High precision studies of the electronic properties in high-Tc $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and skutterudite $\text{LaOs}_4\text{Sb}_{12}$ superconductors

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**High precision studies of the electronic properties
in high- T_c $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and skutterudite
 $\text{LaOs}_4\text{Sb}_{12}$ superconductors**

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Abstract

High temperature superconductors (HTS) are not well understood despite intensive research over the past three decades. Recently, the stripe phase which is a form of charge and spin density modulation has received more attention due to its prevalence in these systems. However, the effects of stripes on the electronic properties of HTS have remained elusive, and new experimental results are needed to shed light on this pressing matter.

In this Thesis, we develop several experimental setups and data analysis methods to perform high-precision magneto-transport experiments including electrical resistivity, thermopower, Nernst effect, and other specially designed measurements for temperatures down to 5 K and magnetic fields up to 16 T. These methods enabled us to perform systematic investigations on $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ where stripe correlations are known to be the strongest among HTS families.

Our experimental results demonstrate that in this high- T_c family, the surface and the bulk of the same sample exhibit two distinct and tunable superconducting transition temperatures, with the value at the surface significantly enhanced – up to 64% relative to the bulk of the sample for the materials we studied. Notably, the occurrence of this novel effect coincides with that of the stripe order, suggesting a possible link between the two. The effects of stripes on superconducting fluctuations and quasiparticle transport are further investigated with Nernst effect measurements. Several unusual features are observed which are discussed in the context of superconducting stripes with preferred spatial arrangements.

The latter part of this Thesis focuses on developing a tunnel-diode-oscillator setup for the measurement of magnetic penetration depth on unconventional superconductors. This technique can be optimized for a part-per-billion precision level which makes it very useful in addressing several fundamental problems such as the determination of pairing symmetry. In particular, its compatibility with dilution refrigerator makes it a valuable probe for low- T_c materials such as heavy-fermion systems. During the construction of the setup, we analyzed earlier penetration depth data of skutterudite superconductor $\text{LaOs}_4\text{Sb}_{12}$ in order to obtain guidance on the physics and parameters required for the abovementioned apparatus. Our results indicate multiband s -wave superconductivity in this compound. The finding is further discussed in reference to the unconventional pairing symmetry observed in the closely related material $\text{PrOs}_4\text{Sb}_{12}$.

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1 Introduction

1.1 Superconductivity

1.1.1 Basic Characteristics and Applications

Superconductivity is a phenomenon where certain materials show zero electrical resistance and the ability to expel magnetic fields from their bulk (Fig. 1.1) when cooled below a critical temperature T_c . The first characteristic is a state of perfect conductivity which was first discovered by Heike Kamerlingh Onnes in 1911 [1]. He found that the resistance of mercury abruptly dropped to zero below 4.2 K. The second characteristic implies perfect diamagnetism which is now known as the Meissner effect and was discovered by Meissner and Ochsenfeld in 1933 [2]. The applied field induces a persistent current on the surface which flows to produce an opposing magnetic field. The overall magnetic field can only penetrate a thin surface layer, and is completely excluded from the interior of the material.

Superconductors have found important applications. Strong magnets that provide magnetic fields up to 30 Tesla can be made using superconductor materials such as niobium-titanium (NbTi) or niobium-tin (Nb₃Sn). Compared with their resistive counterparts, superconducting magnets generally consume much less power and produce more stable fields. For these reasons, they are used in magnetic resonance imaging (MRI) machines that requires strong magnetic fields

Figure 1.1: Schematics of the fundamental properties of a superconductor. (a) The electrical resistivity drops to zero below a certain transition temperature T_c due to the onset of a superconducting state. (b) Magnetic fields are excluded from the interior of the superconductor. Perfect diamagnetism occurs due to the opposing field generated by a persistent current flowing on the surface.

for a wide range of applications in medical diagnosis. Another important application of superconductors is the "magnetic levitation" of vehicles (Maglev). Typically, superconducting and normal electromagnets are mounted on the train and its track, respectively. Magnetic repulsions and attractions levitate, guide, and accelerate the train. Due to the levitation, frictions are greatly reduced and the train can attain speed over 500 km/h.

Despite the usefulness, superconductor technologies are not yet commercialized at large scale. One of the main reasons is the high operating cost which involves complicated vacuum and cryogenic systems in order to cool the superconductor materials to liquid Helium temperature. The situation changed due to the discovery of high-temperature superconductor (HTS) in 1986, where T_c of certain families are found to be above the liquid Nitrogen temperature which requires much less operating cost than for conventional superconductors. Besides the technological potentials, the HTS systems provide a paradigm for fundamental

studies of strongly correlated systems. Intensive studies of HTS have been undertaken over the past three decades. However, the highly complicated systems remain not well understood, and represent one of the most challenging problems in modern condensed matter physics.

