silicone diode sensors (DT-670 from Lakeshore) placed next to the respective heaters (Refer to Fig. 3.9 for the overall schematic). The electronics can is maintained at around 4.6 K while the primary coil stage is maintained at around 2.2 K. The value of the f_{TDO} is closely related to the $-dV/dI$ of the tunnel-diode, which again is dependent on the temperature of the OFHC Copper rectangular plate. Thus the jump in frequency is much more sensitive to fluctuations in the electronics can temperature than the primary coil. So the thermal fluctuation of the electronics is kept less than ± 1 mK. For the primary coil, we found it very easy to control the temperature within the same range as well. The electronics can and the coil stage are thermally anchored (using thick Copper braids) to the 4.2 K head and the 1.5 K pot of the cryostat respectively. This arrangement makes sure that any excess heat load is immediately transferred away from the electronics and the coil. So, as long as there is sufficient liquid Helium-4 in the cryostat dewar, an effective thermal control can be achieved. Before every run, we measure the thermal drift at T_{base} till it becomes monotonically increasing, and then subtract it from the raw data.

With proper thermal control (as explained above) drift as small as 0.01 Hz per minute can be achieved. Just to give a perspective, our raw data is $\sim$ a few hundred Hz over the full temperature range. Even after controlling the thermal drift and noise, sometimes there are unwanted spikes in frequency and it is difficult to ascertain them directly to a particular cause. We took the following precautions to minimize the noise level – (i) I never take measurement immediately after transferring Liquid Helium-4 because there will be noise due to vigorous Helium boil off, (ii) all the pumps are placed on vibration buffers and are provided with vibration dampers to ensure there is no noise transmission either through the ground or the vacuum hoses and (iii) the turbo pumping station is always turned off during measurement.

The least fluctuation we could achieve has been anything between ± 0.05 Hz to ± 0.15 Hz from run to run. The system has an optimum noise level of ~ 2 parts in 10^9 .

Figure 3.10: Full temperature range background signal for the sapphire sample holder. Data from 0.9 K to 16 K have been fitted to a polynomial equation.

Finally we must mention that, even without any sample mounted on the sapphire rod, there is a change in Δf with T . Clearly, this must be the background signal from the sapphire which needs to be measured and then subtracted from the sample raw data. This is extremely crucial especially for BCS-like superconducting samples, which have an almost flat data i.e. extremely small $\Delta f(T)$ at low temperatures. We measured the sapphire background signal (multiple times). The data was measured with a small drop (roughly the same amount used to mount our samples) of GE varnish on top of the sapphire rod. From the T_{base} to ~ 0.85 K the background signal goes downwards, and then it starts going up non-monotonically (shown in

Fig. 3.11 and Fig. 3.10 respectively). We compared the background signal data to that of another TDO thesis [3], and found that the trends are similar. Please note that the overall Δf from 0.4 K to 16 K is < 3 Hz — much smaller than the order of magnitude of usually measured sample data over the same range. Such a small background signal is very easy to subtract and enabled us to measure really small changes in frequency.

Figure 3.11: Sapphire sample holder background signal from 0.4 K to 0.9 K fitted to a linear equation.

3.6 Relation between Inductance and Magnetic Susceptibility

The subsection closely follows the analysis done in [1]. Let us define the following quantities: $\mathbf{B}$ is the magnetic induction, $\mathbf{H}$ is the external magnetic field, $\mathbf{M}$ is the magnetization of the sample, L is the self-inductance of a solenoidal coil when a current I flows through it. Terms with the subscript

‘s’ and subscript ‘0’ refer to values with and without the sample respectively.

The change in the total field energy (Gaussian units) with and without a sample can be written as follows,

$$\Delta U = \frac{1}{8\pi} \int [\mathbf{B} \cdot \mathbf{H} - \mathbf{B}_0 \cdot \mathbf{H}_0] d^3r, \quad (3.9)$$

where,

$$\mathbf{M} = \frac{\chi}{1 + N\chi} \mathbf{B}_0. \quad (3.10)$$

Eq. 3.10 is an approximation assuming the sample is an ellipsoid of revolution and is small enough to be in the uniform part of the coil field. N is the geometrical demagnetization factor and χ the volume susceptibility of the sample.

The change in the self-energy stored in the solenoidal coil when a sample is inserted inside its magnetic field is given as,

$$\frac{1}{2} \Delta L I^2 = \frac{1}{2} (L_s - L_0) I^2. \quad (3.11)$$

Since the total field energy is equal to the self-energy stored in the solenoidal coil, we can write,

$$\frac{1}{2} \int \mathbf{M} \cdot \mathbf{B}_0 d^3r = \frac{1}{2} (L_s - L_0) I^2. \quad (3.12)$$

Dividing the right-hand-side (RHS) and left-hand-side (LHS) in Eq. 3.12 by their respective values without any sample, and using Eq. 3.10 we can write,

$$\frac{L_s - L_0}{L_0} = \frac{4\pi\chi}{1 + N\chi} \frac{V_s}{V_c}. \quad (3.13)$$

Here, V_s and V_c are the volumes of the sample and the coil respectively. The previous expression holds only if the field inside the coil is uniform. If that is not the case, V_s/V_c should be replaced by the *Geometrical filling factor* for a

sample, $F = \left(\int_{V_s} \mathbf{B}_0^2(\mathbf{r}) d^3r \right) / \left(\int_{V_c} \mathbf{B}_0^2(\mathbf{r}) d^3r \right)$. Only in the limit of the coil length being much greater than the coil diameter can we write $F = V_s/V_c$. As we will illustrate later, a smaller value of F gives better data. On the other hand, if the coil diameter is too small, then the thermal radiation from the coil can prevent the sample from reaching the lowest temperatures while cooling down, so there is a trade-off we need to consider.

For the purpose of deriving the calibration factor (G) of our TDO system, we will use F instead of V_s/V_c in Eq. 3.13 as shown below,

$$\frac{L_s - L_0}{L_0} = \frac{4\pi\chi_{CGS}}{1 + N_{SI}\chi_{SI}} F. \quad (3.14)$$

Do note that for using magnetic quantities choosing the correct unit is extremely vital. We have used data and values obtained from a Magnetic Property Measurement System (MPMS) [manufactured by Quantum design] at various points in this thesis. The data generated in MPMS is in CGS units, and we have used the same while analyzing the data later. In Eq. 3.14 the product $N\chi$ can either be in SI or CGS while the numerator is in CGS only. To remind the readers, $\chi_{SI} = 4\pi\chi_{CGS}$ and $N_{CGS} = 4\pi N_{SI}$. From the definition of a perfect Meissner state, we have $\chi_{SI} = -1$. Inserting this value Eq. 3.14 becomes,

$$\frac{L_s - L_0}{L_0} = \frac{-1}{1 - N_{SI}} F. \quad (3.15)$$

Please be reminded that the perfect diamagnetic approximation of $\chi_{CGS} = -1/4\pi$ is only valid at $T = 0$. At any finite temperature, the N_{CGS} factor of the sample causes deviation from this linear relationship.

We can explain the principal of our measurement simply based on Eq. 3.15 as follows. When a sample is cooled below its T_c , the value χ_{CGS} of the superconducting sample changes as a function of temperature, which in turn changes the values of L_s . This change in $L = L_{primary}$ (in our system)

changes the $L_{total} = L_{primary} + L_{tap}$, hence causing a systematic thermodynamic change in the frequency of the self-sustained oscillation which we define as,

$$f_0 = \frac{1}{2\pi\sqrt{L_0 C_0}} \quad (Without \text{ sample}), \quad (3.16)$$

$$f_s = \frac{1}{2\pi\sqrt{L_s C_s}} \quad (With \text{ sample}), \quad (3.17)$$

where $C_s - C_0$ refers to any stray capacitance that might have been introduced while inserting the sample. Assuming $(L_s - L_0 \ll L_0)$, $(C_s - C_0 \ll C_0)$ and $\delta C \ll \delta L$ one can write,

$$\frac{f_0 - f_s}{f_0} = \frac{L_s - L_0}{2L_0} = \frac{2\pi\chi_{CGS}}{1 - N_{SI}} F. \quad (3.18)$$

As briefly stated in Sec. 3.4, we measure the TDO resonant frequency $f_s(T)$ at a finite temperature T relative to $f_s(T_{min})$ at the minimum temperature T_{min} , i.e. we measure $\delta f(T) = f_s(T) - f_s(T_{min})$. Please note that usually $T_{min} = T_{base}$, with certain exceptions as shown in later chapters.

The typical dimensions of the samples we measure are around $1 \times 1 \times 0.1 \text{ mm}^3$. The primary coil has a length $\sim 5 \text{ mm}$ and radius $\sim 1.5 \text{ mm}$. Thus the sample (if centered properly) should be in the uniform part of the coil field, hence we can replace F by V_s/V_c . Taking these two considerations into account and defining $\Delta\chi(T) = \chi(T) - \chi(T_{min})$ [all in CGS], Eq. 3.18 becomes,

$$\frac{\delta f(T)}{f_0} \equiv \frac{f_s(T) - f_s(T_{min})}{f_0} = -\frac{2\pi\Delta\chi(T)}{1 - N_{SI}} \frac{V_s}{V_c}. \quad (3.19)$$

3.7 Relation between Magnetic Susceptibility and Magnetic Penetration Depth

Let us consider our sample to be an infinite slab of thickness $2d$ (cross-section in the x - z plane as shown in Fig. 3.12), with the external magnetic

Figure 3.12: Sample schematic with applied field $\mathbf{B}$ along the x -axis.

field applied along the x -axis. If $z = 0$ coincides with the slab center, the two bounding planes are $z = \pm d$. Then the general solution to Eq. 2.13 with the boundary conditions $B(\pm d) = H_0$ (the peak amplitude) is given as [5],

$$B(z) = H_0 \frac{\cosh\left(\frac{z}{\lambda}\right)}{\cosh\left(\frac{d}{\lambda}\right)}, \quad (3.20)$$

where λ is the absolute value of the magnetic penetration depth.

For the geometry as shown in Fig. 3.12, it can be shown that the magnetization M (induced magnetic moment/sample volume) is given as [6],

$$M = \frac{1}{8\pi d} \int_{-d}^d (B(z) - H_0) dz. \quad (3.21)$$

Substituting $B(z)$ from Eq. 3.20 in Eq. 3.21 and doing the integration one gets [7],

$$M = -\frac{H_0}{4\pi} \left(1 - \frac{\lambda}{d} \tanh \frac{\lambda}{d} \right). \quad (3.22)$$

Thus the volume susceptibility is given as,

$$\chi = \frac{M}{H_0} = -\frac{1}{4\pi} \left(1 - \frac{\lambda}{d} \tanh \frac{\lambda}{d} \right) \approx -\frac{1}{4\pi} \left(1 - \frac{\lambda}{d} \right). \quad (3.23)$$

Here we have assumed that $\lambda \ll d$ (usually true for our single crystal samples) which implies $\tanh \frac{\lambda}{d} \approx 1$.

For practical platelet-shaped superconducting samples with geometry of the form $2w \times 2w \times 2d$; a finite dimension $2w$ exists along the y -axis too, and hence the infinite slab approximation does not strictly apply. This means a component of the external magnetic field will penetrate along the y -direction as well, thus changing the effective superconducting volume element inside the sample. Hence we need to replace d in Eq. 3.23 by an effective sample dimension R_{3D} (shall be mathematically defined later) which depends on sample dimensions, as well as takes into account the geometrical demagnetization effects. Usually R_{3D} has a similar magnitude as d , which implies the approximation $\lambda (\sim nm) \ll R_{3D} (\sim mm)$ still holds true.

Changing d to R_{3D} in Eq. 3.23, the change in the magnetic susceptibility $\Delta\chi$ can be written as,

$$\Delta\chi = \frac{\Delta\lambda}{4\pi R_{3D}} \quad (\lambda \ll R_{3D}). \quad (3.24)$$

Finally, combining Eq. 3.19 and Eq. 3.24 we get,

$$\frac{\delta f(T)}{f_0} = -\frac{V_s}{2V_c(1 - N_{SI}) R_{3D}} \Delta\lambda(T) \quad (\lambda \ll R_{3D}). \quad (3.25)$$

$$i.e. \Delta\lambda(T) = G\delta f(T), \quad (3.26)$$

where the proportionality factor G (we call it the calibration factor) is defined as,

$$G = -\frac{2R_{3D}(1 - N_{SI}) V_c}{f_0 V_s}. \quad (3.27)$$

As briefly mentioned before, it is imperative to point out that what we actually measure using our apparatus is: $\Delta f(T) = f_{IF}(T) - f_{IF}(T_{min})$, where $f_{IF} = f_{LO} - f_s$ is the intermediate frequency output from a mixer. So, to be more precise, Eqn. 3.26 should be written as $\Delta\lambda(T) = G\Delta f(T)$. We choose a fixed local oscillator (f_{LO}) input to the mixer such that f_{IF} is positive with $f_{IF}(T) > f_{IF}(T_{min})$. This is done to ensure that we see a positive diamagnetic jump at the superconducting transition. To achieve the same direction in jump for the converted $\Delta\lambda(T)$, we simply use the positive value G having the same magnitude as in Eq. 3.27.

3.8 System Calibration

It is easily evident from Eq. 3.26 that the raw $\delta f(T)$ we measure for any sample can be immediately converted to $\Delta\lambda(T)$ just by multiplying with a constant factor G . This is one of the biggest advantages of the TDO-based penetration depth measurement technique. Unlike specific heat measurements on superconductors (where one needs to subtract the phonon background to extract the electronic specific heat), here we probe a thermodynamic quantity that is directly related to the underlying electronic interactions. Thus, accurate estimation of G (which involves both sample and coil geometries) for each sample is extremely important.

For most of the samples we measured, we have used a technique for estimating G originally deduced by Prozorov *et al.*. From their analytical solutions, R_{3D} for thin samples ($d \ll w$) can be defined as [8],

$$R_{3D} = \frac{w}{2 \left\{ 1 + \left[1 + \left(\frac{2d}{w} \right)^2 \right] \arctan \left(\frac{w}{2d} \right) - \frac{2d}{w} \right\}}. \quad (3.28)$$

There are different ways to measure the parameters N , R_{3D} , and V_s , some of which have been mentioned below.

The demagnetization factor N which essentially depends on the sample

geometry, can be measured using two different approaches.

(i) Using a MPMS Squid, one can measure the deviation of the $M(H)$ negative slope from $-1/4\pi$ (in the perfect diamagnetic Meissner state) for an applied field $H_{ext} < H_{c1}$ at the base temperature of 1.8 K, according to the equation (using SI units with $N = N_{SI}$),

$$\frac{M}{H_{ext}} = \frac{-1}{4\pi(1 - N)}. \quad (3.29)$$

(ii) For single crystalline samples in the shape of platelets (especially with $T_c < 1.8$ K) with crystal aspect ratio $c : a$ greater than 15 : 1, N can be estimated using the approximate formula [8],

$$\frac{1}{1 - N} \approx 1 + \frac{w}{2d}. \quad (3.30)$$

For calculating R_{3D} , we usually try to measure samples that allow us to use Eq. 3.28. The sample dimensions are measured under a microscope while the sample volume V_s is estimated by dividing the weight of the sample by its density (obtained from volume of the crystal unit cell). For the home-made primary coil, calculating the volume V_c precisely should naturally be difficult. We can find a work-around by observing (from Eq. 3.27) that,

$$G \propto \frac{R_{3D}(1 - N)}{V_s}. \quad (3.31)$$

Eq. 3.31 removes the requirement of measuring V_c . We then estimate G for our unknown sample as follows. We first determine G for Aluminum (Al) — a well-known conventional BCS superconductor.

We have used a 99.9995% pure Al foil (with thickness ~ 0.1 mm) as shown in inset of Fig. 3.13, by fitting the measured Al data to the superfluid density

expression in the pure non-local limit [9],

$$\rho_s(T) = \left[\frac{\Delta(T)}{\Delta(0)} \tanh \frac{\beta \Delta(T)}{2} \right]^{-\frac{1}{3}}. \quad (3.32)$$

Here, the temperature dependence of the superconducting gap is given as [10],

$$\Delta(T) = \delta_{sc} k_B T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\}, \quad (3.33)$$

with all the parameters being already defined in Chapter 2, Page 19. Here we have used, $\delta_{sc} = 1.76$, $\Delta C/C = 1.43$ and $a = 2/3$.

Figure 3.13: Non-local fit to the superfluid density $\rho_s(T)$ data of the 99.9995% pure Al sample yields $G = 10.7 \text{ \AA/Hz}$. Here, $T_c = 1.19 \text{ K}$. Inset shows the pure Al foil cut in the shape of a platelet.

From Fig. 3.13, we see that the best fit between experimental data and the theory is obtained for $G_{Al} = 10.7 \text{ \AA/Hz}$. Using this value of G_{Al} , G_s for an unknown sample (with a *similar geometry*) can be obtained from the

ratio $G_s : G_{Al}$ using Eq. 3.31 as follows,

$$\frac{G_s}{G_{Al}} = \frac{R_{3D,s}(1 - N_s)}{R_{3D,Al}(1 - N_{Al})} \frac{V_{Al}}{V_s}. \quad (3.34)$$

3.9 Extracting pure In-plane and Inter-plane Penetration Depths

Depending on sample growth techniques and other experimental factors, we have encountered a wide variety of sample geometry such as rectangular or square platelets, cylindrical disks and even needle-shaped single crystals. Irrespective of the orientation of the crystallographic planes with respect to the geometrical structure, there are two primary directions of the primary coil ac field that are relevant for discerning the underlying superconducting physics in these samples. The ac magnetic field $H_{ac} = H$ can either be parallel or perpendicular to the crystallographic c -axis, as shown in Fig. 3.14 for a sample with dimensions $\sim 2w \times 2w \times 2d$, with d being parallel to the c -axis. In this particular image $d > w$.

For $H \parallel c$ [Fig. 3.14:– (Left)], non-dissipative eddy currents flow along paths which are parallel to the $2w$ directions i.e. in the ab -plane, and in effect induce penetration depth λ_{ab} *only* along the ab -plane from all four sample sides. This means, with $H \parallel c$, our TDO setup can directly probe the change in the pure in-plane (i.e. in ab -plane) penetration depth $\Delta\lambda_{ab}$ as a function of temperature. On the other hand, with $H \perp c$, the situation is more complicated. As shown in Fig. 3.14:– (Right), now there are two components of the circulating eddy currents – one that flows parallel to the ab -plane and the other that flows perpendicular to it. The component that flows parallel to the ab -plane, induces magnetic field penetration directed along the $2d$ direction. It is important to note that, even though this penetration depth is directed along the c -axis, this component will now be referred to

as λ_{ab} since it originates in response to the ab -plane oriented eddy currents. The other component of the eddy currents is oriented along the c -axis and induces magnetic field penetration along the $2w$ direction (along the a -axis in Fig. 3.14:– (Right)). From the same argument as before, this component will constitute the pure λ_c or inter-plane penetration depth. This implies that for thicker samples i.e. samples with a large aspect ratio, with $H \perp c$, our TDO apparatus ends up probing a mixture of both $\Delta\lambda_{ab}$ and $\Delta\lambda_c$ components — the so called effective penetration depth $\Delta\lambda_{eff}$ as a function of temperature. This problem can also occur in the event that H is inclined at some finite angle to the c -axis due to crystal misalignment (please refer to Chapter 6) or in thick crystals with a strong anisotropy, where significantly different demagnetization fields can have vastly different penetration depths. Using an approach by Prozorov *et. al*, the pure $\Delta\lambda_c(T)$ component for $H \perp c$ can be extracted using the following expression [11],

$$\frac{\Delta\lambda_{eff}(T)}{R_{3D}} = \frac{\Delta\lambda_{ab}(T)}{d} + \frac{\Delta\lambda_c(T)}{w}, \quad (3.35)$$

where R_{3D} is the previously defined effective sample dimension, and depends on the sample geometry.

For the samples we have presented, the aspect ratio varies between 12 : 1 to 16 : 1, with $d \ll w$ in most cases. Some exceptions to this range of aspect ratio values have been the possible multi-gap superconductor $\text{CsMo}_{12}\text{S}_{14}$ and the quasi-one-dimensional superconductor $\text{Tl}_2\text{Mo}_6\text{Se}_6$ – how sample geometry affects their data analysis shall be highlighted in respective chapters. If $d \ll w$ and $R_{3D} \sim w$, it is quite obvious that $\Delta\lambda_{eff}$ in Eqn. 3.35 shall have a larger contribution from $\Delta\lambda_{ab}$, making an accurate extraction of $\Delta\lambda_c$ tricky. The aforementioned possible errors, together with the fact that sample surfaces are not always smooth can result in a substantial error in the magnitude of $\Delta\lambda(T)$ extracted from our raw data. Carrington *et al.* estimated that calculated value of G should have an intrinsic error

up to 20% [12], implying the absolute value of $\Delta\lambda(T)$ measured using our setup is accurate to about $\pm 20\%$. We have considered this error while estimating G for all our samples. Since penetration depth is to an extent surface sensitive, it is quite imperative that we measure extremely clean samples; preferably thin homogeneous single crystal for which the surface mirrors the bulk to a high degree. In addition to single crystals, we have also measured $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$, grown in the form of large polycrystalline samples. Detailed discussion on how sample quality and dimensions affect data acquisition and analysis in these polycrystalline materials shall be discussed later. Do note that we have used the phrases inter-plane and out-of-plane penetration depth synonymously to describe λ_c in this thesis.

Figure 3.14: Schematic of magnetic penetration depths in platelet-shaped superconducting samples with dimensions $\sim 2w \times 2w \times 2d$ for two mutually perpendicular orientations of the sample in the coil H_{ac} field. The orange dashed curves represent the screening eddy currents with the arrows indicating their direction of circulation. The blue shaded regions correspond to the bulk superconducting volume. (Left) $H_{ac} \parallel c$ results in screening currents that allow field penetration *only* along the ab -plane up till the penetration depth designated as λ_{ab} , while (Right) $H_{ac} \perp c$ induces screening currents that allow field penetration along the c -axis as well as in the ab -plane, giving a mixture of in-plane penetration depth λ_{ab} and inter-plane penetration depth λ_c . The ratio of the sample dimensions $w : d$ determines the relative contribution from each penetration depth to the effective penetration depth λ_{eff} in accordance with Eqn. 3.35.

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Chapter 4

α -PdBi₂ and β -PdBi₂

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In this chapter, we present in-plane magnetic penetration depth measurements of the single-crystalline superconductor α -PdBi₂ and its structural isomer, the putative topological superconductor β -PdBi₂. Certain portion of the text in this chapter dealing with α -PdBi₂, contains excerpts and figures (with minor edits) from our own publication (URL above), in accordance with the necessary copyright laws. The chapter contains the following sections: (1) introduction, (2) data and analysis – α -PdBi₂, β -PdBi₂, and (3) conclusion and future work.

4.1 Introduction

Even though the Pd-Bi family of binary compounds have been known for years [1], it was only recently that research interest in them has been reignited

in the condensed matter community due to their potential for being some of the pioneering candidates for stoichiometric topological superconductors. The recently discovered superconductor β -PdBi₂ ($T_c \sim 5.3$ K) [2] has been proposed as a possible candidate to exhibit topological superconductivity. A topological superconductor (TSC) is characterized by a non-trivial Z_2 invariant, which translates to the presence of zero-energy localized modes in its quasiparticle excitation spectrum called Andreev bound states at the surface, or Majorana fermions at the vortex core center, which are topologically protected. In the context of superconductivity this means that a TSC is characterized by a fully gapped bulk while these Majorana dispersing states can exhibit gapless excitation. Spin- and angle-resolved photoemission spectroscopy (ARPES) revealed the existence of several topologically protected surface states crossing the Fermi level in β -PdBi₂, [2] though the experimental detection of Majorana fermions is still elusive [3]. Preliminary low-temperature (down to 2 K) specific heat measurements [4] hinted towards the possibility of a multi-gap superconducting phase in β -PdBi₂, while scanning tunneling microscopy (STM) [5] suggested that it behaves like a single-gap multi-band superconductor. However, later experiments using muon-spin relaxation (μ SR) [6] and calorimetric studies [7] have shown a single isotropic BCS-like gap in β -PdBi₂ with negligible contribution from the topologically protected surface states. Another extensively researched superconducting compound amongst the Pd-Bi binary systems is α -PdBi ($T_c \sim 3.7$ K), that has a monoclinic crystal structure and belongs to the space group P2₁ [1, 8, 9].

Based on the symmetry of the the spin-component of the pairing wave function Ψ , superconductors are classified into spin-singlet (s -wave) and spin-triplet (p -wave) categories (with the later class having very few experimentally verified instances till date). Rashba-type spin-orbit coupling (SOC) is known to occur when mirror inversion symmetry is broken [10]. For

noncentrosymmetric compounds that lack a center of inversion, the enhanced SOC gives rise to helicity states: circular bands in momentum space that have the fermion spins polarized tangential to the momentum. Cooper pairs between these helically polarized spins can only form if the pairing energy is larger than the SOC strength. As qualitatively illustrated by Smidman *et. al*, in 3D noncentrosymmetric materials with helicity states, three key features of superconductivity can be expected – (i) spin-singlet Cooper pairing in the bulk remains unaffected by SOC, (ii) for spin-triplet order parameter, only one of the three allowed Cooper pairing combinations between these helically polarized spins can be ‘topologically protected’ against SOC — evidence of p -wave pairing symmetry thus might be indicative of topologically non-trivial superconductivity, and (iii) once mirror inversion symmetry is broken, symmetry in parity is no longer conserved — a mixture of even parity (spin-singlet in the bulk) and odd parity (spin-triplet in the helicity states) components of the order parameter is expected [11]. Taking these points into account, bulk superconductors possessing helicity states thus provide a unique platform to search for a complex two-component order parameter having the hybrid of spin-singlet and spin-triplet phases. Interestingly, recent ARPES measurements on α -PdBi revealed the presence of similar spin-polarized helicity states at high binding energies but not at the Fermi level, thus negating the possibility of topological superconductivity at the surface [12]. Scanning tunneling spectroscopy (STS) measurements hinted towards a moderately-coupled BCS-like single gap scenario in α -PdBi [13], similar to that reported for β -PdBi₂. Do note that, in our discussion we have not focused on Dresselhaus spin-orbit coupling which can create spin-momentum locked states as well. Instead, we have explicitly talked about Rashba spin-orbit coupling because that is the dominant effect expected in noncentrosymmetric compounds such as α -PdBi.

We thus see that the presence of topological states has been consis-

tently predicted in the Pd-Bi family of superconductors, even though experimental observation of topological superconductivity is yet to be confirmed. Since ~ 2010 , there has been a consistent effort to realize topological superconductors by carrier doping, e.g. Cu- and Nb-intercalated Bi_2Se_3 , [14–16] and In-doped SnTe . [17] In contrast, the Pd-Bi family of binary compounds provide the opportunity for studying some of the first candidates for stoichiometric topological superconductors. [18] Along this line, the less-explored superconductor $\alpha\text{-PdBi}_2$ ($T_c \sim 1.7$ K), [1] which is a structural isomer of $\beta\text{-PdBi}_2$, is interesting to investigate. The tunnel-diode-oscillator (TDO) based penetration depth setup has been shown to be an excellent tool to probe the pairing symmetry of unconventional superconductors such as ruthenates, [19] skutterudites, [20–22] and pnictides, [23–25] due to its ability to discern very small changes (1 part in 10^9) at low temperatures. At low temperatures, isotropic superconducting gaps give an exponential temperature dependence of the penetration depth, whereas nodes in the gap function, whether point nodes or line nodes *result in gapless excitations* and give a power-law temperature dependence. Coupled with the fact that penetration depth measurements are more surface-sensitive than bulk measurements, gapless excitations from the surface states of TSCs may be observable using the TDO technique, thus confirming the presence or absence of the topological nature of superconductivity in this material. For example, in the superconductor intercalated topological insulator $\text{Nb}_x\text{Bi}_2\text{Se}_3$, TDO penetration depth measurements have suggested a spin-triplet p -type order parameter based on observation of point nodal behavior in low temperature data [16]. We do acknowledge that in the unlikely event of the bulk (of a stoichiometric TSC) having a nodal order parameter as well, we can no longer definitively conclude the existence of topologically protected states based on nodal signatures in penetration depth alone.

In this chapter, we present high precision measurements of the in-plane

($H\parallel c$) London penetration depth $\lambda(T)$ of both α -PdBi₂ and β -PdBi₂, down to 0.35 K using a TDO-based technique. For **(I) α -PdBi₂**: The change in penetration depth $\Delta\lambda(T)$ shows an exponential behavior at low temperatures, suggesting the presence of a single isotropic gap in this material. The best fit to the normalized in-plane superfluid density $\rho_s(T)$ is obtained for the zero-temperature superconducting gap $\Delta(0)\sim 2.0k_B T_c$, and the specific heat jump $\Delta C/\gamma T_c\sim 2.0$, where γ is the electronic specific heat coefficient. This suggests that α -PdBi₂ is a moderate-coupling, fully-gapped superconductor. For **(II) β -PdBi₂**: All the samples measured thus far show a reproducible hump (with different magnitudes) in their raw data ~ 1.7 K — much lower than the bulk critical temperature $T_c \approx 4.5$ K, at which the usual diamagnetic jump is observed. Interestingly, the low- T kink coincides with the transition temperature of the α -PdBi₂. However, x-ray diffraction (XRD) of our β -PdBi₂ samples did not show any trace of α -PdBi₂ contamination; thus making the origin of the ~ 1.7 K jump controversial. For the *cleanest* β -PdBi₂ sample we measured, analysis of both low- T $\Delta\lambda(T)$ as well as the extracted normalized superfluid density $\rho_s(T)$ suggests that β -PdBi₂ is a moderate-coupling fully-gapped conventional superconductor with $\Delta(0) \approx 2.1k_B T_c$. Also, we do not see any power-law low-temperature dependence of $\Delta\lambda(T)$ for either phase of the PdBi₂ superconductor. This, however, is not definite evidence of the lack of gapless excitations on the surface of the sample, since the value of the zero-temperature penetration depth $\lambda(0)$ is a few times larger than the surface state thickness (~ 20 -60 nm) in these materials [6, 13].

Figure 4.1: (a) Crystal structure of α -PdBi₂. (b) x-ray diffraction pattern from the cleavage plane of the α -PdBi₂ single crystal as shown in the inset. Data provided by Prof. T. Sasagawa, Laboratory for Materials and Structures Laboratory, Tokyo Institute of Technology, Kanagawa 226-8503, Japan.

4.2 Data and Analysis

4.2.1 α -PdBi₂

α -PdBi₂ has a centrosymmetric monoclinic crystal structure of space group C2/m as shown in Figure 4.1(a). The data presented here were taken on single crystal samples in the shape of platelets with dimensions $\sim 0.8 \times 0.5 \times 0.1$ mm³, the smallest dimension being oriented along the *a*-axis. Single crystals of α -PdBi₂ were grown by a melt growth technique. Elemental Pd (3N5) and Bi (5N) at a molar ratio of 1:2 were sealed in an evacuated quartz

tube, pre-reacted at high temperature until it completely melted and mixed. Then, it was again heated up to 900°C, kept for 20 hours, cooled down slowly at a rate of 2–3°C/h down to room temperature. The obtained single crystals by the optimized growth conditions had a good cleavage, producing flat surfaces as shown in the inset of Figure 4.1(b). The peaks of the x-ray diffraction from the cleavage plane can be assigned to the $(h\ 0\ 0)$ reflections (Figure 4.1(b)), indicating that the cleavage plane is the bc -plane. We report direct measurement of the in-plane penetration depth $\Delta\lambda(T)$ in this chapter.

Figure 4.2: Resistivity vs. temperature data for α -PdBi₂, showing $T_c \sim 1.7$ K. Data provided by Prof. T. Sasagawa, Laboratory for Materials and Structures Laboratory, Tokyo Institute of Technology, Kanagawa 226-8503, Japan.

Resistivity in the bc -plane of the α -PdBi₂ crystal was measured by the four-probe method using a Keithley 2182A Nanovoltmeter and 6221 Current Source. A homemade adiabatic demagnetization refrigerator was used for temperature below 2 K. Temperature dependence of resistivity of α -PdBi₂

in the wide temperature range and around the superconducting transition is shown in Fig. 4.2 and its inset. The residual resistivity below 10 K was adequately low ($18 \mu\Omega cm$) and its ratio to the room temperature value (RRR: residual resistivity ratio) is ~ 15 , indicating the high quality of the crystal. The onset of the superconducting transition is ~ 1.7 K.

Figure 4.3: Low-temperature dependence of the in-plane penetration depth $\Delta\lambda(T)$ in α -PdBi₂. The solid line is the fit to Eqn. (4.1) from 0.35 K ($\sim 0.21T_c$) to 0.58 K ($\sim 0.35T_c$), with the fitting parameters, $\Delta(0)/k_B T_c = 2.00$ and $\lambda(0) = 190$ nm. Inset shows $\Delta\lambda(T)$ for the same sample over the full range.

Figure 4.3 shows $\Delta\lambda(T)$ in Sample#1 of α -PdBi₂ single crystal as a function of temperature up to 0.6 K. The inset shows $\Delta\lambda(T)$ for the sample plotted over the entire temperature range to temperatures above $T_c \approx 1.66$ K (onset of the superconducting transition). The 10%-to-90% transition width is only ~ 0.03 K, showing that the measured crystal is of high quality. The low-temperature $\Delta\lambda(T)$ data is fitted to the standard s -wave BCS model,

[26]

$$\Delta\lambda(T) = \lambda(0)\sqrt{\frac{\pi\Delta(0)}{2k_BT}} \exp\left(-\frac{\Delta(0)}{k_BT}\right), \quad (4.1)$$

with $\Delta(0)$ and $\lambda(0)$ as fitting parameters. As seen in Fig. 4.3, the model fits our data well up to $0.35T_c$ with the best fit obtained for $\Delta(0) = (2.00 \pm 0.02)k_BT_c$ with $\lambda(0) = (190 \pm 10)$ nm. The value of the obtained $\Delta(0)/k_BT_c$ is larger than the weak-coupling BCS value of 1.76, suggesting that α -PdBi₂ is a moderate-coupling superconductor.

In order to extract the in-plane normalized superfluid density $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$ from $\Delta\lambda(T)$ data, we need to know the value of $\lambda(0)$. The previously-obtained value of $\lambda(0)$ is only an estimate, as it was obtained from fitting only low-temperature data. [27] In fitting $\rho_s(T)$ next we allow $\lambda(0)$ to be a fitting parameter. To calculate the theoretical $\rho_s(T)$, we used the expression for superfluid density for an isotropic s -wave superconductor in the clean and local limits as shown below [26],

$$\rho_s(T) = 1 + 2 \int_0^\infty \frac{\partial f}{\partial E} d\varepsilon, \quad (4.2)$$

where $f = [\exp(E/k_BT) + 1]^{-1}$ is the Fermi function and $E = [\varepsilon^2 + \Delta(T)^2]^{1/2}$ is the Bogoliubov quasiparticle energy. The temperature dependence of the superconducting gap $\Delta(T)$ is given by [28]

$$\Delta(T) = \delta_{sc}kT_c \tanh\left\{\frac{\pi}{\delta_{sc}}\sqrt{a\left(\frac{\Delta C}{C}\right)\left(\frac{T_c}{T} - 1\right)}\right\}, \quad (4.3)$$

where $\delta_{sc} = \Delta(0)/k_BT_c$, $a = 2/3$ and $\Delta C/C \equiv \Delta C/\gamma T_c$.

Keeping $T_c = 1.66$ K fixed, and taking into account the $\sim 10\%$ uncertainty in the proportionality factor G , [29], we obtained the best fit with the following parameters: $\lambda(0) = (141 \pm 14)$ nm, $\Delta(0)/k_BT_c = (1.97 \pm 0.04)$, and $\Delta C/\gamma T_c = (2.00 \pm 0.30)$, as shown as a solid line in Figure 4.4. The inset shows the low-temperature fit (up to $0.35T_c$) between the experiment and

Figure 4.4: In-plane superfluid density $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ for α -PdBi₂ Sample#1 calculated from $\Delta\lambda(T)$ data in Fig. 4.3 using $\lambda(0) = 141$ nm. Solid line: Best fitted $\rho_s(T)$ calculated from Eqn. (4.2) using the parameters $\Delta(0)/k_B T_c = 1.97$, $\Delta C/\gamma T_c = 2.00$ and $T_c = 1.66$ K. Dashed line: Calculated $\rho_s(T)$ using weak-coupling s -wave parameters $\Delta(0)/k_B T_c = 1.76$, $\Delta C/\gamma T_c = 1.43$, for $T_c = 1.66$ K. Inset shows $\rho_s(T)$ for the same sample up to $0.35T_c$ along with the best fitting curve.

theory for the same parameters. The dashed line in Figure 4.4, calculated using the BCS weak-coupling values of $\delta_{sc} = 1.76$ and $\Delta C/\gamma T_c = 1.43$, clearly does not fit the data. The fitted value of $\Delta(0)/k_B T_c$ agrees well with that obtained from the $\Delta\lambda(T)$ fit in Figure 4.3.

To check the validity as well as the self-consistency of the obtained parameters, we use the strong-coupling equations [30, 31],

$$\eta_{\Delta}(\omega_0) = 1 + 5.3 \left(\frac{T_c}{\omega_0} \right)^2 \ln \left(\frac{\omega_0}{T_c} \right), \quad (4.4)$$

$$\eta_{Cv}(\omega_0) = 1 + 1.8 \left(\frac{\pi T_c}{\omega_0} \right)^2 \left(\ln \left(\frac{\omega_0}{T_c} \right) + 0.5 \right), \quad (4.5)$$

where η_Δ and η_{Cv} represent the correction factors that are required to be applied over the weak-coupling BCS gap ratio and specific heat jump, respectively, to get the corresponding values in the moderate-to-strong-coupling limits. Here ω_0 is the characteristic (equivalent Einstein) frequency. From $\Delta(0)/k_B T_c = 1.97$, we get the correction factor $\eta_\Delta = 1.97/1.76 = 1.12$. Putting this value into Eqn. (4.4) with $T_c = 1.66$ K gives $\omega_0 \approx 16.9$ K. Using this ω_0 in Eqn. (4.5) gives a specific heat jump of 2.08 — this agrees well with the value of 2.00 obtained from the $\rho_s(T)$ fit and further supports our claim that α -PdBi₂ is a moderately-coupled superconductor.

Figure 4.5: In-plane superfluid density $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ for α -PdBi₂ Sample#2 calculated from $\Delta\lambda(T)$ data in Fig. 4.3 using $\lambda(0) = 134$ nm. Solid line: Best fitted $\rho_s(T)$ calculated from Eqn. (4.2) using the parameters $\Delta(0)/k_B T_c = 2.09$, $\Delta C/\gamma T_c = 2.10$ and $T_c = 1.65$ K. Inset shows $\rho_s(T)$ for the same sample up to $0.35T_c$ along with the best fitting curve.