Before moving to HTS – the main subject of this thesis, we will first revise the BCS theory which provides an excellent microscopic description of conventional superconductivity in metals and alloys. Our subsequent discussions of HTS will be based on certain profound notions inherited from the BCS work.

1.1.2 Cooper Pairs

The pairing of electrons is essential for the occurrence of superconductivity. In 1956, Leon Cooper showed at $T = 0$, the Fermi sea is energetically unstable against the formation of bound electron pairs when the interaction is effectively attractive [3]. The binding occurs as the system tends to achieve a lower energy in the ground state. To see this, consider adding two electrons of energy E_F to the Fermi sea. Suppose they interact attractively with each other, but do not interact with other electrons except via the Pauli-exclusion principle. By the general arguments of Bloch, the lowest-energy state is the one with zero total momentum. This implies that the two electrons must have equal and opposite momentum, which leads to a two-particle wavefunction of the form

$$\psi(r_1, r_2) = \sum g_k e^{ik(r_1 - r_2)} \quad (1.1)$$

where $|g_k|^2$ is the probability of finding the two electrons with momentum k and $-k$. By inserting 1.1 into the Schrödinger equation of the system, the ground state energy E can be shown to be

$$(E - 2\varepsilon_k) g_k = \sum_{k' > k_F} V_{kk'} g_{k'} \quad (1.2)$$

where $V_{kk'}$ is the interaction term which scatters the two electrons from $(k, -k)$ to $(k', -k')$. If one assumes the approximation form

$$V_{kk'} = \begin{cases} -V & , E_F < \varepsilon_k < E_F + \hbar\omega_C \\ 0 & , \text{otherwise} \end{cases} \quad (1.3)$$

where $\hbar\omega_C$ is a cutoff energy for the interaction to be effective, then

$$\begin{aligned} \frac{1}{V} &= \sum_{k' > k_F} \frac{1}{2\varepsilon_k - E} = N(0) \int_{E_F}^{E_F + \hbar\omega_C} \frac{d\varepsilon}{2\varepsilon - E} \\ &= \frac{1}{2} N(0) \ln \left(\frac{2E_F - E + 2\hbar\omega_C}{2E_F - E} \right) \end{aligned} \quad (1.4)$$

where $N(0)$ is the density of state at the Fermi level for one spin orientation. In the weak-coupling limit $N(0)V \ll 1$, this leads to the central result of Cooper's analysis

$$E \approx 2E_F - 2\hbar\omega_c e^{-2/N(0)V} \quad (1.5)$$

which shows that the ground state energy level E is lower than that of two independent electrons at the Fermi level, $2E_F$. This implies that as $T \rightarrow 0$, the electrons have the tendency to form a bound state in order to energetically save the binding energy $\varepsilon = 2\hbar\omega_c e^{-2/N(0)V}$. The formation of such electron pairs, also known as Cooper pairs, leads to the superconducting phase of the system.

The pairing problem is quite general in the sense that the mechanism that leads to the attractive interaction is not specified. Clearly, there needs to be some "glue" to overcome the Coulomb repulsion between the bare electrons. In conventional superconductors such as metals and alloys, the pairing of electrons

typically is mediated through lattice distortion, as first proposed Fröhlich in 1950 [4,5]. In simple terms, the electrons are moving at Fermi velocity $v_F = \hbar k_F / m_e$ which is much faster than the characteristic velocity of the surrounding ions $v_i = v_F m_e / m_i$, where m_e and m_i are the masses of the electron and the ion respectively (Fig.1.2). Suppose an electron enters a region at time $t = 0$ and attracts the surrounding oppositely charged ions. The ions, however, take a finite amount of response time $\tau \sim 2\pi/\omega_D \sim 10^{-13}$ s to polarize themselves, where ω_D is the Debye frequency of the system. By the time this happens, the electron has moved a distance $v_F \times \tau \sim 1000$ Å away. A second electron that passes by the region before the ionic fluctuation relaxed away will experience an attraction that lowers down its energy. This process causes an effective attraction between the two electrons, which may be strong enough to overcome the repulsive Coulomb interaction. Importantly, the latter is largely screened out over the long distance ~ 1000 Å.