In order to check the robustness and reproducibility of our data and analysis, we measured another single-crystal sample designated Sample#2. The best fit of the superfluid density data, using the method described earlier, was obtained for the parameters $\lambda(0) = (134 \pm 13)$ nm, $\Delta(0)/k_B T_c$

$= (2.09 \pm 0.04)$, and $\Delta C/\gamma T_c = (2.10 \pm 0.29)$. We can see that (1) the fitted parameters of $\Delta(0)/k_B T_c$ and $\Delta C/\gamma T_c$ are consistent with each other via strong-coupling corrections, and (2) the obtained parameters for both α -PdBi₂ samples are consistent with each other.

Based on the analysis of the in-plane data in both the samples, we infer that α -PdBi₂ is a single-gap isotropic moderately-coupled BCS superconductor with zero-temperature superconducting gap $\Delta(0) \sim 2.0 k_B T_c$, and specific heat jump $\Delta C/\gamma T_c \sim 2.0$, with superconducting transition temperature $T_c \sim 1.7$ K.

4.2.2 β -PdBi₂

Figure 4.6: Measurement of the magnetic susceptibility (χ) on single crystalline β -PdBi₂ after demagnetization correction as a function of temperature, in an external ac field of 10 Oe applied parallel to the c -axis. The figure shows both zero-field-cooled (ZFC) and field-cooled (FC) data measured following conventional protocol. The diamagnetic jump at the superconducting transition is complete at $T_c \sim 4.6$ K.

β -PdBi₂ has a tetragonal structure belonging to the space group I4/mmm

[4,32,33] as shown in Fig. 4.8(c) and single crystals for our measurement were grown by a melt growth method described in detail elsewhere [2]. To fit on our sample coldfinger, the single crystal samples were cut into platelets with dimensions $\sim 0.8 \times 0.7 \times 0.1 \text{ mm}^3$, the smallest dimension being oriented along the c -axis. The ac field H of the TDO solenoidal coil was oriented along the crystalline c -axis, i.e. we present in-plane penetration depth data of β -PdBi₂ in this chapter.

As shown in Fig. 4.6, ZFC and FC measurement of the in-plane ac susceptibility from 1.8 K to 7 K in an external field of 10 Oe, shows a bulk superconducting transition with $T_c \sim 4.6 \text{ K}$ for β -PdBi₂. The sharp diamagnetic jump, in addition to the superconducting volume fraction $>90\%$ at 1.8 K is indicative of high quality of the measured crystal and strong bulk superconductivity.

Figure 4.7: Low-temperature change in frequency Δf (Hz) measured using the TDO setup for three different single crystalline samples (denoted by $\square$, $\circ$ and $\triangle$) of β -PdBi₂, plotted on the same graph. All the samples show similar distinctive jumps $\sim 1.7 \text{ K}$ with different magnitudes.

Figure 4.7 shows the change in frequency data Δf for three different

single crystalline samples of β -PdBi₂ with similar dimensions from 0.4 K to 2.7 K. A reproducible feature in the form of a sharp jump is observed for all three samples, with an onset temperature ~ 1.7 K. This temperature is uncannily similar to the T_c of the counterpart superconductor α -PdBi₂. For PdBi₂, the low-temperature α -phase is obtained below 380°C with slow cooling, while the high-temperature β -phase can be stabilized at low temperatures by rapid quenching between 380°C to 490°C [34,35]. We considered

Figure 4.8: (a) XRD pattern for the same batch of single crystalline β -PdBi₂ samples, which we have used to probe $\lambda(T)$. (b) XRD image for β -PdBi₂ crystals in which α -phase has been introduced on purpose. The * symbols and arrow heads point to the small peaks corresponding to α -PdBi₂ crystal structure, which seem to be quite spaced apart from the peaks due to the intrinsic crystal structure of the β -phase. (c) Crystal structure of β -PdBi₂. Data provided by Prof. T. Sasagawa, Laboratory for Materials and Structures Laboratory, Tokyo Institute of Technology, Kanagawa 226-8503, Japan.

the possibility that perhaps different volume fractions of *all* our β -PdBi₂ crystals had undergone a structural phase transition to the α -phase, and

that is why the diamagnetic jump of α -PdBi₂ manifests in the raw data. To dispense off our doubts, our collaborator Prof. T. Sasagawa performed XRD measurements on the measured β -PdBi₂ crystals (grown by his group), which showed no signature of α -phase contamination. The XRD image of the pristine β -PdBi₂ single crystals has been shown in Fig. 4.8 (a). Additionally, the crystal grower performed XRD of α -phase-contaminated β -PdBi₂ as shown in Fig. 4.8 (b). Comparison of these two images deems unlikely the possibility of coexistence of both α - and β - phases in our measured samples.

Figure 4.9: Low-temperature in-plane penetration depth $\Delta\lambda_{ab}(\text{\AA})$ for the single crystalline superconductor β -PdBi₂ disk#1 from 0.45 K to 1.3 K. Till $0.25T_c$, data have been fitted quite nicely to Eqn. 4.1 with the fitting parameter $\Delta(0) = (1.97 \pm 0.08)k_B T_c$. The dashed and dotted curves are fits to the the nodal expression $\Delta\lambda = BT^n$ for $n = 1$ and 2 respectively. The inset shows the full- T range data with the superconducting transition having an onset $T_c \approx 4.5$ K.

In the subsequent paragraphs, we have presented data and analysis of the β -PdBi₂ crystal designated disk#1, that shows the smallest jump at

~ 1.7 K. Fig. 4.9 shows magnetic penetration depth $\Delta\lambda_{ab}(T)$ for this crystal from 0.45 K to 1.3 K with the coil ac field $H\parallel c$ -axis. The red solid curve is the fit up till $0.25T_c$ to the standard s -wave BCS model, as shown in Eqn. 4.1, with the fitting parameter $\Delta(0) = (1.97 \pm 0.08)k_B T_c$. This value is higher than the BCS weak-coupling value of 1.76, suggesting that β -PdBi₂ is a moderate-coupling superconductor as well. The onset T_c is found to be ≈ 4.5 K (Inset of Fig. 4.9) and agrees quite well with the 4.6 K value obtained from χ - T measurement in Fig. 4.6. We have also tried fitting data over the same T -range to the power-law expression $\Delta\lambda = BT^n$ with the exponents $n = 1$ (line nodes) and $n = 2$ (point nodes), as shown by the dashed and dotted curves respectively. Clearly, they do not fit our data well.

Figure 4.10: In-plane superfluid density $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ for single crystalline β -PdBi₂ disk#1 calculated using $\lambda(0) = 2630$ Å. Solid line: Best fitted $\rho_s(T)$ calculated from Eqn. 4.2, using the parameters $\Delta(0)/k_B T_c \approx 2.1$, $\Delta C/\gamma T_c = 2.00$ and $T_c = 4.55$ K. Dashed line: Calculated $\rho_s(T)$ using weak-coupling s -wave parameters $\Delta(0)/k_B T_c = 1.76$, $\Delta C/\gamma T_c = 1.43$, for the same $T_c = 4.55$ K.

Using $\lambda(0) = \lambda_{ab}(0) = 2630$ Å from μSR [6], we have plotted in-plane

$\rho_s(T)$ for our β -PdBi₂ disk#1 crystal as shown in Fig. 4.10. Then, we used the same theoretical model as that used for α -PdBi₂, and calculated theoretical $\rho_s(T)$ using Eqn. 4.2, with Eqn. 4.3 describing the T -dependence of the gap. To fit our experimental data for β -PdBi₂ disk#1, we varied the parameters $\Delta(0)/k_B T_c$ and T_c , while using $\Delta C/\gamma T_c = 2.00$, obtained from electronic specific heat measurements [3, 7]. As shown by the solid curve in Fig. 4.10, best fit is obtained using the parameters $\Delta(0)/k_B T_c = (2.1 \pm 0.04)$ and $T_c = (4.55 \pm 0.02)$ K. The curve can not convincingly fit the kink ~ 1.7 K corresponding to the low- T jump in $\Delta\lambda(T)$ — the origin of which is still doubtful to us. We have also plotted theoretical $\rho_s(T)$ using BCS weak-coupling values of $\Delta(0)/k_B T_c = 1.76$ and $\Delta C/\gamma T_c = 1.43$, with the same $T_c = 4.55$ K. The dashed curve in Fig. 4.10 represents the same, and quite clearly does not fit the data well. The obtained value of $\Delta(0)/k_B T_c = 2.1$ from our fit and the experimentally measured $\Delta C/\gamma T_c = 2.00$ are consistent with each other via the strong-coupling corrections by Orlando *et al.* [31].

4.3 Conclusion and Future Work

To conclude, we have presented in this chapter magnetic penetration depth measurements on single crystalline samples α - and β -PdBi₂, with intrinsic transition temperatures $T_c \approx 1.7$ K and 4.6 K respectively. For β -PdBi₂, $\Delta\lambda(T)$ in all the samples exhibit a reproducible hump ~ 1.7 K — the feature resembling a sharp discontinuity, observed at phase transition boundaries. Our initial guess that this jump was the superconducting response of sparsely scattered α -PdBi₂ containment, has been refuted by XRD data, which clearly showed no signature of α -phase in our measured crystals. Another possibility is that the jump is indicative of two-gap behavior in β -PdBi₂, with one of the gaps manifesting the characteristic diamagnetic jump at its intrinsic transition temperature ~ 1.7 K. This would imply that in all likelihood, more than one energy band crosses the Fermi level E_F , with

weak-interband coupling between these Fermi pockets on which the two gaps open up. Even though ARPES measurements have observed multiple surface (NOT bulk) bands crossing E_F in β -PdBi₂ — *theoretical* analysis have clearly discerned them to be the topologically non-trivial surface states [2]. This implies that, if our high-resolution apparatus is indeed probing these topological states; then we should have seen a power-law behavior in low- T $\lambda(T)$ data owing to the expected gapless excitations of the Majorana Fermions. But $\Delta\lambda(T)$ data (till $0.25 T_c$) for β -PdBi₂, does not fit to a power-law expression. The low- T hump is then most likely some sort of an artifact, the origin of which we expect to figure out soon.

Table 4.1: PdBi₂: summary of measurements

$\Delta(0)/k_B T_c$	μSR	Calorimetric studies	STM	STS	PCAR	TDO
α -PdBi	—	1.90	—	1.90	Possible mixed phase	—
β -PdBi ₂	1.87	2.05	1.85	—	2.05	2.10
α -PdBi ₂	—	—	—	—	—	2.00

In Table 4.1, we have summarized the extracted values of the $\Delta(0)/k_B T_c$ for the PdBi₂ family of superconductors, from different measurements. As clearly evident, both surface-sensitive measurements viz. μSR , STM, STS and point-contact Andreev reflection (PCAR), as well as bulk-measurements such as AC calorimetry, yield a moderate-coupling scenario, in line with our observations, with consistent parameters [3, 7, 13, 36]. Thus, based on our consistent penetration depth results of both α - and β -phase PdBi₂, together with the fact that electronic structure calculations show a metallic normal-state of α -PdBi₂, similar to β -PdBi₂ as well as α -PdBi [37], we conclude that all of them have a similar nature of the superconducting state.

In both β -PdBi₂ and α -PdBi, even though multiple theoretical calculations as well as experimental observations have clearly pointed out the existence of topological states, the bulk superconducting ground state always seems to be topologically trivial, as already shown. It has been suggested that for Type-II superconductors, the surface Andreev bound states con-

Figure 4.11: Schematic showing the possible extent of surface states in α - and β -PdBi₂, relative to the spatial scale of TDO-based penetration depth measurements.

sisting of Majorana Fermions are expected to decay into the bulk within a few coherence lengths ξ . Using the value of $\xi \approx 20 \text{ nm}$ for β -PdBi₂ from calorimetric measurements [7], and $\xi \approx 66 \text{ nm}$ for α -PdBi from STS measurements [13], these states should have a spatial extent of $\sim 100 \text{ nm}$ from the surface. Given our fitted value of $\lambda(0) \approx 140 \text{ nm}$ for α -PdBi₂, our penetration depth measurements is able to measure field penetration from $\sim 140 \text{ nm}$ *inwards*, with Angstrom resolution. To elaborate on this, even at zero temperature, the magnetic field has already penetrated through the sample over a distance of $\sim 140 \text{ nm}$ in our sample. Hence any gapless excitation, which exists over the aforementioned length scale of $\sim 100 \text{ nm}$ from the surface, will not be detected by our technique. As schematically illustrated in Fig. 4.11, this implies that we are barely able to probe the topological surface states in α -PdBi₂. Extending this argument to β -PdBi₂ with a higher $\lambda(0) \approx 260 \text{ nm}$, clearly suggests that — observation of these non-trivial surface states would be even more improbable in this compound.

Thus, the absence of a low- T power law in our data does not necessarily rule out the presence of surface states in these materials. More surface-sensitive spectroscopic measurements such as point-contact Andreev spectroscopy and ARPES should give direct evidence of topologically-protected surface states in this class of possible stoichiometric TSCs. Additionally, μ SR and calorimetric measurements should be performed on α -PdBi₂ to validate the parameters we have reported. It should be noted that introducing external non-magnetic impurities in the sample can be an interesting prospect. This is because the order parameter in the helicity states would be topologically protected against this perturbation, while the bulk superconductivity would be affected due to enhanced scattering. This in turn can change the overall penetration depth behavior, therefore might give more specific information regarding the pairing symmetry in these helicity states and possible Majorana excitations. We would discuss with our collaborators regarding the feasibility of executing this experiment.

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Chapter 5

CsMo₁₂S₁₄: Multi-band Superconductor?

In this chapter, magnetic penetration depth and magnetization measurements on the Chevrel phase superconductor CsMo₁₂S₁₄ have been presented. The chapter contains the following sections: (1) introduction, (2) data and analysis – penetration depth, magnetization and thermodynamic critical fields, superfluid density, and (3) conclusion and future work.

5.1 Introduction

CsMo₁₂S₁₄ belongs to the family of ternary molybdenum chalcogenides having the stoichiometric formula M_xMo₆X₈ [M = Na, K, Ca, Sr, Ba, Sn, Pb, rare earth metal, 3d element; X = S, Se or Te] commonly known as Chevrel phases. These family of materials were discovered by Chevrel *et al.* in 1971 [1] and over the years have been shown to be promising candidates for unconventional superconductivity. Critical transition temperature T_c has been found to vary over a wide range with values as small as 1.4 K in Gd_{1.2}Mo₆S₈ [2] to as high as 15.2 K in PbMo₆S₈, in which a value greater than 80 T of the upper critical field H_{c2} has been reported [1, 3, 4]. Despite providing an exciting avenue to investigate unconventional superconducting

features such as high- T_c , H_{c2} value higher than the Pauli limit amongst others, the Chevrel phase-based compounds have been largely neglected in comparison to the cuprates and the iron-based superconductors. For years condensed matter physicists have tried to explain a high value of the critical temperature using multi-band superconductivity, which basically relates the increase in T_c to the enhanced effective density of states (DOS) due to interband interaction between non-degenerate bands crossing the Fermi level E_F . Band structure calculations have shown the presence of two distinct Mo d -bands at E_F for these Mo_6X_8 [$\text{X} = \text{S}, \text{Se}$]-based compounds [5]. Later, low-temperature experiments using scanning tunnelling spectroscopy (STS), together with thermodynamic measurements of the electronic specific heat found evidence of two-gap superconductivity in SnMo_6S_8 and PbMo_6S_8 , with the two superconducting gaps being attributed to the two different energy bands [4]. This is similar to the well known example of MgB_2 in which interaction between a quasi-2D σ -band and a quasi-3D π -band gives rise to multi-gap superconductivity [6].

Here, we present and analyze both in-plane and out-of-plane London penetration depth (λ) data on single crystal samples of the related ternary reduced molybdenum sulphide $\text{CsMo}_{12}\text{S}_{14}$ [due to lack of perfect stoichiometry, a more accurate representation would be $\text{Cs}_{\sim 1}\text{Mo}_{12}\text{S}_{14}$], from T_c down to 0.4 K. Even though this particular Chevrel phase-based compound was first reported back in 2009 [7], there has not been much experimental study of the superconducting phase since then. We also provide data for both field- and temperature-dependent magnetization, $M(H)$ and $M(T)$ respectively, which we have used to extract essential parameters, such as the lower critical magnetic field H_{c1} and penetration depth at absolute zero $\lambda(0)$ — integral to our data analysis. The penetration depth has been probed using a tunnel-diode-oscillator (TDO) based penetration depth technique [8]. Our analysis of the raw data reveals that, for both field orientations, a sharp downturn

is observed in $\Delta\lambda(T)$ data at a temperature ~ 1.2 K, which is significantly lower than the bulk $T_c \approx 7.4$ K; at which the usual diamagnetic jump is seen. Additionally, a distinctively broad *hump* is seen in both extracted $H_{c1}(T)$ as well as the normalized superfluid density $\rho_s(T)$ data at $T \sim 5.5$ K. We found that instead of using a conventional single superconducting gap model, we need to use a *two-gap* model – one isotropic *s*-wave gap and the second an anisotropic *s*-wave gap, to get a reasonably good fit between data and theory. Our analysis of both in-plane and out-of-plane $\rho_s(T)$ suggests that, $\text{CsMo}_{12}\text{S}_{14}$ has at least two superconducting gaps, one weakly-coupled isotropic gap and one anisotropic gap, with respective intrinsic T_c 's of ~ 1.2 K and ~ 7.4 K respectively. Our claim for multi-gap behavior is supported by electronic structure calculations, that show three distinct bands crossing the Fermi level and enhancing the DOS in $\text{CsMo}_{12}\text{S}_{14}$.

5.2 Data and Analysis

5.2.1 Penetration Depth

Data presented here were taken on hexagonal bipyramidal-shaped single crystal samples with the largest diagonal ~ 0.7 mm and smallest diagonal ~ 0.6 mm, the smallest dimension being oriented along the *c*-axis. $\text{CsMo}_{12}\text{S}_{14}$ crystallizes in the trigonal space group $P\bar{3}1c$ and details of the crystal growth and characterization can be found elsewhere [7]. As mentioned in the previous chapters, below T_c it can be shown that the change in the London penetration depth $\Delta\lambda(T) = \lambda(T) - \lambda(0.4 \text{ K})$ is related to the change in the resonant frequency $\Delta f(T)$ of our TDO setup as follows [9],

$$\Delta\lambda(T) = G\Delta f(T). \quad (5.1)$$

Here, G is the calibration factor that depends on the coil and sample geometries. Our usual approach to determine G for an unknown sample is to first obtain G for a pure Al sample (of known dimensions) and then use the R_{3D} approach (described in Chapter 3). However, this sort of comparison approach has one drawback in that it is primarily valid for samples which resemble the shape of the platelet-shaped Al sample, with thickness ($2t$) $\ll$ width ($2w$). For our bipyramidal-shaped $\text{CsMo}_{12}\text{S}_{14}$ samples without planar surfaces and having $t \approx w$, we anticipate that calculating G using the R_{3D} approach might not be correct. Instead, we have estimated G by comparing our TDO $\Delta\lambda(T)$ to that extracted from $H_{c1}(T)$ data, as shall be discussed later in this chapter. One more point of concern is that, for out-of-plane measurement ($H\parallel ab$), an effective penetration depth $\Delta\lambda_{eff}$ is probed, which has contributions from both $\Delta\lambda_{ab}$ and $\Delta\lambda_c$. We have used the expression $(\Delta\lambda_{ab}/t) + (\Delta\lambda_c/w) = (\Delta\lambda_{eff}/R_{3D})$ by Prozorov *et. al* to extract the $\Delta\lambda_c$ component from this mix [10]. Here, the effective sample dimension R_{3D} is calculated following the standard approach described in Chapter 3. For clarity, direction of the TDO ac field H (<50 mOe) relative to the crystallographic axes have been shown in each graph.