Figure 1.2: Phonon mediated electron pairing mechanism. Open and filled circles represent the lattice ions and an electron moving at the Fermi velocity v_F . At $t = 0$ an electron distorts the nearby lattice. Since the ions move at a much lower velocity $v_i < v_F$, the lattice remains distorted after the electron has moved away, creating a concentration of positive charge. At time $t = t_1$ a second electron passes by this distortion and is attracted towards it. The mediation through lattice distortion effectively causes an attractive interaction between the two electrons.

Quantum-mechanically, the attractive interaction is described as an exchange of virtual phonon between the two electrons. The phonon-mediated interaction can

be anisotropic in real space, but spin-independent. This imposes the conditions that the two-particle wavefunction needs to be symmetric with respect to the spatial coordinates and antisymmetric in the spin sector in order to achieve the lowest energy level. As a result, electrons pair up as a singlet state ($k \uparrow, -k \downarrow$) with opposite spin and momentum.

1.1.3 BCS Theory

The first successful microscopic theory of superconductivity was formulated by Bardeen, Cooper, and Schrieffer in 1957 [6]. The theory extends the Cooper pairing to the case of many interacting electrons. Besides, phonon-mediate pairing mechanism is assumed in the theory.

Parameter	Physical Meaning
ε_k	Energy of an electron of momentum $\hbar k$, relative to the Fermi sea
E_k	Excitation energy of a quasi-particle of momentum $\hbar k$, relative to the condensate ground state
Δ	Superconducting energy gap
μ	Fermi energy
$V_{k,k'}$	Interaction term that scatters a pair from the state $(k' \uparrow, -k' \downarrow)$ to $(k \uparrow, -k \downarrow)$
v_k^2	Occupation probability of a Cooper pair of $(k \uparrow, -k \downarrow)$
θ	relative phase of u_k and v_k
$c_{k,\sigma}^+, c_{k,\sigma}$	Creation and annihilation operators for a single-particle of momentum $\hbar k$ and spin σ

Table 1.1: A list of parameters used in the BCS theory.

As pointed out by Cooper in 1956, the Fermi sea is unstable against the formation of bound pairs where there is an effectively attractive interaction. The pairs will condensate until an equilibrium point is reached where the binding energy

for an additional pair become zero. The challenge that arises, then, is to determine the many-body wavefunction that describes the condensate state, which is identical to the superconductor ground state. This is elegantly described by the BCS wavefunction

$$|\text{BCS}\rangle = \prod_k (u_k + e^{i\theta} v_k c_{k,\uparrow}^+ c_{-k,\downarrow}^+) |0\rangle \quad (1.6)$$

The parameters u_k and v_k are real numbers that satisfy $u_k^2 + v_k^2 = 1$. v_k^2 is the probability that the paired state of $(k, -k)$ is full, and u_k^2 the probability that it is empty.

To determine $\{u_k\}$ and $\{v_k\}$, the so-called pairing Hamiltonian

$$\mathcal{H} = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^+ c_{k,\sigma} + \sum_{k,k'} V_{k,k'} c_{k,\uparrow}^+ c_{-k,\downarrow}^+ c_{k',\uparrow} c_{-k',\downarrow} \quad (1.7)$$

is used, which only includes terms that are important for superconductivity (e.g. it omits other terms for unpaired electrons) The first term represents the kinetic energy of individual electrons, with $\varepsilon_k = \hbar^2 k^2 / 2m_e - \mu$. The second term $V_{k,k'}$ represents the interaction that scatters a pair from the state of $(k, -k)$ to the state of $(k', -k')$. The BCS theory then assumes the form of V_{kk} shown in Eqn. 1.3. Further, variational method is applied by setting $\delta \langle \text{BCS} | \mathcal{H} | \text{BCS} \rangle = 0$, which leads to

$$v_k^2 = \frac{1}{2} \left(1 - \frac{\varepsilon_k}{E_k} \right) = \frac{1}{2} \left(1 - \frac{\varepsilon_k}{(\Delta^2 + \varepsilon_k^2)^{1/2}} \right) \quad (1.8)$$

and

$$u_k^2 = 1 - v_k^2 \quad (1.9)$$

where E_k is the excitation energy of a quasi-particle of momentum $\hbar k$, while Δ

is a system parameter which as we shall show shortly, is an energy gap. Fig. 1.3 shows the occupation probability v_k^2 as function of single-particle energy ε_k .