Figure 5.1 shows $\Delta\lambda(\text{\AA})$ for both in-plane and out-of-plane measurements in single crystalline $\text{CsMo}_{12}\text{S}_{14}$, as a function of temperature till 2.6 K. The lower inset shows $\Delta\lambda(\text{\AA})$ for the same crystal plotted over the entire temperature range to temperatures above a well-defined superconducting transition with $T_c \approx 7.4$ K. This value agrees well with the reported $T_c \approx 7.7$ K from resistivity measurements [7]. For both data sets, a sharp change in T -dependence is observed at ~ 1.2 K, with the magnitude of $\Delta\lambda(\text{\AA})$ being $\sim 50\%$ larger for $H\parallel c$ than for $H\parallel ab$ over the same range. For the rest of the temperature range from 1.3 K to 7 K, ratio of $\Delta\lambda(\text{\AA})$ between both data sets is ~ 1 , thus suggesting an isotropic behavior in the crystal between in-plane and out-of-plane data. An exponential function

Figure 5.1: Low-temperature dependence of the in-plane ($\circ$) and out-of-plane ($\square$) penetration depth $\Delta\lambda(T)$ in single crystalline samples of $\text{CsMo}_{12}\text{S}_{14}$. The solid lines are fit to Eqn. $\Delta\lambda(T) = A + BT^n$ from 0.4 K to 1.1 K, with the fitting parameters, A , B and n . Both data sets show a distinctive kink at ~ 1.2 K and a similar power law exponent $n \sim 2.65$ from the fits. Dashed curves show fits to the s -wave exponential expression (see main text), from 1.4 K ($0.2T_c$) to 2.6 K ($0.35T_c$), and yield: $\Delta_{ab}(0) = 1.51k_B T_c$ ($H\parallel c$) and $\Delta_c(0) = 1.76k_B T_c$ ($H\parallel ab$). Lower inset shows $\Delta\lambda(T)$ for the same sample over the full- T range, showing $T_c \approx 7.4$ K. $H\parallel ab$ data have been vertically shifted for clarity. Upper inset shows low- T $\Delta f(T)$ in a second single crystal Sample#2 of $\text{CsMo}_{12}\text{S}_{14}$ with $H\parallel c$, showing a similar anomaly at ~ 1.3 K.

of the form $\Delta\lambda(T) \propto \exp(-\Delta(0)/k_B T)$, which is expected for conventional superconductors, did not fit the low- T $\Delta\lambda$ data well. A better fit is obtained using a power-law expression of the form $\Delta\lambda(T) = A + BT^n$ to this range, which gives an exponent $n = 2.67 \pm 0.03$ for $H\parallel c$ and $n = 2.63 \pm 0.08$ for $H\parallel ab$ respectively. A kink similar to the ~ 1.2 K kink in Sample#1 is reproducible in another single crystalline $\text{CsMo}_{12}\text{S}_{14}$ Sample#2 at ~ 1.3 K, as shown in the upper inset of Fig. 5.1. It is worth mentioning that, we obtained better exponential fits when we fitted data after the anomaly from

1.4 K ($0.2T_c$) to 2.6 K ($0.35T_c$), as shown by the dashed curves in Fig. 5.1. Using $\lambda(0) = 2840 \text{ \AA}$ and $2760 \text{ \AA}$ for $H\|c$ and $H\|ab$ respectively (extracted from magnetization measurements as shown later), the exponential fits yield: $\Delta_{ab}(0) = (1.51 \pm 0.01)k_B T_c$ for $H\|c$, and $\Delta_c(0) = (1.76 \pm 0.02)k_B T_c$ for $H\|ab$ respectively. Clearly, a detailed investigation of the normalized superfluid density $\rho_s(T)$ is necessary to discern if this feature corresponds to a superconducting transition from a second gap in this sample.

In order to extract $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ from $\Delta\lambda(T)$ data, we need to know the value of $\lambda(0)$. $\lambda(0)$ for Type-II superconductors can be calculated by solving the following equations [11, 12],

$$H_{c2}(0) = \sqrt{2}\kappa H_c(0), \quad (5.2)$$

$$H_{c1}(0) = \frac{H_c(0)}{\sqrt{2}\kappa} \ln \kappa + 0.08, \quad (5.3)$$

$$H_{c1}(T) = \left[\frac{\phi_0}{\lambda^2(T)} \right] \ln \kappa, \quad (5.4)$$

where $\kappa = \lambda(0)/\xi(0)$ is the Ginzburg-Landau (GL) parameter, $\phi_0 = 2.07 \times 10^{-7} \text{ Oe cm}^2$ is the magnetic-flux quantum, ξ is the superconducting coherence length with H_{c1} and H_{c2} being the lower and upper critical magnetic fields respectively. Eqn. 5.2 and Eqn. 5.3 can be solved to obtain κ . Then, putting this value of κ in Eqn. 5.4, we can find out $\lambda(0)$ using the measured values of $H_{c1}(T)$. A Quantum Design Magnetic Property Measurement System (MPMS) has been used to measure the sample magnetization M as a function of temperature as well as applied field, and extract the values of H_{c1} .

5.2.2 Magnetization and Thermodynamic Critical Fields

Figure 5.2 shows the temperature dependence of the magnetic susceptibility of the $\text{CsMo}_{12}\text{S}_{14}$ single crystal measured by following the zero-field-cooled

Figure 5.2: Temperature dependence of the magnetic susceptibility $4\pi\chi$ after demagnetization correction in an external field of 10 Oe applied along the c -axis of $\text{CsMo}_{12}\text{S}_{14}$ single crystal. The figure shows both zero-field-cooled (ZFC) and field-cooled (FC) data measured following standard protocol.

(ZFC) and field-cooled (FC) procedures after subtracting the linear diamagnetic background signal from the sample holder, in an external field of 10 Oe applied along the crystallographic c -axis. The ZFC data shows a sharp diamagnetic signal with the transition mid-point temperature being ~ 7.3 K. This value agrees well with the T_c reported from Fig. 5.1. The corresponding superconducting volume fraction at 1.8 K is around 90% thus confirming bulk superconductivity in this sample. The fact that $4\pi\chi = -1$, indicative of total flux expulsion, is *not* reached even at temperatures well below the bulk T_c , might correspond to a second superconducting transition as indicative from Fig. 5.1. Our MPMS $T_{base} = 1.8$ K being higher than 1.2 K at which the feature appears — we cannot see the feature in $\chi(T)$ data. For the same reason, the extracted values of $\lambda(0)$ might be a slight overestimate.

Determining the correct values of the lower critical field $H_{c1}(T)$ from $M(H)$ curves is not easy. The standard approach involves estimating H_{c1} as the point where the $M(H)$ curve at different constant temperatures deviates from a Meissner-like linear response to a non-linear one. This transition corresponds to vortex penetration in the sample and is usually not abrupt, thus introducing a substantial error. We have used an approach described in [13] to determine the values of $H_{c1}(T)$ for both in-plane and out-of-plane data. We fit the low- H magnetization data to a linear fit from $H = 0$ Oe to different upper limits of H , and for each fit calculate the regression coefficient R . H_{c1} is then taken to be the point at which this function $R(H)$ drops from a maxima ~ 1 . Figure 5.3 shows field-dependent magnetic moment (at some of the fixed temperature points) for $\text{CsMo}_{12}\text{S}_{14}$ with $H \parallel c$, obtained after subtracting the sample holder background. The deviation from Meissner-like linear diamagnetic response with increasing H is clearly visible in all the curves. Data for $H \parallel ab$ have been obtained in a similar manner but not shown here.

Figure 5.4 shows the T -dependence of $\lambda(\text{\AA})$, for both in-plane and out-of-plane orientations in $\text{CsMo}_{12}\text{S}_{14}$ Sample#1, which have been calculated from $H_{c1}(T)$ data. Inset shows these source $H_{c1}(T)$ curves, extracted from $M(H)$ data by the regression factor technique (described before). For both field orientations, $H_{c1}(T)$ can be fit nicely (solid and dashed line respectively in the inset) to the formula $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^n]$, with the fitting parameters $H_{c1}(0) = (86.6 \pm 1.7)$ Oe and $n = (1.3 \pm 0.1)$ for $H \parallel c$, and $H_{c1}(0) = (92.9 \pm 2.7)$ Oe and $n = (1.4 \pm 0.1)$ for $H \parallel ab$. Using these values of $H_{c1}(0)$, we solve Eqn. 5.2 and Eqn. 5.3 with $H_{c2}(0) = 19.36$ T to get $\kappa \sim 70$ for both crystal orientations. This high value of κ puts $\text{CsMo}_{12}\text{S}_{14}$ in the extreme local limit [12], similar to the other extensively investigated compound PbMo_6S_8 , for which $\kappa \approx 100$ [14]. Then, for each value $H_{c1}(T)$, $\lambda(T)$ is calculated using Eqn. 5.4 and fitted to the formula $\lambda(T) = \lambda(0)[1 - (T/T_c)^n]^{-0.5}$, with

Figure 5.3: Experimentally obtained in-plane ($H\parallel c$) magnetic moment (emu) plotted as a function of external magnetic field H (Oe) for $\text{CsMo}_{12}\text{S}_{14}$ for different temperatures. Inset shows data till 200 Oe, with the main panel showing low-field data till 35 Oe.

n obtained from the corresponding $H_{c1}(T)$ fits. We obtain the following parameters: $\lambda_{ab}(0) = (2840 \pm 10) \text{ \AA}$ for $H\parallel c$, and $\lambda_c(0) = (2760 \pm 25) \text{ \AA}$ for $H\parallel ab$. $H_{c2}(0)$ has been evaluated through the slope of $dH_{c2}/dT|_{T_c}$ close to T_c , according to the well-known Werthamer-Helfand-Hohenberg (WHH) approximation $H_{c2}(0) = -0.69T_c(dH_{c2}/dT)$ [12].

We would like to draw attention to the distinctive kink at ~ 5.3 K in Fig. 5.4, observed in $H_{c1}(T)$ and extracted $\lambda(T)$ curves for both the field orientations. Such a feature can be indicative of either a single anisotropic gap or in the more exciting scenario, can point to the existence of multiple gaps. Now, in a very general sense it can be shown that: $\rho_s(T) \propto [\lambda(T)]^{-2} \propto H_{c1}(T)$, i.e. if this feature at ~ 5.3 K is intrinsic to the superconducting phase; then it should be visible in superfluid density data as well. This is precisely what we observed in the extracted $\rho_s(T)$ data, as visible in Fig. 5.6 where a convex curvature can be seen between ~ 5 -6 K. However, we do not have a clear reason as to why a similar kink is not observed in the TDO

Figure 5.4: Absolute penetration depth $\lambda(\text{\AA})$ in $\text{CsMo}_{12}\text{S}_{14}$ single crystal as a function of temperature for $H\parallel c$ ($\circ$) and $H\parallel ab$ ($\square$), calculated using Eqn. 5.4 from 1.8 K to 7 K. $H\parallel ab$ data has been offset for clarity. The lines are fits to the Eqn. $\lambda(T) = \lambda(0)[1 - (T/T_c)^n]^{-0.5}$, where n is obtained from fits to $H_{c1}(T)$ data. Solid line: Fit to $H\parallel c$ data with the parameters $n = 1.3$ and $\lambda(0) = 2840 \text{ \AA}$, Dashed line: Fit to $H\parallel ab$ data with the parameters $n = 1.4$ and $\lambda(0) = 2760 \text{ \AA}$. Inset shows respective lower critical field $H_{c1}(T)$ data for both in-plane and out-of-plane measurements with fits to Eqn. $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^n]$.

$\Delta\lambda(T)$ curve in Fig. 5.5.

We should describe here how we estimated the calibration factor G for our $\text{CsMo}_{12}\text{S}_{14}$ sample in order to convert $\Delta f(\text{Hz})$ to $\Delta\lambda(\text{\AA})$. As already mentioned, we did not use the R_{3D} method to calculate G . Instead, we compared $G \times \Delta f(T)$ from our TDO measurement, to $\Delta\lambda(T) = \lambda(T) - \lambda(1.8 \text{ K})$, obtained from magnetization measurements, and used G as the fitting parameter. This sort of comparison is valid because similar to magnetization measurements, our TDO setup basically measures the magnetic susceptibility. We considered the 1.8 K data as the T_{min} data point, thus ensuring consistency between TDO and MPMS data sets. The least square

Figure 5.5: Estimating the TDO calibration factor G for $\text{CsMo}_{12}\text{S}_{14}$ single crystal sample by comparing in-plane $\Delta\lambda(T)$ data from the TDO measurement ($\circ$) to that obtained from magnetization measurements ($\square$).

fits between the two curves was obtained for $G_c = (6.3 \pm 0.3) \text{ \AA/Hz}$ and $G_{ab} = (4.9 \pm 0.4) \text{ \AA/Hz}$; relevant for $H \parallel c$ and $H \parallel ab$ data respectively. Figure 5.5 shows the best fit for $H \parallel c$. Just to verify, we found out that the usual R_{3D} approach of calculating G gives a value of $G_c = 10.3 \text{ \AA/Hz}$: higher than the previously obtained value.

5.2.3 Superfluid Density

Using the obtained values of $\lambda_{ab}(0) = 2840 \text{ \AA}$ and $\lambda_c(0) = 2760 \text{ \AA}$, we plot the experimental $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$ for $\text{CsMo}_{12}\text{S}_{14}$. Figure 5.6 shows the in-plane $\rho_s(T)$ curve with the inset showing the anisotropy for the second superconducting gap as shall be discussed subsequently. The similar dependence on temperature for the two curves is clear. Additionally, two features are reproduced in both data sets — (1) a point of inflection

at ~ 1.2 K and (2) a broad valley/hump-like feature (from 4.5 K to 6.5 K) centered around $T \approx 5.5$ K, where a dip is also observed in $H_{c1}(T)$ curves. Motivated by the possibility of multi-gap induced smearing of superfluid density, we tried to fit $\rho_s(T)$ data for both crystal orientations to the well established α -model for multi-gap superconductors. Briefly mentioned in Chapter 2, this model originally proposed by Padamsee *et al.* [15] has been successfully extended to account for two-gap behavior in MgB_2 [16, 17]. According to this model, the temperature dependence of two arbitrary gaps can be written as: $\Delta_1(T) = \alpha_1 \Delta_{BCS}(T)$ and $\Delta_2(T) = \alpha_2 \Delta_{BCS}(T)$, where $\alpha_i = \Delta_i(0)/k_B T_{ci}$ with $i = 1, 2$ designating the two gaps. This model also takes into account the possibility of the two gaps being characterized by two separate intrinsic transition temperatures T_{c1} and T_{c2} .

Theoretical $\rho_s(T)$ for each gap is calculated using the expression for superfluid density for an isotropic s -wave superconductor in the clean and local limits as shown below [12],

$$\rho_s(T) = 1 + 2 \int_0^\infty \frac{\partial f}{\partial E} d\varepsilon, \quad (5.5)$$

where $f = [\exp(E/k_B T) + 1]^{-1}$ is the Fermi function and $E = [\varepsilon^2 + \Delta(T)^2]^{1/2}$ is the Bogoliubov quasiparticle energy. Next, the overall superfluid density is obtained by adding the contributions from the gaps Δ_1 and Δ_2 with a multiplicative weight factor as follows,

$$\rho_{Total}(T) = w\rho_1(T) + (1 - w)\rho_2(T), \quad (5.6)$$

with $w \leq 1$ being the contribution from Gap 1.

We first tried to fit our experimental data assuming both gaps to have an isotropic s -wave like nature. Using an interpolation formula by Gross *et al.*, the temperature dependence of each gap $\Delta_i(T)$, relevant for the α -model,

can be written as follows [18],

$$\Delta_i(T) = \alpha_i k_B T_{ci} \tanh \left\{ \frac{\pi}{\alpha_i} \sqrt{a \left(\frac{\Delta C}{C} \right)_i \left(\frac{T_{ci}}{T} - 1 \right)} \right\} \quad i = 1, 2. \quad (5.7)$$

Here, $a = 2/3$ is a constant and $\Delta C/C \equiv \Delta C/\gamma T_c$, is the jump in electronic specific heat. Using the weak-coupling BCS parameters: $\alpha_i = 1.76$ and $(\Delta C/C)_i = 1.43$ for both gaps $i = 1, 2$; the obtained two-gap fit is shown in Fig. 5.6 as a black solid curve. Considering two separate T_c 's, this model can fit the sharp downturn at ~ 1.2 K quite nicely, with the fitting parameters $T_{c1} \approx 1.2$ K, $T_{c2} \approx 7.4$ K, and the weight factor $w \approx 0.15$ for Gap 1. However, the fit is really poor over the broad valley surrounding $T \sim 5.5$ K. The orange solid curve shows the single gap BCS fit, which clearly does not fit our data.

Next, we considered the possibility of the second gap to be anisotropic. In very general terms, the gap function for spin-singlet superconductors can be written as $\Delta(T, \mathbf{k}) = \Delta(T)g(\mathbf{k})$, where $g(\mathbf{k})$ is a dimensionless function of maximum magnitude of unity (for isotropic s -wave), describing the angular variation of the gap on the Fermi surface. In addition to the gap anisotropy $g(\mathbf{k})$, the shape of the Fermi surface on which the gap opens up can influence the shape of the $\rho_s(T)$ curve as well. The electronic band structure calculations for $\text{CsMo}_{12}\text{S}_{14}$ have been performed by our theoretical collaborators, and show that three bands cross the Fermi level E_F , with the Fermi surfaces having non-spherical contours. Our collaborator Dr. Alexander Petrović performed zero-field measurement of the electronic specific heat $C(T)$ on the same $\text{CsMo}_{12}\text{S}_{14}$ Sample#1 (see Fig. 5.9), which showed a bulk- $T_c \sim 7.3$ K with $\Delta C/\gamma T_c \approx 0.7$, which is much lower the weak-coupling value of 1.43. Keeping the parameters for Gap 1 fixed as $\Delta_1(0) = 1.76 k_B T_{c1}$, $(\Delta C/C)_1 = 1.43$, $T_{c1} \approx 1.2$ K and using $(\Delta C/C)_2 \approx 0.7$ for Gap 2, we next tried to fit $\rho_{ab}(T)$ considering the second gap to possess the following

anisotropy factors $g(\mathbf{k})$ –

(I) For the first possibility, we assumed that $\Delta(T, \mathbf{k})$ for Gap 2 possesses a spheroidal geometry of the form shown below [19],

$$g(\theta) = \frac{1}{\sqrt{1 - \varepsilon \cos^2(\theta)}}, \quad (5.8)$$

where the parameter $-\infty \leq \varepsilon \leq 1$ is related to the eccentricity e of the gap as $\varepsilon = e^2$, and θ is the polar angle with respect to the c -axis. Depending on the sign of ε the gap can be prolate ($\varepsilon > 0$), oblate ($\varepsilon < 0$) or a sphere ($\varepsilon = 0$). This specific form of anisotropy was suggested by Prozorov *et al.*, who used it to show that CaAlSi is an anisotropic s -wave superconductor [19].

(II) For the second scenario, we assumed that the second gap has a $s+g$ -wave like pairing symmetry, similar to that suggested for some borocarbide superconductors [20]. $g(\mathbf{k})$ for this model is of the following form,

$$g(\theta, \phi) = \frac{1 + \sin^4(\theta)\cos(4\phi)}{2}. \quad (5.9)$$

The solid red curve in Fig. 5.6 shows the fit to the two-gap α -model with two separate T_c 's, with Gap 1 having a weak-coupling s -wave like order parameter, and Gap 2 having an anisotropic s -wave nature of type (I). In addition to the ~ 1.2 K downturn, this model can fit the broad valley ~ 5.5 K in our experimental $\rho_{ab}(T)$ data reasonably well, if we use $\Delta_2(0) \approx 1.8k_B T_{c2}$, $T_{c2} \approx 7.4$ K, $\varepsilon \approx 0.4$ for Gap 2, with Gap 1 contributing only $\sim 15\%$ to the overall superfluid density. The positive value of ε implies that the superconducting gap is prolate-shaped, with the gap maxima oriented along the c -axis, and our estimated value of $1.8k_B T_{c2}$ corresponds to gap minima $[\Delta_2(0)]_{min}$ lying in the ab -plane. Using the ratio between gap maxima and gap minima – $[\Delta_2(0)]_{max}:[\Delta_2(0)]_{min} = 1/\sqrt{1-\varepsilon} \approx 1.3$ for $\varepsilon \approx 0.4$, the expected zero- T gap along the c -axis should be $[\Delta_2(0)]_{max} \approx 2.3k_B T_{c2}$. The inset of Fig. 5.6 shows the Gap 2 anisotropy obtained using the anisotropic

Figure 5.6: Normalized superfluid density $\rho_{ab}(T) = \lambda_{ab}^2(0)/\lambda^2(T)$ ($\circ$) for single crystalline $\text{CsMo}_{12}\text{S}_{14}$ Sample#1, calculated using $\lambda_{ab}(0) = 2840 \text{ \AA}$. The **orange solid curve** is the fit to a single-isotropic-gap fit, with $\Delta(0) = 1.76k_B T_c$, $\Delta C/C = 1.43$ and $T_c \approx 7.4 \text{ K}$. All the other curves are fits to Eq. 5.6 with the details as follows: **Black solid curve** – Gap 1 and Gap 2: $\Delta_i(0) = 1.76k_B T_{ci}$, $(\Delta C/C)_i = 1.43$, ($i = 1, 2$), $T_{c1} \approx 1.2 \text{ K}$, $T_{c2} \approx 7.4 \text{ K}$ and $w \approx 0.15$. **Red solid curve** – Gap 1: $\Delta_1(0) = 1.76k_B T_{c1}$, $(\Delta C/C)_1 = 1.43$, $T_{c1} \approx 1.2 \text{ K}$, $w \approx 0.15$ and Gap 2: anisotropic s -wave of type **(I)**, with $\Delta_2(0) \approx 1.8k_B T_{c2}$, $T_{c2} \approx 7.4 \text{ K}$, $(\Delta C/C)_2 = 0.7$, and $\varepsilon \approx 0.4$. **Dot curve** – Gap 1: $\Delta_1(0) = 1.76k_B T_{c1}$, $(\Delta C/C)_1 = 1.43$, $T_{c1} \approx 1.2 \text{ K}$, $w \approx 0.05$ and Gap 2: anisotropic s -wave of type **(II)**, with $\Delta_2(0) \approx 1.8k_B T_{c2}$, $T_{c2} \approx 7.4 \text{ K}$ and $(\Delta C/C)_2 = 0.7$. **Dash-dot curve** – Gap 1: $\Delta_1(0) = 1.76k_B T_{c1}$, $(\Delta C/C)_1 = 1.43$, $T_{c1} \approx 1.2 \text{ K}$, $w \approx 0.05$ and Gap 2: anisotropic s -wave of type **(II)**, with $\Delta_2(0) \approx 3.0k_B T_{c2}$, $T_{c2} \approx 7.4 \text{ K}$ and $(\Delta C/C)_2 = 0.7$. The inset shows a cross-sectional comparison between $\Delta_2(0)/k_B T_{c2}$ along the c -axis and in the ab -plane for the type **(I)** Gap 2 anisotropy.

s -wave model **(I)**.

As shown in Fig. 5.7, $\rho_c(T)$ can be fit nicely to the same two-gap model (shown by the red solid curve), using a weakly-coupled BCS-like Gap 1 with $T_{c1} \approx 1.3 \text{ K}$, and a type **(I)** anisotropic Gap 2 having the parameters $\Delta_2(0) \approx 2.3k_B T_{c2}$, $\varepsilon \approx 0.4$ and $T_{c2} \approx 7.4 \text{ K}$, with Gap 1 contributing $\sim 10\%$

Figure 5.7: Normalized superfluid density $\rho_c(T) = \lambda_c^2(0)/\lambda^2(T)$ ($\square$) for single crystalline $\text{CsMo}_{12}\text{S}_{14}$ Sample#1, calculated using $\lambda_c(0) = 2760 \text{ \AA}$. The solid red curve is the fit to Eq. 5.6 with a BCS-like Gap 1, and Gap 2 having an anisotropic s -wave nature of type (I). The fitting parameters are – Gap 1: $\Delta_1(0) = 1.76k_B T_{c1}$, $(\Delta C/C)_1 = 1.43$, $T_{c1} \approx 1.3 \text{ K}$, $w \approx 0.10$ and Gap 2: anisotropic s -wave of type (I), with $\Delta_2(0) \approx 2.3k_B T_{c2}$, $T_{c2} \approx 7.4 \text{ K}$, $(\Delta C/C)_2 = 0.7$, and $\varepsilon \approx 0.4$.

to the overall superfluid density. Thus we see that, between the two-gap fits for in-plane and out-of-plane data in $\text{CsMo}_{12}\text{S}_{14}$, there is a small offset of $\sim 0.1 \text{ K}$ in T_{c1} , while the bulk critical temperature $T_{c2} \approx 7.4 \text{ K}$ remains the same. We should also point out that the ratio of $[\Delta_2(0)]_{\max}:[\Delta_2(0)]_{\min} \approx 1.3$, is quite close to the ratio of $\Delta_c(0):\Delta_{ab}(0) = 1.76/1.51 \approx 1.2$ that we obtained from the low- T s -wave fits to $\Delta\lambda(T)$, as shown in Fig. 5.1.

On the other hand, using the type (II) anisotropy for the second gap, did not yield good fits between experiment and theory. The dot and dash-dot curves in Fig. 5.6, represent the two-gap α -model fits, considering the same weakly-coupled BCS-like Gap 1, and Gap 2 having $s + g$ -type pairing symmetry — in both weak-coupling [$\Delta_2(0) \approx 1.8k_B T_{c2}$] and strong-coupling

$[\Delta_2(0) \approx 3.0k_B T_{c2}]$ limits. For both these fits, $T_{c2} \approx 7.4$ K, while $w \approx 0.05$ for Gap 1. Both these fitting curves are way off from our experimental $\rho_{ab}(T)$ curve for almost the entire T -range above $T \sim 1.3$ K.

5.3 Conclusion and Future Work

In conclusion, we reported the first measurements of the magnetic penetration depth λ in single crystal samples of $\text{CsMo}_{12}\text{S}_{14}$ down to 0.4 K using a tunnel-diode based, self-inductive technique at 26 MHz. A sharp downturn is observed in the TDO signal ~ 1.2 K for both in-plane λ_{ab} and out-of-plane λ_c measurements, in both crystals measured. In addition, a broad hump is observed ~ 5.5 K in $H_{c1}(T)$, as well as in $\rho_s(T)$ curves for both field orientations. Based on fits of $\rho_s(T)$ to the two-gap α -model, we suggest that $\text{CsMo}_{12}\text{S}_{14}$ is a two-gap superconductor — the first gap having an isotropic s -wave pairing symmetry with weak-coupling BCS parameters, while for the second gap, the order parameter has an anisotropic s -wave like nature, which is found to have a prolate-shaped gap function, with gap maxima along the crystallographic c -axis. We attribute the second jump at low- T to the superconducting transition from the first gap with $T_{c1} \approx 1.2$ K (in-plane) and $T_{c1} \approx 1.3$ K (out-of-plane), while the second gap closes at $T_{c2} \approx 7.4$ K — the bulk superconducting transition temperature. From Suhl’s model of multi-gap superconductivity this would imply very weak interband interaction between the individual electron/hole pockets on which the two gaps open up below the respective T_c ’s [21].

Calculations of the band dispersion curves by our collaborator Dr. Régis Gautier, show three non-degenerate bands crossing the Fermi level E_F in $\text{CsMo}_{12}\text{S}_{14}$ as shown in Fig. 5.8. We suggest that Gap 1 opens up on a relatively isotropic hole pocket, while anisotropy in Gap 2 can be either due to anisotropic topography of the other hole pockets or due to interband-coupling between two separate band-specific gaps.

Figure 5.8: (Left) DFT calculations (using the Win2K package) showing the band dispersion curves in $\text{CsMo}_{12}\text{S}_{14}$, with the three bands that cross E_F labeled as 1, 2 and 3. (Right) Top and side views of the Brillouin zone showing the band-specific Fermi surfaces. Calculations have been performed by Dr. Régis Gautier, ENSCR Professor, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes Cedex, France

As shown in Fig. 5.9, the jump in the zero-field electronic specific heat $\Delta C/\gamma T$ at T_c , is found to be only 0.7 — nearly half the value of 1.43 for BCS weak-coupling gaps. This can be due to fractional contributions to the overall Sommerfeld coefficient γ from band-specific γ for individual gaps, as observed in other multi-gap superconductors [22]. Note that the area above and below the invisible line (corresponding to the normal-state heat capacity C_N) not being equal implies that our estimated C_N is not correct. This is because the $T^3 + T^5$ phonon background C_{ph} which we have used to fit $C_N(T)$ (and then extrapolate to $T = 0$) is not valid for $\text{CsMo}_{12}\text{S}_{14}$. We are currently in the process of completing the field-dependent specific heat measurements to obtain C_N more accurately by strongly suppressing C_{ph} . Based on the preliminarily observed anomaly between ~ 1.3 – 2.5 K in Fig. 5.9, we anticipate that the analysis of bulk specific heat data will further strengthen the possibility of multi-gap superconductivity in $\text{CsMo}_{12}\text{S}_{14}$. We also plan to perform single crystal XRD using a synchrotron facility to discern the

Figure 5.9: Zero-field electronic specific heat data on single crystalline $\text{CsMo}_{12}\text{S}_{14}$ Sample#1 showing a jump $\Delta C/\gamma T \approx 0.7$ at $T = T_c$. Measurements have been performed by Dr. Alexander Petrović, School of Physical and Mathematical Sciences, Nanyang Technological University.

existence of surface impurities. In the event that the ~ 1.2 K anomaly is found to be intrinsic and not related to some surface containment, we would strongly believe that we are indeed dealing with at least two separate band-specific gaps with weak coupling between these two bands. That would strongly reaffirm our claim that $\text{CsMo}_{12}\text{S}_{14}$ is a unique multi-gap superconductor. Additionally, we plan to perform magnetization measurements in the normal phase to discern the presence of any long-range magnetic ordering in the material immediately above T_c , in order to explore the possibility of magnetism induced superconductivity. We should however point out that, till date there is no known long-range magnetic order in any Mo-cluster compound which does not contain magnetic rare earth elements. As for the superconducting phase, our estimated value of $H_{c2}(0)$ for $\text{CsMo}_{12}\text{S}_{14}$ exceeds the Pauli paramagnetic limit, thus deeming unlikely the possibility

of interplay between superconductivity and paramagnetism. We would also like to investigate the enhancement and anomalous T -dependence of H_{c2} – a feature reported for multi-gap MgB_2 .

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Chapter 6

Tl₂Mo₆Se₆: Two-step

Superconducting Transition

In this chapter, we present measurements of both in-plane and out-of-plane magnetic penetration depth $\lambda_{ab,c}(T)$ in single crystals of the quasi-one-dimensional superconductor Tl₂Mo₆Se₆. We also show data and analysis of electrical transport measurements on the same sample as supporting information. The chapter contains the following sections: (1) introduction, (2) data and analysis – penetration depth and superfluid density, electrical transport measurements, and (3) conclusion and future work.

6.1 Introduction

We define a “quasi-one-dimensional” (q1D) superconductor to be a crystalline material which can (structurally and electronically) be considered as an array of weakly-coupled one-dimensional filaments with a superconducting instability. The phrase *quasi*-1D implies that the diameter of each filament is greater than the superconducting coherence length ξ , therefore the filaments are not identical to true 1D superconductors — Mermin-Wagner theorem is thus not violated. This instability can however be overcome if the inter-chain (transverse) coupling becomes strong enough,

so as to allow Cooper pair hopping between these filamentary chains [1]. This coupling drives a dimensional crossover from 1D (intra-chain) to 2D or 3D (intra *and* inter-chain) behavior, depending on the array anisotropy. Dimensional crossover out of a 1D state is governed by the transverse electron hopping integral $t_{\perp}$ and $e^{-}e^{-}$ interaction strength [2]. In the non-interacting limit, coherent single-particle inter-chain hopping occurs for temperatures $\leq t_{\perp}/k_B$. The $e^{-}e^{-}$ interactions renormalize this crossover to lower temperatures, and for sufficiently strong electronic interactions, single-particle hopping becomes irrelevant. Another factor which may suppress single-particle hopping is the opening of a spin gap due to back-scattering between Fermi surface sheets, creating a Luther-Emery liquid in which the charge transport remains metallic and 1D [3]. However, a lack of single-particle hopping does not preclude the establishment of long range order, since coherent two-particle hopping eventually occurs below temperature $T_J \geq t_{\perp}^2/t_{\parallel}k_B$, where $t_{\parallel}$ is the intra-chain hopping along the 1D axis and T_J is the Josephson coupling temperature between the chains [4]. This creates a ground state featuring ordered pairs, i.e. a superconductor or density wave. Most q1D materials studied to date exhibit large $t_{\perp} \gtrsim 100$ K and/or weak pairing instabilities, undergoing single-particle dimensional crossover in their normal (metallic) states [5–7]. In contrast, dimensional crossover via two-particle hopping remains experimentally unexplored.

For our investigated superconductor $\text{Tl}_2\text{Mo}_6\text{Se}_6$, the DFT-calculated band structures have been verified by angle-resolved photoemission spectroscopy (ARPES) and give $t_{\perp} \approx 230$ K: suggesting this material to be a 3D system in the normal state [8]. Even then, a two-step transition has been seen in related materials, and can be expected across an energy scale $\sim T_J$, if T_J is lower than the temperature T_{ons} at which Cooper pairs form within individual chains [9]. Experimentally, T_{ons} can be identified as the temperature at which the electrical resistance begins to fall from the corresponding

value of R_{NS} in the resistive normal state. For $T_J < T < T_{ons}$, the material behaves as an array of uncoupled 1D superconductors, with a finite electrical resistance due to the inevitable formation of elementary topological excitations such as phase slips within each filament. In this context, a phase slip refers to a relative shift of 2π in the phase φ of the superconducting order parameter $\Psi(x, t) = e^{i\varphi(x, t)}|\Psi|$ over a finite length scale, which in turn can momentarily change the conjugate variable $|\Psi|$ to zero over the same spatial scale along the length of the filament [10]. Do note that $|\Psi|$ does not wind around the crystal axis. At T_J , transverse phase coherence is established: a dimensional crossover from 1D to a 3D superconducting ground state exhibiting zero resistance and a Meissner effect is therefore anticipated.

In recent years, advancement in nanofabrication techniques have facilitated high-precision tailoring of q1D superconductors in the form of individual nanowires, arrays or carbon nanotubes [11, 12]. Understandably, naturally occurring crystalline nanocomposites should provide an easier and cheaper alternative route to realizing the next generation of novel superconductors. Some of the earliest known examples of crystalline q1D superconductors were members of the organic Bechgaard salt family such as $(\text{TMTSF})_2\text{PF}_6$ [13]. The Chevrel phase-based superconductors, with the stoichiometric formula $M_2\text{Mo}_6X_6$ (M = Group IA or Group III metal, X = chalcogen [8, 14]), are made up of building blocks of c -axis oriented infinitely-long $(\text{Mo}_6X_6)_\infty$ chains as shown in Fig. 6.1. The M -ions intercalated between these filamentary chains; act as charge reservoirs and facilitate transverse Josephson coupling. The strong uniaxial anisotropy arising from their intrinsic crystal structure renders the q1D properties to these class of materials. In addition, members of this family have been reported to exhibit T_J smaller than T_{ons} : for example, $T_J = 1.0$ K, $T_{ons} = 1.6\text{--}5.5$ K for $\text{Na}_2\text{Mo}_6\text{Se}_6$ [15, 16]. All of these factors suggest that, the $M_2\text{Mo}_6X_6$ -based

nanofilamentary composites might be some of the pioneering candidates for realizing superconductivity with reduced dimensionality in pure single crystalline compounds.

Figure 6.1: Crystal structure of $\text{Tl}_2\text{Mo}_6\text{Se}_6$, viewed parallel and perpendicular to the c -axis. The space group is $P6_3/m$.

Discovered in 1980, $\text{Tl}_2\text{Mo}_6\text{Se}_6$ has been found to be one of the most strongly anisotropic q1D superconductors with T_{ons} varying between 3 K to 6.5 K [9, 17]. The $(\text{Mo}_6\text{Se}_6)_\infty$ chains are weakly-coupled by Tl^+ ions, with Tl vacancy concentration of $\sim 2.5\%$ giving imperfect stoichiometry [18]. It is worth pointing out that, the vacancy disorder (δ) in $\text{Tl}_2\text{Mo}_6\text{Se}_6$ is significantly smaller than in $\text{Na}_2\text{Mo}_6\text{Se}_6$; for which δ has been suggested to enhance the experimental T_J relative to the theoretical value [15]. Although, electrical transport has previously been measured in this compound, and supports a two-step scenario [17], magnetic penetration depth has not yet been probed in this sample. We have therefore measured and present in this chapter the anisotropic penetration depth $\Delta\lambda_{ab,c}(T)$ in single crystals of $\text{Tl}_2\text{Mo}_6\text{Se}_6$, with two principal objectives: (1) to determine whether the magnetic signatures of the superconducting transition also display two-step

characteristics and (2) to obtain a detailed quantitative understanding of the onset of transverse coherence in q1D superconductors.

The change in the magnitude of the penetration depth $\Delta\lambda_c(T)$ probed with the ac magnetic field H perpendicular to the filamentary chains ($H \perp c$), clearly shows a two-step superconducting transition with *apparent* $T_{ons} \approx 6.7$ K, and an unusually wide transition region. Note that, we define the true onset of the 1D superconducting phase by the symbol T_p denoting Cooper pair formation, which we shall show is lower than the apparent T_{ons} . We have also shown that, both low- T normalized superfluid densities $\rho_{ab,c}(T)$ give near-perfect fits to the single-gap BCS model with moderate-coupling. We have additionally performed electrical transport measurements, which reveal that a globally coherent superconducting ground state with $R(T) = 0$ is established below 4.2 K in this material. This value is in close proximity to the transverse coupling temperature $T_J = 4.4$ K as reported previously [15, 16]. However, $\Delta\lambda_{ab}(T)$ measured with $H \parallel c$; which probes transverse phase coherence alone, clearly shows a long-tail extending from ~ 3 K to 4.8 K. We suggest that, fluctuation-induced broadening by finite-size effects and sample inhomogeneity might be responsible for rendering these long tails in the ultra-phase-sensitive penetration depth data. We have also shown that, with the exception of a fluctuation-dominated finite T -width near T_{ons} , the 1D superconducting regime above T_J can be described by a model of phase slips with contribution from both thermal and quantum fluctuations.