Figure 1.3: Occupation probability v_k^2 for the superconducting (solid) and normal (dashed) states at $T = 0$. Even at absolute zero the momentum distribution of the electrons in a superconductor does not show an abrupt discontinuity at the Fermi level E_k as is the case of a normal metal. Such behavior is due to quantum pairing correlations rather than thermal fluctuations.

The energy level of the many-body ground state is lower than that of the Fermi-sea state (i.e. a normal metal) by an amount of $\frac{1}{2}N(0)\Delta^2(0)$. This is known as the condensation energy at $T = 0$, which also equals to $H_c^2(0)/8\pi$, where $H_c(0)$ is the thermodynamic critical field. The excitations of the system can be described by the one-body energy spectrum

$$E_k = (\varepsilon_k^2 + \Delta^2)^{1/2} \quad (1.10)$$

where E_k is the excitation energy required to create a quasi-particle of momentum $\hbar k$ from the condensate, ε_k is the electron energy relative to the Fermi sea, and Δ is the energy gap that separates the ground state from the continuum of

excited states. The energy gap is given by

$$\Delta = \frac{\hbar\omega}{\sinh [1/N(0)V]} \quad (1.11)$$

or in the weak-coupling limit $N(0)V \ll 1$,

$$\Delta \approx 2\hbar\omega_c e^{-2/N(0)V} \quad (1.12)$$

Intuitively, one can interpret the energy spectrum as follows. ε_k is the energy of an electron in state k . After the pairing is "switched on", it is modified to E_k by the inclusion of the energy gap Δ . Because of the modifications, one speaks of a *quasi-particle* instead of electron. The energy gap to excitations leads to the zero-resistance property, since small excitations due to scattering of electrons are forbidden.

Figure 1.4: The quasi-particle excitation energy E_k as a function of ε_k . The latter is the energy of an independent electron (relative to the Fermi level) before the pairing interaction is switched on. An energy gap Δ exists in the spectrum, which is responsible for many of the superconducting properties.

1.2 High- T_c Superconductors

1.2.1 Discoveries

The 1986 discovery of the copper-oxide La-Ba-Cu-O by J.G.Bednorz and K. A. Muller [7] stimulated an explosion of research activities on superconductivity. More excitements were stirred a year later when the Y-Ba-Cu-O system was synthesized by Chu and co-workers, which showed a much higher $T_c \sim 93$ K [8]. Their T_c exceed the limit put forward by conventional BCS theory, hence were given the name high- T_c superconductors. Shortly afterwards came the reports of Bi-Sr-Ca-Cu-O and Tl-Sr-Ca-Cu-O systems with $T_c \sim 105$ K and ~ 120 K, respectively [9–13]. In 1993, $T_c \sim 133$ K was discovered in the Hg-Ba-Ca-Cu-O system $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+d}$ [14], which can be further increased to ~ 164 K under hydrostatic pressure [15, 16]. The Hg-based system has remained the record holder of T_c over the last twenty years.

1.2.2 Copper-Oxide Plane

All HTS have layered perovskite structure, with the common structural unit of CuO_2 plane formed by Cu-O bonds along the [001] and [010] directions. Fig. 1.5 shows the crystallographic structure of La_2CuO_4 which is a parent compound of HTS. The lattice parameters of the tetragonal system are $a = b = 3.78$ Å and $c = 13.2$ Å [17]. The CuO_2 plane is a two-dimensional Mott insulator with long-range AFM order. The oxidation state of La and O ions in the material are +3 and -2, respectively. Therefore, the Cu ion is in the +2 state ($3d^9$ configuration) with one unpaired electron. According to band theory, the conduction band is half-filled and must be metallic. However, strong on-site Coulomb repulsions between electrons make double occupancy of a Cu site energetically costly, and the hopping of electrons is suppressed. In addition, virtual hopping of electrons

to the adjacent O ions produces antiferromagnetic super-exchange interaction between the neighboring Cu ions. This leads to a long-range AFM ordering of Cu spins below the Néel temperature $T_N \approx 325$ K [18–21].

Figure 1.5: Crystallographic structure of La_2CuO_4 (left panel). The lattice parameters are $a = b = 3.78$ Å and $c = 13.2$ Å. Copper-oxide plane with doped holes (right panel).

1.2.3 Doping the Mott Insulator

Holes can be introduced to the CuO_2 plane by substituting divalent rare-earth ions (e.g. Sr^{2+} or Ba^{2+}) for the trivalent La^{3+} ion. The introduction of holes drastically reduce the Néel temperature T_N and suppress the long-range magnetic order at $x \approx 0.02$. However, short-range magnetic correlations persist to the ground states of higher doping levels including the superconducting phase.