6.2 Data and Analysis

6.2.1 Penetration Depth and Superfluid Density

Measurements were performed on needle-shaped $\text{Tl}_2\text{Mo}_6\text{Se}_6$ single crystals designated Sample#1 and Sample#2, with length ~ 1.5 mm and diameter ~ 0.07 mm: the c -axis oriented along the length. The crystal growth and

Figure 6.2: Schematic representation of the two-step superconducting transition in q1D systems as expected in magnetic penetration depth data, relative to crystal orientation. Individual filaments have been shown as small cylinders within the outline of the bigger cylinder representing the crystal. The direction of the external magnetic field H , and the crystallographic axes c and a have been shown by arrows. (Top) With $H \parallel c$, only transverse coupling between the filaments should be probed. (Bottom) With $H \perp c$, both transverse phase coherence below T_J , as well as phase slip (white patches) dominated 1D longitudinal phase coherence above T_J can be detected.

characterization have been described elsewhere [15]. As derived in Chapter 3, the change in the diamagnetic susceptibility $\Delta\chi(T) = \chi(T) - \chi(0.35 \text{ K})$ is related to the change in the resonant frequency $\Delta f(T)$ of our TDO setup as follows,

$$4\pi\Delta\chi(T) = \frac{G}{R_{3D}}\Delta f(T), \quad (6.1)$$

which in turn gives,

$$\Delta\lambda(T) = G\Delta f(T), \quad (6.2)$$

where $\Delta\lambda(T) = \lambda(T) - \lambda(0.35 \text{ K})$, is the change in the magnetic penetration depth. For the TDO ac field $H \perp c$, an effective penetration depth $\Delta\lambda_{eff}$ is probed; which has contributions from both in-plane $\Delta\lambda_{ab}$ and out-of-plane $\Delta\lambda_c$. We have used the expression $(\Delta\lambda_{ab}/t) + (\Delta\lambda_c/w) = (\Delta\lambda_{eff}/R_{3D})$ by Prozorov *et. al* to extract the $\Delta\lambda_c$ component from this mix [19]. Here, $2t$ and $2w$ stand for the sample length and diameter respectively. Since $w < t$ for our crystal, $\Delta\lambda_{eff}$ should naturally have a much higher contribution from $\Delta\lambda_c$. For the q1D sample $\text{Ti}_2\text{Mo}_6\text{Se}_6$ being probed, we anticipate that two-step superconducting transition should be observed in $\Delta\lambda_{eff}(T)$, and in effect in the dominant $\Delta\lambda_c(T)$ component. This is because in response to $H \perp c$, the superconducting eddy currents allow magnetic field penetration along all the crystallographic directions, and therefore should pick up signatures for both c -axis directed longitudinal phase coherence with phase slips above T_J , and inter-filamentary transverse phase coherence below T_J . On the other hand, $H \parallel c$ should ideally probe only transverse coupling along the ab -plane when $T < T_J$. The schematic of the anticipated two-step transition in our penetration depth data has been shown in Fig. 6.2. Do note that, the spatial extent of the phase slips within each filament have been enlarged for clarity, and do not represent the true length scale. Phase slips happen on a length scale $\sim \xi_{\parallel}$ — the superconducting coherence length parallel to the filaments, with $\xi_{\parallel}$ being orders of magnitude smaller than the length of each

$(\text{Mo}_6\text{Se}_6)_\infty$ filamentary chain.

Figure 6.3: Anisotropic $\Delta\lambda(T)$ data for $\text{Tl}_2\text{Mo}_6\text{Se}_6$ Sample#1, obtained from the TDO experiment. Dashed lines indicate the apparent $T_{ons} \approx 6.7$ K, a second kink ~ 5.7 K and $T_J = 4.4$ K. $\Delta\lambda_{ab}$ is the penetration depth probed by the TDO magnetic field parallel to the 1D filamentary axis, while $\Delta\lambda_c$ is probed with the field applied perpendicular to the chains. T_{ons} is defined as the intersection point of the extrapolated linear regions immediately before and after $\Delta\lambda_c(T)$ starts to fall from the normal state value. Inset shows corresponding magnetic susceptibilities $4\pi\chi_{ab}(T)$ and $4\pi\chi_c(T)$ respectively, obtained using Eqn. 6.1 with $4\pi\chi(6.75 \text{ K}) = 0$.

We have plotted $\Delta\lambda_{ab,c}(T)$ for $\text{Tl}_2\text{Mo}_6\text{Se}_6$ Sample#1 from 0.35 K to 9 K in Fig. 6.3, extracted from the raw frequency shift $\Delta f(T)$ using Eqn. 6.2, with $H < 50$ mOe. It is immediately clear from the $\Delta\lambda_c(T)$ curve, that the superconducting transition is unusually wide, stretching from ~ 2.6 – 6.7 K, despite such a small applied field. Such a broad transition over a similar T -range is reproducible in another $\text{Tl}_2\text{Mo}_6\text{Se}_6$ single crystal that we have measured (not shown here). Previously done magnetization measurements on $\text{Tl}_2\text{Mo}_6\text{Se}_6$, observed a similarly broad transition in $M(T)$ data as well. [17] The two extreme dashed lines in Fig. 6.3 indicate the

apparent $T_{ons} \approx 6.7$ K and the theoretical $T_J = 4.4$ K in this compound. In between these two key temperatures, $\Delta\lambda_c(T)$ shows a sharp kink ~ 5.7 K shown by the middle dashed line: a similar feature is observed in $R(T)$ data, as illustrated later. Converting $\Delta f(T)$ to diamagnetic susceptibility using Eqn. 6.1, yields effective superconducting volume fractions $\sim 39\%$ for $H\|c$ and $\sim 99\%$ for $H\|ab$, as shown in the inset of Fig. 6.3. This is in line with theoretical expectations for q1D superconductors with $\lambda_{ab} \gg \lambda_c$ and previous experiments on $\text{Ti}_2\text{Mo}_6\text{Se}_6$ [9,20]. It is worth noticing that, the apparent superconducting onset temperature also varies with field orientation: ~ 6.7 K for $\Delta\lambda_c(T)$ versus ~ 4.8 K for $\Delta\lambda_{ab}(T)$. Within a two-step transition scenario, this result is entirely expected if one considers that $H\|c$ probes inter-filamentary phase coherence alone, which should only be established around $T_J = 4.4$ K, whereas $H\|ab$ probes a mixture of inter- and intra-filamentary coherence. Since intra-filamentary phase coherence is initiated within individual filaments due to Cooper pair formation below T_{ons} , the apparent onset temperature for superconductivity is higher for $H\|ab$. A faint trace of the transition at ~ 6.7 K is nevertheless visible in $\Delta\lambda_{ab}(T)$ — this is likely due to a crystal alignment error with the field, which we estimate to be within $\pm 1\%$ in our apparatus.

Converting our $\Delta\lambda(T)$ data to normalized superfluid densities $\rho_s(T) = [\lambda^2(0)/\lambda^2(T)]$ using $\lambda_{ab}(0) = 1.5 \mu\text{m}$ and $\lambda_c(0) = 0.12 \mu\text{m}$ values, deduced from earlier magnetic and thermodynamic data, [8] we plot $\rho_{ab,c}(T)$ in Fig. 6.4. The experimental $\rho_s(T)$ have been fitted to the expression for superfluid density for a conventional s -wave superconductor in the clean and local limits as shown below [21],

$$\rho_s(T) = 1 + 2 \int_0^\infty \frac{\partial f}{\partial E} d\varepsilon, \quad (6.3)$$

where $f = [\exp(E/k_B T) + 1]^{-1}$ is the Fermi function and $E = [\varepsilon^2 + \Delta(T)^2]^{1/2}$ is the Bogoliubov quasiparticle energy. We have considered temperature

dependence of the gap $\Delta(T)$ of the form [22],

$$\Delta(T) = \delta_{sc} k T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\}, \quad (6.4)$$

where $\delta_{sc} = \Delta(0)/k_B T_c$, $a = 2/3$ and $\Delta C/C \equiv \Delta C/\gamma T_c$. We find that, low- T $\rho_{ab,c}(T)$ data till ~ 3 K can be fitted nicely to Eqn. 6.3 as shown by the solid red and blue curves in Fig. 6.4. The obtained fitting parameters are $\delta_{sc} = 2.2 \pm 0.1$, $\Delta C/C = 2.3 \pm 0.3$ and $T_c = (2.95 \pm 0.05)$ K for $\rho_{ab}(T)$, and $\delta_{sc} = 2.0 \pm 0.1$, $\Delta C/C = 2.2 \pm 0.3$ and $T_c = (2.65 \pm 0.05)$ K for $\rho_c(T)$; suggesting that $\text{Ti}_2\text{Mo}_6\text{Se}_6$ is a moderate-coupling superconductor. The moderate-coupling scenario, as well as the obtained value of $\Delta C/C \approx 2.3$, is in close agreement to previously done electronic specific heat measurements [8].

Do note that, T_c has been used here in a general sense, and refers to the temperature around which the drop in ρ_s is abruptly reduced and the “tail” in the superconducting transition starts — it does not refer to the mean-field critical temperature corresponding to a true phase transition. As clearly seen, these theoretical fits cannot reproduce such broad transitions, yielding T_c lower than T_J at which a bulk superconducting ground state is established. Plotting $\rho_{ab,c}(T)$ on a logarithmic scale (inset of Fig. 6.4) reveals these pronounced tails extending up to ~ 4.8 K (ρ_{ab}) and ~ 6.7 K (ρ_c). The fact that $\rho_{ab,c}(T)$ only rise steeply below $T \sim 3$ K is indicating that the phase stiffness is weak at higher temperatures. This is consistent with phase coherence between the 1D filaments only being established at $T_J < T_{ons}$, while phase fluctuations continue to broaden the transition even below T_J .

Figure 6.4: Normalized superfluid densities $\rho_{ab,c}(T)$ for $\text{Tl}_2\text{Mo}_6\text{Se}_6$ Sample#1, extracted from $\Delta\lambda_{ab,c}(T)$ in Fig. 6.3 using $\lambda_{ab}(0) = 1.5 \mu\text{m}$ and $\lambda_c(0) = 0.12 \mu\text{m}$. Solid curves are fits to Eqn. 6.3 with the following parameters: Red curve [$\rho_{ab}(T)$] - $\delta_{sc} = 2.2 \pm 0.1$, $\Delta C/C = 2.3 \pm 0.3$ and $T_c = (2.95 \pm 0.05) \text{ K}$, Blue curve [$\rho_c(T)$] - $\delta_{sc} = 2.0 \pm 0.1$, $\Delta C/C = 2.2 \pm 0.3$ and $T_c = (2.65 \pm 0.05) \text{ K}$. Inset shows full T -range data with $\rho_{ab,c}(T)$ plotted on a logarithmic scale. The dashed lines indicate the apparent $T_{ons} \approx 6.7 \text{ K}$ and $T_J = 4.4 \text{ K}$.

6.2.2 Electrical Transport Measurements

I. Physics of the Two-step Superconducting Transition below T_J

Let us now try to model this two-step transition. Taking into consideration the fact that the observed tails in both $\Delta\lambda_{ab}(T)$ and the extracted $\rho_{ab}(T)$ curves seem to saturate in close vicinity of T_J ; it seems quite apparent that we need to explicitly consider how intra-filamentary phase fluctuations just above T_J , give rise to a globally coherent phase below it. We propose that inter-filamentary transverse phase coupling in $\text{Tl}_2\text{Mo}_6\text{Se}_6$ is achieved

via vortex-antivortex pair (VAP) binding phase transition. Such a phase transition is of infinite order within the theoretical framework of the 2D-XY model, and is described by the Berezinskii-Kosterlitz-Thouless (BKT) model [23–25]. The parallel with BKT physics in the $M_2\text{Mo}_6X_6$ -based q1D superconductors was first highlighted in 2011, following the observation of a differential resistance plateau for $T_J < T < T_{ons}$ and power-law $I(V)$ scaling in $\text{Tl}_2\text{Mo}_6\text{Se}_6$ [17]. Subsequently, similar BKT-type behaviour was observed in a variety of other q1D materials [15, 26, 27] and confirmed by Monte-Carlo simulations [28]. In spite of all the available evidence, the very concept that a q1D material might exhibit a BKT transition has so far failed to gain traction within the academic community, primarily for two reasons.

The first reason is quite understandable, and it addresses the very obvious issue that how can a model that was developed for 2D materials, be applicable to a q1D system. As nicely illustrated by Anserment *et. al* for the case of $\text{Na}_2\text{Mo}_6\text{Se}_6$ [15], if we consider a cross-sectional view of a q1D superconductor, i.e. viewed parallel to the 1D axis, we are now looking at a 2D array of superconducting filaments, each with a distinctive 1D superconducting phase. The symmetry of this problem now falls into the 2D XY universality class, and the system would therefore be expected to undergo a BKT-type transition at T_J , at which the correlation length $\xi_\perp$ perpendicular to the filamentary axis diverges exponentially and pairing up of free Josephson vortices and antivortices parallel to the filaments take place, as shown schematically in Fig. 6.5.

The second reason for skepticism is that by claiming q1D materials exhibit 2D XY physics, we are neglecting the spatial and temporal evolution of the phase and amplitude of the order parameter within individual filaments. However, the intense anisotropy of q1D materials such as $\text{Tl}_2\text{Mo}_6\text{Se}_6$ suggests that, we may in fact be justified in ignoring these fluctuations — the coherence length parallel to the filaments $\xi_\parallel$ is 10-20 times longer

than $\xi_{\perp}$ [8, 17]. This implies that the two-dimensionality normal to the filamentary axis is merely instantaneously violated on short timescales and at large length scales.

Figure 6.5: Schematic representation of the proposed vortex-antivortex binding transition in our q1D superconductor $\text{Tl}_2\text{Mo}_6\text{Se}_6$. If Josephson vortices and antivortices (shown as cylinders) parallel to the direction of the $(\text{Mo}_6\text{Se}_6)_{\infty}$ filaments (shown as hexagonal rods) get paired up via some mechanism below T_J , Josephson coupling and thereby transverse phase coherence between the filaments can be facilitated.

Our collaborator Dr. Alexander Petrović from School of Physical and Mathematical Sciences, Nanyang Technological University has performed the electrical transport measurements on the same $\text{Tl}_2\text{Mo}_6\text{Se}_6$ crystal, and we present the corresponding data analysis in the following paragraphs. For BKT-like phase transitions, two pivotal features in electrical transport data are expected — (1) $V(I)$ curves should exhibit a power-law scaling of the form $V \propto I^{\alpha(T)}$; with the power law-exponent $\alpha(T)$ expected to show

Figure 6.6: (a) $V(I)$ curves for Tl₂Mo₆Se₆ Sample#1 from $T = 1.95$ K to 6.55 K. (b) Inset shows $V(I)$ data plotted on a log-log scale, with solid lines showing the power-law fits of the form $V \propto I^{\alpha(T)}$. The power-law exponent α , shows a change from $\alpha \approx 1$ for $T > 5$ K, to $\alpha \approx 10$ for $T < 3$ K. The main panel shows this change in $\alpha(T)$, and also highlights a sudden Nelson-Kosterlitz jump from $\alpha \approx 3$ to $\alpha \approx 1.5$, at $T_{BKT} \approx 4.2$ K. (c) Exponential scaling over a range ~ 0.3 K above T_{BKT} in $R(T)$ data obtained with $I = 0.2$ mA. The linear fit (red solid line) to the scaling regime can be extrapolated back to obtain $T_{BKT} \approx 4.1$ K. Inset shows T_{BKT} obtained in a similar manner for $I = 0.05$ mA, 0.1 mA, 0.2 mA and 0.5 mA.

a discontinuous “Nelson-Kosterlitz jump” from $\alpha = 3$ to $\alpha = 1$ at T_{BKT} [29, 30], and (2) resistance $R(T)$ should show an exponential scaling of the form $R(T) = R_0 \exp(-bt^{-1/2})$ over a narrow T -range above T_{BKT} , where $t = (T/T_{BKT} - 1)$ and R_0, b are material constants [31–33].

Figure 6.6(a) shows the V – I curves for Tl₂Mo₆Se₆ Sample#1, obtained

using a standard ac transport technique, over a T -range from 1.95–6.55 K. Inset of Fig. 6.6(b) shows $V(I)$ data plotted on a double logarithmic scale. The straight solid lines represent power-law fits to the same. From the apparent $T_{ons} \approx 6.7$ K down to 5 K, data seem to follow an Ohmic trend, with a large fitting-range ~ 0.1 –7 mA. Below 5 K, the slope α changes sharply with decrease in temperature, and curves become more steeper. Finally, below 3 K, α seems to saturate. At low- T , data can be fitted to power-law only over a small I -range. Many factors such as quantum-fluctuations at low- T , finite-size effects and vortex-unbinding at elevated currents can affect the $V(I)$ curves, and in effect, hamper the accurate determination of $\alpha(T)$ and the discontinuity in the jump at T_{BKT} [34,35]. This is reflected in the larger error-bars in $\alpha(T)$ at low- T , as shown in the main panel of Fig. 6.6(b). From the definition of a Nelson-Kosterlitz jump, we get $T_{BKT} = (4.17 \pm 0.02)$ K in close agreement to the value of $T_J = 4.4$ K.

Resistivity measurements were performed using a standard four-probe technique. Fig. 6.6(c) illustrates the exponential scaling of $R(T)$ [for $I = 0.2$ mA] over ~ 4.3 –4.6 K, which can be extrapolated to obtain $T_{BKT} = (4.09 \pm 0.03)$ K. This is in close agreement to the value of 4.17 K, obtained from the $\alpha = 3$ definition [shown in Fig.6.6(b)]. Our data analysis thus suggests that, the dimensional crossover from the 1D to the 3D superconducting phase in our q1D system across T_J can be perhaps attributed to a BKT-like phase transition involving the pairing up of vortices and antivortices.

One might now quite understandably ask, if a superconducting ground state is expected to form below ~ 4.2 K, how do we then justify the long tails and the low values of the apparent $T_c \approx 3$ K obtained from the $\rho_{ab,c}(T)$ fits shown earlier? One plausible reason would be the presence of intrinsic inhomogeneities: similar to other thermodynamic phase transitions, they can lead to the broadening of the transition region here around the critical temperature as well. The other factor that is expected to contribute

even more strongly to the fluctuation is finite-size effect. Finite dimension of our strongly anisotropic crystal can limit the exponential divergence of $\xi_{\perp}$ around T_J , and in effect render a long tail in the transition [33, 34]. It is also possible that longitudinal phase fluctuations within individual chains, that can either source or sink free vortices; behave similarly to a finite-size effect or inhomogeneity. Another factor that might contribute to the broadening of the dimensional cross-over, is competition between line-vortices and vortex-loops. In addition to line-vortices formed within the Josephson junctions parallel to the chains, vortex-loops can form across the filaments at a finite $T > T_J$. Since the energy required to create a vortex (line or loop) is proportional to its enclosed volume, the energy required to generate a vortex-line (that can theoretically be as long as the crystal length) should therefore be higher than that of a vortex-loop which has a smaller dimension ($\sim$ separation between the chains). However, disorder can limit the length of line-vortices thus making the energy scale comparable. In such a scenario, the energy required to bind free line-VAP in order to establish transverse phase coherence might be affected: this in turn can broaden the dimensional crossover as we approach T_J from above.