For $x < 0.05$, commensurate magnetic correlations (static) are observed with a correlation length of the order of the average separation between the holes [22–26]. The spin-spin correlation length, $\xi \approx 3.8/\sqrt{x}$ [22] decreases rapidly with increasing the hole concentration, indicating the formation of AFM domains. For

$x > 0.05$, magnetic fluctuations (dynamic) that are *incommensurate* with the lattice are observed [27–30]. The correlation length is larger than the separation between the holes, and only weakly depends on the concentration of the latter [27].

Figure 1.6: Schematic phase diagram of hole-doped HTS. The antiferromagnetic (AF), spin glass (SG), and superconducting (SC) states develop on increasing the hole concentration p . Dashed line indicates that the SG phase persists up to $p \sim 0.19$ which is inside the SC phase. Pseudogap (PG), non-Fermi-liquid (non-FL), and Fermi-liquid (FL) behaviors are observed in the high-temperature regimes shown in the diagram. Around $1/8$ doping, T_c is suppressed which causes a dip in the SC dome as indicated by the green arrow. The $1/8$ anomaly is due to the onset of stripe order.

The added holes provide vacancies for the electron hopping. For $x < 0.05$, the system shows metallic behaviors ($dR/dT > 0$) at moderate temperatures but eventually crosses over to an insulating ($dR/dT < 0$) ground state as $T \rightarrow 0$ [31]. The insulating behaviors have been attributed to the short-range freezing of holes at low temperature. For $x > 0.05$, superconductivity occurs, with T_c showing a dome shape in the $T - x$ phase diagram which demises at $x \approx 0.27$. The

highest T_c occurs at optimal doping $x_{opt} \approx 0.16$. Besides, there exists a critical doping $x_c \approx 0.19$ at which many electronic properties such as the low-energy spin fluctuations [32], the quasiparticle spectrum [33], the pair condensation energy [33, 34], and the superfluid density [35, 36] show abrupt changes. In particular, the superfluid density is the highest at this point. Since the changes occur at $T = 0$, this has been interpreted as a quantum critical point.

Strong correlations in the underdoped side of the superconducting dome cause electronic heterogeneity [37, 38] and glassy behaviors [39]. In several HTS families, a suppression of T_c occurs at $x = 1/8$. The $1/8$ anomaly is caused by the onset of ‘stripe phase’ which is a form of charge- and spin-density-wave. In the next section, we will further elaborate on the stripe phase, and discuss its role on high- T_c superconductivity.

1.3 Stripe Phase

1.3.1 Strong Interactions

Soon after the discovery of HTS, Hubbard model analysis predicted the emergence of "stripe phase" from the hole-doped Mott insulator [40–42]. The phenomenon is due to strong interactions in the Mott system. The energy level is lowered if neighboring spins are antiferromagnetically aligned. Consequently, the antiferromagnetic background has the tendency to expel holes [43] to form hole-rich and hole-poor regions [44]. On the other hand, the long-range Coulomb interaction between holes tends to generate local charge inhomogeneity which leads to the confinement of mobile holes in one-dimensional stripes [45, 46]. As a result, the holes self-segregate into unidirectional stripes that form antiphase boundaries between hole-poor antiferromagnetic domains. The stripe phase is the most pronounced at hole concentration $x = 1/8$, where every eighth electron

is removed from the system. This produces 4-unit-cell-wide antiferromagnetic domains that behave like narrow ribbons of Mott insulator, and 1-unit-cell-wide charge lines along which conductivity occurs.

1.3.2 Experimental Observations

The first evidence of stripe phase was discovered in $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x = 0.12$) by Tranquada and co-workers [47]. Through elastic neutron scattering, they observed magnetic superlattice peaks at $(\frac{1}{2} \pm \varepsilon, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2} \pm \varepsilon)$ in the $(kh0)$ zone of reciprocal space (i.e. the copper-oxide planes were probed), with $\varepsilon \approx x = 0.12$. The wave vector is specified in terms of the reciprocal lattice unit $2\pi/a$. Also found were charge-related superlattice peaks at positions $(0, 2 \pm 2\varepsilon)$ and $(\pm 2\varepsilon, 2)$. These results are consistent with neutron reflections off the magnetic structure shown in Fig. 1.7, with uni-directional charge stripes running along the CuO direction separated by four lattice constants a . The magnetic moments on Cu atoms are antiferromagnetically aligned, and the hole density on the stripe is 0.5 per Cu site.