II. Physics of the Two-step Superconducting Transition for $T_J < T < T_{ons}$

The complete set of $R(T)$ curves obtained for different driving currents I (mA) have been shown Fig. 6.7. The two-step superconducting transition is outright clear; showing stark similarity to the $\Delta\lambda_c(T)$ curve in Fig. 6.3, as apparent from the first two dashed lines which indicate the apparent $T_{ons} \approx 6.7$ K and the second kink in TDO data at $T \sim 5.7$ K. The extreme left dashed line indicates $T_J = 4.4$ K. Figure 6.8 shows the zoomed in $R(T)$ data from 4.3 K to 6.6 K. The humps in the region ~ 4.3 – 4.8 K might be attributed to pair-breaking effects as suggested for $\text{Na}_2\text{Mo}_6\text{Se}_6$, and as expected, they

Figure 6.7: $R(T)$ curves for $\text{Tl}_2\text{Mo}_6\text{Se}_6$ Sample#1, with $I = 0.05$ mA, 0.1 mA, 0.2 mA and 0.5 mA, from which we extract $R_{NS} \approx 0.009 \Omega$. The extreme two dashed lines indicate the apparent $T_{ons} \approx 6.7$ K and $T_J = 4.4$ K, while the middle dashed line corresponds to the second kink ~ 5.7 K: observed in TDO $\Delta\lambda_c(T)$ data in Fig. 6.3. Near the ~ 5.7 K dashed line, a clear hump can be seen in the $R(T)$ curves as well.

get smeared out with increase in magnitude of I [15]. In a generic sense, these humps might be signatures of the transition to the transverse coherent phase.

Within the two-step scenario, $R(T)$ data above T_J should correspond to 1D superconductivity within individual $(\text{Mo}_6\text{Se}_6)_\infty$ chains, with a strong contribution from longitudinal phase slips. However, an additional anomaly can be observed in the form of minor humps from ~ 6.0 K to 6.2 K for $I \leq 0.2$ mA, which shifts up to 6.5 K to 6.7 K at the higher value of $I = 0.5$ mA. We anticipate Cooper pair fluctuations above the superconductor-normal phase transition boundary, to be predominantly responsible for broadening the $R(T)$ curves from ~ 6 K to 6.7 K. These fluctuation Cooper pair

formations behave distinctively different from conventional quasiparticles and do not contribute to the superfluid density: instead they broaden the superconducting transition in the vicinity of the mean-field phase transition temperature T_{mf} . In the context of q1D systems, the relevant temperature range ΔT , over which interaction between fluctuations need to be essentially considered, is given by the product $T_{ons}G_{1D}$, where G_{1D} is the 1D Ginzburg-Levanyuk number [36]. To give a perspective, critical region width $\Delta T \sim 1.5$ K for $\text{Ti}_2\text{Mo}_6\text{Se}_6$ and $\Delta T \sim 2.0$ K for $\text{In}_2\text{Mo}_6\text{Se}_6$ have been reported in the past [8]. Based on the original microscopic theory developed by Aslamazov and Larkin (A-L), the fluctuation-induced excess conductivity (called paraconductivity) within the mean-field region can be described by the following expression [37–39],

$$\frac{\Delta\sigma}{\sigma_{300}} = A \left(\frac{T}{T_{mf}} - 1 \right)^\lambda, \quad (6.5)$$

where $\Delta\sigma = \sigma(T) - \sigma_N(0)$ is the excess conductivity, σ_{300} is the conductivity at 300 K, and A and λ are constants related to the dimensionality (D) of the superconducting phase, with $\lambda = 2 - D/2 = 1.5$ for 1D A-L fluctuations. $\sigma_N(0)$ is equal to the intercept a of the normal phase conductivity fitted to a linear equation of the form $\sigma(T) = a + bT$.

To illustrate the contribution from fluctuations to our experimental data above 6 K, we plotted $\ln(\Delta\sigma/\sigma_{300})$ as a function of $\ln(T/T_{mf} - 1)$ with $T_{mf} = T_p$, as shown in the inset of Fig. 6.8 for $I = 0.05$ mA. A linear fit to the same plot from ~ 6.2 K to 6.6 K yields the slope $\lambda = 1.45 \pm 0.14$, in close proximity to 1.5: validating the contribution of A-L 1D fluctuations over the specified T -range. This would then suggest that, phase slip-dominated 1D Ginzburg-Landau superconductivity should exist below this region. We used the well-known Langer-Ambegaokar-McCumber-Halperin (LAMH) model of thermally activated phase slips (TAPS) [40,41], together with a contribution from quantum phase slips (QPS) [42] to fit $R(T)$ data from 4.9 K to 5.9 K.

Figure 6.8: Zoomed in $R(T)$ data shown from $T = 4.3$ K to 6.6 K. The solid curves are fits to the TAPS+QPS model, as represented by Eqn. 6.11, from $T = 4.9$ K to 5.9 K. Inset shows log-log plot of Eqn. 6.5 for conductivity $\sigma(T)$ obtained with $I = 0.05$ mA. A linear fit from 6.2 K to 6.6 K yields the parameter $\lambda \approx 1.5$: suggesting strong 1D Aslamazov-Larkin fluctuations in this T -range.

Brief discussion on these models is given below.

A. LAMH Model of Thermally Activated Phase Slips: Here, phase slips are thermally activated over an energy barrier ΔF , proportional to $\xi(T) = \xi(0)(1 - T/T_p)^{-1/2}$ and the length of the nanowire L . The frequency of random excursions in the superconducting order parameter is given by a prefactor $\Omega(T)$, that sets the time scale of the fluctuations. The LAMH contribution to the total resistance can be expressed as follows,

$$R_{LAMH}(T) = \frac{\pi \hbar^2 \Omega}{2e^2 k_B T} \exp\left(-\frac{\Delta F}{k_B T}\right), \quad (6.6)$$

where the attempt frequency is given by,

$$\Omega = \frac{L}{\xi(T)} \left(\frac{\Delta F}{k_B T} \right)^{1/2} \frac{1}{\tau_{GL}}, \quad (6.7)$$

and $\tau_{GL} = [\pi\hbar/8k_B(T_p - T)]$ is the GL relaxation time. Following a development of the energy barrier by Lau *et al.*, [43] we can write $\Delta F(T)$ as,

$$\Delta F(T) = Ck_B T_p \left(1 - \frac{T}{T_p} \right)^{3/2}, \quad (6.8)$$

where C is a dimensionless parameter relating the energy barrier for phase slips F to the thermal energy near T_p and is defined as,

$$C \approx 0.83 \left(\frac{L}{\xi(0)} \right) \left(\frac{R_q}{R_F} \right). \quad (6.9)$$

Here, $R_q = h/4e^2 = 6.45 \text{ k}\Omega$ is the resistance quantum for Cooper pairs and R_F the normal state resistance of the entire nanowire. [44]

Our macroscopic single crystalline sample with crystal diameter $D \gg \xi$, can not be considered to be equivalent to a single nanowire within the framework of the LAMH model. Recently a generalized version of the LAMH theory has been successfully used to model $R(T)$ data in macroscopic crystals of the q1D superconductor $\text{Na}_2\text{Mo}_6\text{Se}_6$ [15, 16]. In their model, the authors considered the crystal to be a $m \times n$ array of identical parallel 1D filaments/nanowires, each of length L . In Eqn. 6.9, this leads to the replacement of R_F by the *total* crystal resistance R_{NS} , as well as a geometric renormalization of L to $L_{eff} = Lm/n$, where Lm is the experimental voltage contact separation on a crystal and n is the typical number of 1D filaments within the crystal cross-section. Their model thus facilitates application of the LAMH theory even beyond the single nanowire limit, with the small assumption that all the filaments are geometrically alike.

B. Quantum Phase Slips: Thermal fluctuations cease to exist with decrease in temperature and, hence, TAPS become progressively less important

and eventually die out in the limit $T \rightarrow 0$. However, quantum phase slips originating from quantum fluctuations in the order parameter still persist in ultra-thin superconducting wires. The QPS contribution to the resistivity in a 1D superconductor becomes relevant when $k_B T < \Delta(T)$, where $\Delta(T)$ is the superconducting gap. We anticipate that, QPS should play an equally important role as TAPS in contributing to the experimentally obtained $R(T)$ data for our $\text{Ti}_2\text{Mo}_6\text{Se}_6$ single crystals, even in the relatively higher T -range. We attribute this argument to the moderate-coupling strength of the superconducting order parameter, obtained from single-gap fits to the superfluid density. The enhanced pairing strength implies that, the cut-off temperature $T \approx 0.9T_{ons}$ below which QPS is applicable, as well as the relevant T -range, would be enhanced in our system beyond the weak-coupling limit. Additionally, it has been suggested that, for superconducting nanowires with a constriction arising due to non-uniform or fluctuating cross sections; the QPS component from the constriction can have a significant contribution even at higher temperatures. [42] Naturally occurring non-uniformity or disorder-induced fluctuations in the diameter of the infinitely extended $(\text{Mo}_6\text{Se}_6)_\infty$ chains in our crystal is a finite possibility. For the QPS contribution, we used the following expression, [42]

$$R_{QPS}(T) = A_Q B_Q \frac{R_q^2}{R_F} \frac{L^2}{\xi(0)^2} \exp \left[-A_Q \frac{R_q}{R_F} \frac{L}{\xi(T)} \right], \quad (6.10)$$

where A_Q and B_Q are constants. In a similar manner to the TAPS contribution, we treat our crystals as macroscopic arrays of nanowires and rewrite Eqn. 6.10 in terms of L_{eff} and the normal state resistance R_{NS} of the entire crystal. Finally, the total theoretical $R(T)$ is calculated by considering a parallel combination of the TAPS and QPS components, with an additional quasiparticle contribution R_{NS} as follows,

$$R = (R_{NS}^{-1} + (R_{LAMH} + R_{QPS})^{-1})^{-1}. \quad (6.11)$$

The solid curves in Fig. 6.8 show the least-square fits to our experimental $R(T)$ data from 4.9 K to 5.9 K, using Eqn. 6.11 with the fitting parameters T_p , $L_{eff}/\xi(0)$, A_Q and B_Q . $R_{NS} = 0.0095 \Omega$ is used for all the fits. The fitting parameters with the error bars have been listed in Table 6.1. The fits for all the $R(T)$ curves can reproduce our data well, and yield $T_p \approx 6$ K — lower than the apparent onset temperature ~ 6.7 K at which resistance starts to drop. It is important to mention that, we have used the TAPS+QPS fitted value of $T_p = 5.9$ K for $I = 0.05$ mA, to extract the A-L parameter $\lambda \approx 1.5$ using Eqn. 6.5. In q1D superconductors whose resistance is influenced by QPS, A_Q is expected to be of order unity, in agreement with our data. Comparing to the fitting parameters from the LAMH model fits to the corresponding q1D superconductor $\text{Na}_2\text{Mo}_6\text{Se}_6$ [15], we see that our obtained values for $L_{eff}/\xi(0)$ are substantially smaller. This is expected considering the larger value of $\xi(0)$ parallel to the filamentary axis, for our less disordered $\text{Tl}_2\text{Mo}_6\text{Se}_6$ crystals.

Table 6.1: Phase slip fit parameters for $\text{Tl}_2\text{Mo}_6\text{Se}_6$

Fits are shown in Fig. 6.8				
I (mA)	T_p (K)	$L_{eff}/\xi(0)$	A_Q	B_Q
0.05	5.89 ± 0.02	$(1.44 \pm 0.12) \times 10^{-4}$	0.43 ± 0.04	$(20 \pm 2.2) \times 10^{-4}$
0.10	6.02 ± 0.02	$(1.08 \pm 0.07) \times 10^{-4}$	0.45 ± 0.04	$(40 \pm 3.1) \times 10^{-4}$
0.20	6.16 ± 0.02	$(7.82 \pm 0.52) \times 10^{-5}$	0.52 ± 0.05	$(70 \pm 5.3) \times 10^{-4}$
0.50	6.00 ± 0.08	$(5.71 \pm 0.36) \times 10^{-5}$	0.92 ± 0.04	$(70 \pm 20) \times 10^{-4}$

6.3 Conclusion and Future Work

In conclusion, we present measurements of magnetic penetration depth $\lambda_{ab,c}(T)$ on single crystalline q1D superconductor $\text{Tl}_2\text{Mo}_6\text{Se}_6$, using a TDO-based penetration depth probing tool. With ac field H applied perpendicular to the direction of the 1D filamentary axis, our $\Delta\lambda_c(T)$ data clearly shows signature for a two-step superconducting transition, with an apparent $T_{ons} \approx 6.7$ K. Similar to related q1D nanocomposite systems, this two-step superconduct-

ing transition can be broadly divided into the longitudinally coherent intra-filamentary 1D superconducting regime with phase slips above the transverse Josephson coupling temperature T_J , and a globally coherent superconducting ground state below it.

For $T > T_J$, we have shown that $R(T)$ data can be fitted to a model of phase slips with contribution from both thermal and quantum fluctuations, over a fitting range ~ 1 K. The same model however fails above 5.9 K, due to Cooper pair fluctuation-enhanced broadening within the 1D chains. Transition from the enhanced fluctuation-laden critical transition region to the 1D phase slip regime is in all likelihood responsible for the kinks ~ 6.0 – 6.5 K in $R(T)$ data, and ~ 5.7 K in $\Delta\lambda_c(T)$ data.

Our ac transport measurements also show power-law scaling in $V(I)$, and exponential scaling in $R(T)$ around T_J — both experimental signatures of a BKT-type phase transition involving binding of free Josephson line-vortices. We also fit the extracted normalized superfluid densities $\rho_{ab,c}(T)$ to BCS-like single superconducting gap model, with moderate-coupling pairing strength $\Delta(0) \sim 2.00 k_B T_c$, and apparent $T_c \approx 3$ K. We suggest that, this low value of T_c relative to T_J can be attributed to fluctuation-induced broadening of the superconducting transition below T_J due to combined effects of free vortices, finite-size effects and inhomogeneities. We are currently awaiting theoretical simulations that we anticipate will validate our suggested model and strengthen our data analysis for this q1D system.

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Chapter 7

$\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ Skutterudites

In this chapter, magnetic penetration depth measurements of the filled skutterudite superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ have been presented for $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 . The chapter contains the following sections: (1) introduction, (2) data and analysis, and (3) conclusion and future work.

7.1 Introduction

The filled skutterudite compounds with the chemical formula $\text{MPt}_4\text{Ge}_{12}$ (M = alkaline earth, lanthanide, or actinide) belong to the family of heavy-fermion superconductors (HFSC) and have attracted a lot of research interest in recent years [1, 2]. Numerous experiments probing the pairing symmetry of the superconducting order parameter have yielded contrasting reports of both nodal as well as nodeless gap function in these family of compounds. For example, magnetic penetration depth measurement of the first Pr-based HFSC $\text{PrOs}_4\text{Sb}_{12}$ ($T_c = 1.85$ K) revealed it be a strong-coupling superconductor with two point nodes on the Fermi surface [3], even though muon spin resonance (μSR) had initially suggested it to be a fully-gapped superconductor [4]. Recently another stoichiometrically similar skutterudite superconductor $\text{PrPt}_4\text{Ge}_{12}$ ($T_c \simeq 7.9$ K) has been discovered, which ex-

hibits T^3 -dependence of the electronic specific heat suggesting the presence of point nodes in the gap function with μ SR showing signature of time reversal symmetry breaking (TRSB), thus hinting towards unconventional superconductivity [5]. Interestingly, it was observed that substitution of Pr by Ce leads to suppression of the TRSB phenomenon as well as T_c in $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ [6] and leads to a crossover from a nodal to a nodeless superconducting gap [7]. A similar crossover from a weak-coupling to moderate-coupling conventional superconductivity with increase in Ru doping concentration had been reported previously in $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$ as well [8]. Based on a detailed analysis of the low- T electronic specific heat, it has eventually been reported that for $x \leq 0.07$ two-gap superconductivity exists in $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ with a dominant nodal gap function but for $x > 0.07$, only nodeless gaps persist [9]. Two-gap behavior for $\text{PrPt}_4\text{Ge}_{12}$ has been suggested based on other measurements such as magnetization [10] and photoemission spectroscopy [11] as well. Thermal conductivity data on the structurally similar skutterudite $\text{LaPt}_4\text{Ge}_{12}$ have also suggested the strong possibility of multi-gap order parameter, with the authors emphasizing that $\text{PrPt}_4\text{Ge}_{12}$ should exhibit similar unconventional superconductivity as well [12]. Nuclear magnetic resonance/nuclear quadrupole resonance studies on the other hand found that the experimental results of $\text{PrPt}_4\text{Ge}_{12}$ could be consistently reproduced by not only an isotropic s -wave gap model but also an anisotropic s -wave gap model with a point node [13].

Here we present measurements of the magnetic penetration depth λ down to 0.35 K on polycrystalline samples of $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ for $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 using a tunnel-diode based resonant oscillator technique. These samples were measured towards the end of this PhD and a detailed analysis is still underway. We observed that with the exception of $x = 0.02$ and $x = 0.04$, low- T data for all other doping concentrations exhibited a sharp downturn at temperatures below ~ 0.7 K, which resemble

diamagnetic jumps usually observed at superconducting transitions. We suspect that accidental contamination from perhaps a higher doping value of Ce causes these sharp jumps which constitute almost 75% of the raw-data below 1 K. For the relatively *cleaner* samples with $x = 0.02$ and $x = 0.04$, low- T $\lambda(T)$ data cannot be fit to an exponential function, thus suggesting unconventional nature of the pairing symmetry. Power-law fittings to $\lambda(T)$ gives an exponent $n \sim 2.6$ for both doping concentrations; thus suggest presence of possible point nodes similar to that reported from electronic specific heat measurements. Additionally, normalized superfluid density $\rho_s(T)$ for $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ with $x = 0, 0.02$ and 0.04 , can be fit to a two-gap model using a nodal Gap 1 and a nodeless Gap 2; with a gradual reduction in the contribution from the nodal gap with increase in x .

7.2 Data and Analysis

Polycrystalline samples of $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ were prepared by an arc-melting and annealing procedure, and were found to have a cubic unit cell belonging to the space group $\text{Im}\bar{3}$ for all values of x [7]. Big chunks of these polycrystalline samples were cut using a clean razor blade and rectangular platelet-shaped samples were obtained. The samples had moderately flat basal planes with dimensions $\sim 0.6 \times 0.6 \text{ mm}^2$, while the thickness ranged from 0.2 mm in the thinner ones to as high as 0.5 mm in the bulkier samples. The samples were placed inside the primary coil of our TDO system such that the coil ac field H was perpendicular to the planar surface of the samples. We used an approach similar to that described by Prozorov *et al.* to estimate the calibration factor G for all the polycrystalline samples [14]. However, due to reasoning already described in Chapter 3, the calculated value of G for the thicker samples are expected to have a higher error bar.