Figure 1.7: Schematic of the stripe phase in a CuO_2 plane with hole density $p = 1/8$. Oxygen sites which surround the Cu sites are omitted for clarity - only the Cu sites are shown. Arrows indicate the spin ordering, which rotates by a π phase across the domain wall. Holes (red circles) are located at anti-phase domain walls. The hole density on an individual stripe is 0.5 per Cu site.

The stripe phase has been subsequently observed in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [17, 48–51] and $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ [52–55]. In these systems, it is believed that the stripes are stabilized by the low temperature tetragonal (LTT) structure which onsets

Figure 1.8: Superlattice peaks observed in $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x = 0.12$), taken from Ref [47]. a, Diagram of the $(kh0)$ zone of reciprocal space. Solid circles indicate the spin and charge superlattice peaks, whereas open circles indicate Bragg peaks for the LTT crystal structure. b, Scan along $(\frac{1}{2}, \frac{1}{2} + q, 0)$ through the superlattice peaks at $(\frac{1}{2}, \frac{1}{2} \pm \varepsilon, 0)$ which were measured with a neutron energy of 13.9 meV. c, Scan along $(0, 2 + q, 0)$ through the $(0, 2 - 2\varepsilon, 0)$ peak using 14.7 meV neutrons.

just above the charge-stripe ordering temperature [56–58]. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, stripes were observed by *inelastic* neutron scattering [27–30]. The magnetic peaks are characterized by wave vectors of similar position in the k -space, namely $(\frac{1}{2} \pm \varepsilon, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2} \pm \varepsilon)$ with $\varepsilon \approx x$. However, the scattering is inelastic, which means a finite amount of energy ($\sim \text{eV}$) is required to excite the superlattice peaks. This indicates that the stripes in this system are dynamic or fluctuating.

1.3.3 Stripes and Superconductivity

An important question that arises is whether the stripe phase is relevant to the mechanism of high- T_c superconductivity. It is generally understood that *static*

stripes destroy the long-range order of superconductivity. In HTS system where the stripes are pinned, such as in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [17,59] and $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ [56,60], a strong suppression on T_c is observed around the doping level $x = 1/8$. The suppression causes a dip in the T_c dome, which leads to a local minimum with $T_c < 5$ K (e.g. Fig. 1.10). In other HTS systems where the stripes are dynamic, such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ [61–65], a plateau is observed instead near the 1/8 doping.

Figure 1.9: The incommensurability δ of low-energy spin fluctuations as a function of hole concentration p in $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+y}$ (Bi2201), $\text{La}_2\text{Sr}_x\text{CuO}_4$ (LSCO), and $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (YBCO). A linear dependence $\delta \sim p$ is observed below the 1/8 doping. Taken from Ref. [66].

While the 1/8-anomaly suggests that the stripe phase has adverse effects on superconductivity, there are experimental clues indicating *dynamic* stripes may help superconductivity. A remarkable linear relationship (Fig. 1.9) between the incommensurability δ and the hole concentration p is observed in $\text{La}_2\text{Sr}_x\text{CuO}_4$ [67–69], $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ [70, 71], and $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+y}$ [66]. Since δ means the distance between the stripes and T_c is linearly proportional to p in the underdoped regime, the results suggest that T_c gets enhanced as the stripes move closer to one another.

There have been theoretical efforts to investigate the role of stripes in high- T_c superconductivity. Emery and co-workers proposed a pairing mechanism based on spin-gap proximity effects in the stripe phase [72, 73]. It has been suggested that the spatial confinement of the Mott-insulating antiferromagnetic domains by charge stripes induces a spin gap in the regions [74]. Through pair hopping between the two locally distinct regions, i.e. the stripes and the domains, the mobile holes acquire a local pairing gap which causes superconducting correlations on individual charge stripes. At lower temperatures, global superconducting phase coherence is achieved due to inter-stripe Josephson coupling.

1.4 $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$

Due to their strong interplay, understanding the role of stripes in high- T_c superconductivity has been one of the most important problems in HTS research [75–78]. From the experimental point of view, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO) is the ideal system for the investigations. This is because stripe correlations in this system are much stronger compared to other HTS systems in terms of amplitude and correlation length [79]. Despite being the first discovered HTS, this system is not well characterized near $x = 1/8$ where the stripe order is the most pronounced. This is mainly due to the difficulty of growing single crystals of good quality and sufficiently large size for this particular doping range [80, 81]. Traveling-solvent-floating-zone (TSFZ) growth techniques have been attempted to improve the crystal quality [49, 80, 82–84]. Neutron scattering experiments on large piece of single crystals were performed in 2004 by Fujita and co-workers, providing the first direct evidence of stripe phase in this system. Notably, this is about 20 years after the initial discovery of the material [7].