Measurement of $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ samples with Ce concentrations $x = 0.06, 0.07$ and 0.085 revealed the existence of a significantly large jump in

the resonant frequency of the TDO that starts from $T_{min} \approx 0.35$ K of our cryostat and seem to saturate ~ 0.7 K, while for $x = 0$ a distinctive upturn ~ 1.2 K followed by a downturn similar to other doping concentrations is observed. Figure 7.1 shows these low- T jumps with the inset showing $\Delta f = f(T) - f(T_{min})$ data over the full temperature range. The onset temperature for the bulk diamagnetic transitions are found to be $T_c = 7.7$ K, 4.6 K, 4.1 K and 3.6 K for $x = 0, 0.06, 0.07$ and 0.085 respectively. These values agree well with the transition temperatures for the respective doping concentrations reported elsewhere [9]. Since penetration depth $\Delta\lambda(T)$ is directly proportional to Δf with a multiplicative calibration factor G , these humps should be visible in $\Delta\lambda(T)$ as well, and eventually in the extracted superfluid density $\rho_s(T)$ data. As already discussed for the superconductor $\text{CsMo}_{12}\text{S}_{14}$ in a previous chapter, such abrupt inflection points in TDO-measured data can be hinting towards possible multi-gap behavior in $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$, a possibility that has been consistently suggested for this particular skutterudite superconductor. But the occurrence of these humps around the same temperature range in these samples, each crystal having a visibly different T_c suggests that contamination by some superconducting specimen might be a stronger possibility. Since penetration depth measurements can probe surface of superconducting compounds with a high resolution, perhaps these jumps are the response from some surface-bound impurities (which might have percolated inside during the crystal growth) to the TDO coil ac field H . We have already expressed our concern regarding this issue to the sample growers.

Figure 7.2 shows penetration depth data for Ce concentrations $x = 0.02$ and 0.04 of the $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ superconductor. Unlike the doping concentrations shown in Fig. 7.1, there is no distinctive hump-like feature in the low- T data for these two samples. Choosing the onset of the diamagnetic jump as the transition temperatures, we get $T_c = 6.6$ K for $x = 0.02$ and

Figure 7.1: Change in magnitude of the resonant frequency $\Delta f = f(T) - f(T_{min})$ of the TDO in the low- T range for the polycrystalline superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$, with Ce doping concentrations $x = 0, 0.06, 0.07$ and 0.085 . Inset shows full temperature range data showing the superconducting transitions for the respective samples. The black open circles highlight the sharp downturn < 1 K that is visible in frequency data for all the samples. The sample with $x = 0.085$ shows an additional hump ~ 2 K, which is not reproducible in other data sets.

$T_c = 5.6$ K for $x = 0.04$ respectively. An exponential function of the form $\Delta\lambda(T) \propto \exp(-\Delta(0)/k_B T)$ did not yield a good fit to our data till $0.3T_c$. The best fit was obtained using a power-law expression of the form $\Delta\lambda(T) = A + BT^n$ (till $0.3T_c$) with the fitting parameter $n \approx 2.4$ and 2.8 for $x = 0.02$ and 0.04 respectively. Naively speaking, for unconventional superconductors having a nodal gap function, $n = 1$ can point to a d -wave like order parameter in the clean limit, while $n = 2$ can be indicative of either a dirty d -wave scenario or a gap function with point nodes. Since the obtained exponent $n \sim 2.6$ is higher than both, perhaps we are not dealing with a gap function that is purely nodal. A similar possibility has been

Figure 7.2: Low- T magnetic penetration depth $\Delta\lambda(\text{\AA})$ for the polycrystalline superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ for $x = 0.02$ (Top plot) and $x = 0.04$ (Bottom plot). Inset shows the respective superconducting transitions over the full temperature range. The red curves are fits to the power-law expression $\Delta\lambda(T) = A + BT^n$, with intercept $A = 0$. Best fits are obtained for $n = 2.41 \pm 0.02$ for $x = 0.02$ and $n = 2.81 \pm 0.02$ for $x = 0.04$ respectively.

suggested for $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ from specific heat measurements, which too found out that for $x \leq 0.04$ data can be fit to a power-law expression with an exponent that is too high for point nodes [9].

It has been shown that for d -wave superconductors having a nodal gap function, the normalized $\rho_s(T)$ varies linearly with temperature even though $\lambda(T)$ can have a quadratic T -dependence [15]. Scientifically speaking, this implies that our measured $\Delta\lambda(T)$ data should be converted to $\rho_s(T)$ to check whether the gap function is truly nodal or not. As already stated, specific heat measurements on the $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ family, as well as on related skutterudite compounds have shown the existence of multi-gap superconductivity with one nodeless gap and one nodal gap. We tried to fit $\rho_s(T)$ for the undoped $\text{PrPt}_4\text{Ge}_{12}$ sample, and for the relatively cleaner samples with doping concentration $x = 0.02$ and 0.04 to the same multi-gap model in order to see if similar signatures of two-gap superconductivity exist in our penetration depth data. For $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0$), we have already shown in Fig. 7.1 that an anomalous feature is seen in $\Delta f(T)$ data for $\text{PrPt}_4\text{Ge}_{12}$ from 0.35 K to ~ 1.3 K. Since we are not yet sure about the origin of this plateau, we have shown $\rho_s(T)$ curve for this particular data set from 8 K down to 1.6 K only. For $x = 0.02$ and 0.04 , full T -range data have been shown. To calculate the theoretical $\rho_s(T)$, we used the expression for superfluid density as shown below [16],

$$\rho_s(T) = 1 + 2 \int_0^\infty \frac{\partial f}{\partial E} d\varepsilon, \quad (7.1)$$

where $f = [\exp(E/k_B T) + 1]^{-1}$ is the Fermi function and $E = [\varepsilon^2 + \Delta(T, \theta)^2]^{1/2}$ is the Bogoliubov quasiparticle energy. Here $\Delta(T, \theta) = \Delta(T)g(\theta)$, with the anisotropy factor $g(\theta) = 1$ for nodeless conventional superconductors. For the nodeless gap, we used an isotropic gap function with $\Delta(T, \theta) = \Delta(T)$ of

the form shown below [17],

$$\Delta(T) = \delta_{sc} k T_c \tanh \left\{ \frac{\pi}{\delta_{sc}} \sqrt{a \left(\frac{\Delta C}{C} \right) \left(\frac{T_c}{T} - 1 \right)} \right\}, \quad (7.2)$$

where $\delta_{sc} = \Delta(0)/k_B T_c$, $a = 2/3$ and $\Delta C/C \equiv \Delta C/\gamma T_c$. For the multi-band analysis, we used the two-gap phenomenological model by Bouquet *et al.* [18], according to which the total superfluid density $\rho_s(T)$ can be expressed as a linear combination of superfluid densities from individual gaps as follows,

$$\rho_s(T) = \rho_{Total}(T) = w \rho_1(T) + (1 - w) \rho_2(T), \quad (7.3)$$

where ρ_i [$i = 1, 2$] represents individual gap superfluid densities of the form shown in Eq. 7.1, with w being a weight factor accounting for the contribution from Gap 1. For the nodal gap, we have used gap anisotropy of the form found in the superfluid ^3He A-phase as shown below,

$$\Delta(T, \theta) = \Delta(T) \sin(\theta). \quad (7.4)$$

Gap anisotropy similar to Eqn. 7.4 has been used for the multi-gap analysis of specific heat data on $\text{PrPt}_4\text{Ge}_{12}$ as well [9]. $\Delta(T)$ for both Gaps 1 and 2 have been considered to be similar to Eq. 7.2. To fit our experimental $\rho_s(T)$ data to the two-gap theoretical model, we used a fixed value of T_c equal to the onset of the superconducting transition as seen in raw $\Delta\lambda(T)$ data: $T_c = 7.7$ K, 6.6 K and 5.6 K for $x = 0$, 0.02 and 0.04 respectively.

The parameters zero- T penetration depth $\lambda_i(0)$, $\Delta_i(0)/k_B T_c$, $(\Delta C/C)_i$, and w have been used as variables to obtain the best fits with minimum mean square error (MSE). Do note that $i = 1$ and 2 denote the nodal and the nodeless gap respectively, with w being the fractional contribution from the nodal gap to overall $\rho_s(T)$. The fits have been shown by red solid curves

Figure 7.3: Normalized superfluid density $\rho_s(T) = \lambda^2(0)/\lambda^2(T)$ extracted from $\Delta\lambda(T)$ for polycrystalline $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$. (a) shows $\rho_s(T)$ for $x = 0$ from 1.6 K onwards, while (b) and (c) show $\rho_s(T)$ curves for $x = 0.02$ and $x = 0.04$ respectively over the full T -range. The solid red curves are fits up-till respective T_c 's to Eq.7.3, using a nodal Gap 1 with anisotropy $g(\theta) = \sin(\theta)$ and a nodeless Gap 2. The obtained fitting parameters have been listed in Table 7.1. The black dashed curve in (a) is the fit to a single nodeless gap with the BCS weak-coupling parameters $\Delta(0)/k_B T_c = 1.76$, $\Delta C/C = 1.43$ with $T_c = 7.7$ K and $\lambda(0) = 1300$ Å.

in Fig. 7.3. The parameters have been listed in Table 7.1, as shown below.

The fitted value of $\lambda(0) = 1300$ Å for $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0$) is in close agreement to $\lambda(0) = 1140$ Å for the same doping, as available from literature [5]. The black dashed curve in Fig. 7.3(a) represents the single-gap

Table 7.1: $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$: fitting parameters

x	$\lambda(0)(\text{\AA})$	$\Delta_1(0)/k_B T_c$	$\Delta_2(0)/k_B T_c$	$(\Delta C/C)_1$	$(\Delta C/C)_2$	w
0	1300 ± 300	3.6 ± 0.3	2.4 ± 0.1	0.73 ± 0.01	1.08 ± 0.03	0.78 ± 0.02
0.02	2800 ± 500	2.6 ± 0.1	1.6 ± 0.4	0.16 ± 0.01	1.65 ± 0.68	0.67 ± 0.01
0.04	3500 ± 900	2.1 ± 0.1	1.8 ± 0.1	0.12 ± 0.01	0.73 ± 0.03	0.47 ± 0.02

fit to $\rho_s(T)$ calculated using the weak-coupling BCS parameters $\delta_{sc} = 1.76$, $\Delta C/C = 1.43$ and $T_c = 7.7$ K. Clearly, the curve does not fit our experimental data for $x = 0$ extracted with $\lambda(0) = 1300$ $\text{\AA}$. The distinctive curvature stretching from ~ 6 K to 7.7 K in Fig. 7.3(a), i.e. smearing of $\rho_s(T)$ near the superconducting transition, can be indicative of multi-gap behavior [19], and hence further strengthens our claim for using two separate band-specific superconducting gaps in the fits. Observing the parameters listed in Table 7.1, we can clearly see that the contribution from the nodal gap decreases monotonically with increase in x , with the weight factor w becoming $< 50\%$ for $x = 0.04$. This is in line with the increase in the value of $\Delta_2(0)/k_B T_c$ for the nodeless gap as x changes from 0.02 to 0.04, while $\Delta_1(0)/k_B T_c$ for the nodal gap continues to decrease. This trend is in agreement to that reported from earlier specific heat measurements [9], albeit the numerical values do not agree perfectly possibly due to the following reasons — (1) the fact that specific heat is more of a bulk measurement than penetration depth which is largely surface-sensitive, the absolute values of $\Delta(0)$ may not align, (2) more importantly, we are clearly dealing with poor/contaminated sample quality — this can directly affect the bulk superconducting ground state being probed. Additionally, there is a linear increase in the fitted values of $\lambda(0)$ as we move away from $x = 0$. This contradicts the behavior of T_c , which decreases with increase in x . This trend is similar to that reported for other doping-based superconductors such as Cu_xTiSe_2 [20], but needs to be verified experimentally.

7.3 Conclusion and Future Work

To conclude, we report magnetic penetration depth $\lambda(T)$ measurements on polycrystalline samples of the filled skutterudite superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ for the Ce concentrations $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 . With the exception of $x = 0.02$ and $x = 0.04$, all other doping concentrations show an anomalous jump in the low- T penetration depth data below 1 K. We have consulted the sample growers regarding the possibility of these jumps being superconducting response from some surface-bound impurities in these samples. We are awaiting their response. The superconducting transition temperatures are in close agreement to that reported from previous thermodynamic and electronic specific heat data. Low- T $\lambda(T)$ data for the cleaner samples with $x = 0.02$ and 0.04 can be fit to a power law exponent $n \sim 2.6$. This value points to an unconventional pairing symmetry of the superconducting order parameter and is probably indicative of a multi-gap scenario in these family of superconductors.

As part of the preliminary analysis, we have shown that for $x = 0, 0.02$ and 0.04 ; superfluid density $\rho_s(T)$ can be fitted nicely to a two-gap model, with one point-nodal gap and one nodeless conventional gap. Our fitting parameters show a gradual reduction in the contribution of the nodal gap to the overall superfluid density with increase in Ce doping, with a transition from a dominant nodal gap to a dominant nodeless gap from $x = 0.02$ to $x = 0.04$. These findings are in line with reports from electronic specific heat measurements by Singh *et al.*, whose work has primarily motivated us to do the multi-band analysis in $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ [9]. Additionally, our findings are in-line with penetration depth data on the related skutterudite $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$, which showed low- T power-law behavior for $x \leq 0.02$ and exponential T -dependence for samples with $x \geq 0.04$, suggesting a crossover from nodal to nodeless superconductivity across $x = 0.03$ [8]. Similar to our data that show an increase in the magnitude of $\Delta_2(0)$ for

the nodeless gap in $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ as x increases from 0.02 to 0.04, the magnitude of $\Delta(0)$ for the nodeless gap in $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$ increased as well — going from weak-coupling ($x = 0.04, 0.06$) to moderate-coupling ($x = 0.08$). Based on previous measurements and also current data provided by us, it would seem that the occurrence of low-lying excitations giving a nodal superconducting phase, which gets suppressed with enhanced dopant substitution is a common phenomenon in many of the filled skutterudite compounds. A systematic investigation of the origin of these low-lying quasiparticle excitations and the role of dopant elements in suppressing TRSB might provide crucial information regarding the pairing symmetry of the heavy-fermion skutterudite family of superconductors.

As an integral part of the future work, we plan to measure more samples from a separate batch of crystals on different doping concentrations, including those which have thus far shown poor data. This should allow us to do more precise analysis of $\rho_s(T)$, and discern the point where superconductivity makes the anticipated transition from the two-gap to the pure nodeless gap scenario. We would additionally perform magnetization measurements, and verify the values of $\lambda(0)$. Preliminary local density approximation calculations in $\text{PrPt}_4\text{Ge}_{12}$ have shown a large DOS at E_F , with a relatively strong coupling constant between the bands [21]. We would seek theoretical collaboration to solve the coupled-Eliashberg equations taking into account the correct interband/intraband coupling, and hence do an even more rigorous analysis to discern whether the observed anisotropy is indeed due to two separate superconducting gaps or due to an effectively single anisotropic gap.

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Chapter 8

Conclusion

In this thesis we present measurements of the temperature-dependence of the penetration depth of a number of unconventional superconductors using a TDO based self-resonating technique. Our analysis quite conclusively shows that penetration depth is a very direct way of probing the symmetry of the order parameter of the superconducting gap — for both single gap as well as multi-gap superconductors. Additionally, we have attempted to probe unconventional features such as: quasiparticle excitations from topologically non-trivial surface states and two-step superconducting transition in a quasi-one-dimensional superconductor using our home-build penetration depth apparatus.

For the Pd-Bi based superconductor α -PdBi₂ ($T_c \approx 1.7$ K), we obtain an exponential dependence of the low- T penetration depth data, suggesting a conventional single-gap moderate-coupling pairing symmetry of the order parameter. The conventional BCS-like pairing scenario is further validated by analyzing the extracted superfluid density, which can be fit to a single-gap BCS model. We also present measurements on the structural isomer β -PdBi₂ ($T_c \approx 4.5$ K) superconductor, for which evidence of topologically protected surface states have been reported experimentally [1]. Results very similar to α -PdBi₂ were obtained, with a moderately

coupled superconducting gap $\Delta(0) \sim 2.0k_B T_c$ for both these materials. This value is very close to that reported from other bulk as well as surface-sensitive measurements [2–5]. Contrary to expectation, we did not observe any power-law temperature-dependence of penetration depth that might originate from the gapless excitations from the surface states. We attribute this to an experimental limitation of the TDO probe.

We have also studied some novel superconducting materials belonging to the family of ternary molybdenum chalcogenides, commonly known as Chevrel phases. The first investigated sample $\text{CsMo}_{12}\text{S}_{14}$ seems to be a promising candidate for multi-band superconductivity with two separate transition temperatures. Both in-plane and out-of-plane penetration depth show a sharp kink ~ 1.2 K, even though the bulk T_c as confirmed by our magnetization measurements and previous resistivity measurements [6] is ~ 7.4 K. Additionally, a broad convex curvature can be observed in the superfluid density curves at ~ 5.5 K. We also present data for temperature dependent lower critical magnetic field $H_{c1}(T)$ for both field orientations, which show kinks at ~ 5.5 K as well. We have used the multi-gap model by Padamsee *et al.* [7], and show that the superfluid density data can be fit using two superconducting gaps — one conventional weak-coupled *s*-wave gap with $T_c \sim 1.2$ K, and one anisotropic *s*-wave gap with $T_c \sim 7.4$ K. We also present electronic band structure calculations that show three bands crossing the Fermi level, and support our claim for multi-band superconductivity.

The other Chevrel phase-based superconductor that we show, is the quasi-one-dimensional material $\text{Tl}_2\text{Mo}_6\text{Se}_6$, which is made up of a weakly-coupled array of (theoretically) infinitely extended $(\text{Mo}_6\text{Se}_6)_\infty$ chains. Penetration depth data clearly show a two-step superconducting transition involving a dimensional crossover from a longitudinally coherent 1D superconducting phase with fluctuations in the temperature range $T_J < T < T_{ons}$, to a globally coherent 3D bulk superconducting phase below T_J , with

$T_{ons} \approx 6.7$ K and $T_J \approx 4.4$ being the onset temperature of superconducting transition and the theoretical Josephson coupling temperature respectively. Based on the transport data, we suggest that transverse Josephson coupling below T_J between the chains can be attributed to a Berezinskii-Kosterlitz-Thouless (BKT) phase transition involving pairing of Josephson vortices and antivortices [8–10]. Our findings are consistent with resistivity data on $\text{Ti}_2\text{Mo}_6\text{Se}_6$ that we present, and also in agreement with electrical transport measurements on the related compound $\text{Na}_2\text{Mo}_6\text{Se}_6$ [11].

The last compound we show in this thesis is the filled skutterudite superconductor $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$. Penetration depth was probed in polycrystalline samples with the Ce doping concentrations $x = 0, 0.02, 0.04, 0.06, 0.07$ and 0.085 . Anomalous jumps are observed in penetration depth data for majority of the samples measured, even though bulk T_c values are consistent with previous measurements [12, 13]. We suspect poor sample quality to be responsible for the observed jumps. For $x = 0.02$ and 0.04 with relatively clean data, low-temperature penetration depth can be fit to a power-law exponent $n > 2$ — suggesting a probable gap function that is not purely nodal. We have used the two-gap model with one nodeless conventional gap and one unconventional gap with point nodes to fit the extracted superfluid density data for $x = 0, 0.02$ and 0.04 . Preliminary data analysis suggests that the contribution from the nodal gap decreases monotonically, while the nodeless gap contribution increases simultaneously with increasing Ce concentration. The multi-gap behavior of $\text{Pr}_{1-x}\text{Ce}_x\text{Pt}_4\text{Ge}_{12}$ has been reported before from magnetization and photoemission spectroscopy measurements [14, 15], while the decrease in nodal contribution with increase in x has been observed in electronic specific heat measurements [12].

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