Fig. 1.10 shows the phase diagram of LBCO. The stripe phase occurs over a doping range around $x = 1/8$. A series of transitions take place before the onset

Figure 1.10: The phase diagram of LBCO. The onset temperatures of bulk superconductivity (T_c), charge stripe order (T_{CO}), spin stripe order (T_{SO}), and structural transition (T_d) are indicated. Solid and dashed lines are guides to the eye. Taken from Ref. [17]

of superconductivity. The system first undergoes a structural transition from low-temperature-orthorhombic (LTO) to low-temperature-tetragonal (LTT) at T_d which is immediately followed by the charge-stripe ordering at $T_{CO} \lesssim T_d$ [85–87]. The spin stripe ordering occurs at a lower temperature T_{SO} , prior to the onset of bulk superconductivity at T_c . On superconducting transition, the system undergoes another structural transition to the low-temperature less-orthorhombic (LTLO) phase. The suppression of superconductivity is strongest at $x \approx 1/8$, with $T_c \approx 4$ K.

In this thesis, we performed a range of systematic characterizations on the electrical and thermoelectric transport properties of LBCO. High quality single crystals over the doping range $0.076 < x < 0.139$ were prepared by our collaborators at AIST, Japan, with the recently developed laser-diode-heated floating zone (LDFZ) growth method [81]. The use of laser beams delivers a more focused and homogeneous heating than the conventional TSFZ that uses halogen lamps. Consequently, incongruently melting materials such as LBCO can be grown with high quality, and reliable results of transport measurements can be obtained.

2 Methods

This chapter introduces the experimental methods employed in this thesis. The growth technique for our samples of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ is described. We discuss the different voltage-contact configurations used to probe the ab-plane surface and the bulk of the same sample. Electrical and thermoelectric transport measurements over the temperature range of 5-300 K are performed with homebuilt probes which provide high signal-to-noise level and temperature stability, both of which are important for low signal measurements. A custom-made superconducting magnet supplies fields up to 16 Tesla for magneto-transport experiments. The use of commercial facilities such as the Quantum Design PPMS, MPMS, and Helium recovery plant are described.

2.1 Crystal Growth of LBCO

High-quality single crystals of cuprates, such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, can be grown with the traveling-solvent floating-zone (TSFZ) method [88]. However, it is difficult to grow $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ single crystals with this technique due to the low solubility of Ba atoms [82]. Ba compounds such as $\text{La}_4\text{BaCu}_5\text{O}_{13}$ and $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ form in the feed rod, which affect the chemical homogeneity of the grown crystals [80]. Several steps have been taken to improve the growth process of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, including the use of reduced atmosphere which minimizes impurity phases in the crystals.

Despite progress, growth of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ single crystals remains challenging with the conventional TSFZ method. A main problem is the use of halogen lamps for the heating. The focusing of light with ellipsoidal mirrors is often broad and can not produce a sharp temperature gradient at the solid-liquid interface. This causes the melt to spill over to the crystal making the growth unstable. Furthermore, the growth process is sensitive to crystal misalignment which often causes inhomogeneous heating on the sample. For example, when the sample is decentered from the growth axis, the side that is closer to the lamps receives a higher intensity of light than the opposite side.

Figure 2.1: Schematic of the laser-diode-heated floating zone (LDFZ) method. The sample is irradiated with homogeneous laser beams of rectangular cross-section. The sharp edge of beam produces a steep temperature gradient at the solid-liquid interface, which is essential to prevent the flow of molten component to the crystal. The beam size is large to ensure an uniform heating over the entire sample. Taken from Ref. [81].

Recently, Dr. Toshimitsu Ito from the National Institute of Advanced Industrial Science and Technology (AIST), Japan developed the laser-diode-heated floating zone (LDFZ) method which employs laser beams as the heating source [81]. Homogenous laser beams of rectangular cross-section are irradiated to the molten zone through the use of light pipes. The sharp cutoff of the beam enforces a steep temperature gradient at the solid-liquid interface which stabilize the crystal growth. The beam width is designed to be larger than the size of the crystal. This ensures uniform heating on the sample and makes the growth process less sensitive to crystal misalignment than the conventional TSFZ method.

In this Thesis, we measured $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ single crystals grown with the LDFZ method. The well focused and homogeneous laser heating produces samples with exceptionally high degree of homogeneity, as we will demonstrate in chapters 3 & 4 through a range of measurements.

2.2 Transport Measurements

This section describes our experimental setups of resistivity, thermopower, and Nernst effect measurements. Particular attention is placed on the use of different contact configurations in the experiments which enabled our finding of surface-enhanced superconductivity (chapter 3). The designs and uses of high-performance homebuilt probes and commercial Quantum Design PPMS are described.

2.2.1 Experimental Setups

The electronic instruments and cryogenic equipment used in this project are fairly standard for a low-temperature research laboratory. Several customizations on the experimental setup, however, are implemented to achieve the optimal results for transport measurements.

Fig. 2.2 shows the schematic of the experimental setup of transport measurements in a custom-made superconducting magnet (Janis Research Company). The magnet supplies strong fields to the limit of 16 Tesla. Measurements at zero field are carried out in another Helium dewar with the same set of apparatus. Photographs for the two cases are shown in Fig. 2.3.

A homebuilt probe is inserted into the superconducting magnet filled with liquid Helium. The sample is mounted inside the vacuum can of the probe, and is positioned to the field center of the magnet. The liquid Helium thermally anchors

the vacuum can at 4.2 K, which in turn provides cryogenic cooling to the sample through solid conduction (e.g. copper braids). In a typical run, the sample space is evacuated to a pressure $\lesssim 1 \times 10^{-6}$ mbar in order to minimize heat exchanges between the sample and the environment.

Figure 2.2: Schematic of the experimental setup of transport measurements in a superconducting magnet. The homebuilt probe is loaded into the magnet through a sliding-seal adaptor. Nitrogen and vacuum jackets provide thermal insulation to the chamber. The sample is positioned to the center of the magnet solenoid which is heat sunk in liquid Helium. Two nanovoltmeters, Agilent 34420A #1 and #2, are used to measure the voltage of sample and thermocouple, respectively. Dc source Yokogawa 7651 supplies current to the sample during an electrical transport measurement, or to the $1\text{k}\Omega$ heater mounted on the sample during a thermoelectric transport measurement. Sample temperature is monitored and stabilized by temperature controller Lakeshore 336. Data acquisition is automated by Labview programs.

The temperature of the sample is monitored with a calibrated cernox sensor and stabilized by temperature controller Lakeshore 336. Both the sensor and sample are mounted next to each other on a sapphire block which is a good

thermal conductor. The temperature range 5-300 K can be readily accessed with a stability of 1 mK at low temperatures. Normally, data is taken after the sample temperature and magnetic field are stabilized to the setpoints. This avoids errors in temperature reading due to a thermal inequilibrium between the sensor and the sample.

Figure 2.3: Photographs of the experimental setup of transport measurements. (a) The “Nernst probe” is mounted on the custom-made 16T superconducting magnet. The bellows are connected to vacuum pumps located in the pump room (not shown). A Helium reliquefier Cryomech PT410 is mounted next to the magnet to recover the Helium boil-off of the experiment. (b) The “zero-field probe” is mounted on a Helium dewar. When magnetic field is not required, configuration (b) is preferably used for a lower Helium consumption. Details of the two homebuilt probes are given in sec. 2.2.2.

A set of nanovoltmeters Agilent 34420A and dc source Yokogawa 7651 is used for both dc electrical and thermoelectric measurements. In the former case, the dc source supplies excitation currents typically $0.1 - 5$ mA to the sample. The induced voltage is measured with the nanovoltmeter which has a resolution better than ± 3 nV. In the case of thermoelectric measurements, two nanovoltmeters are used to measure the thermoelectric signal, and the thermocouple signal which determines the temperature gradient. The dc source supplies a small current

$\sim 0.1 - 1$ mA to the $1\text{k}\Omega$ heater mounted on the sample to generate a sizable temperature gradient.

In a typical field measurement, the Nernst probe is loaded into the custom-made 16T superconducting magnet. Helium boil-off from the magnet is collected for recovery. To further improve the Helium recovery, we load a portable Helium reliquefier (Cryomech PT410) on the magnet. Zero-field measurements are typically done with the zero-field probe in a small Helium dewar.

Sample Mounting and Contacts

Consider a high- T_c copper-oxide with the crystal c -axis pointing along the vertical direction. Due to its strongly-layered structure, in a transport measurement, placing the voltage contacts on the top *surface* or on the side of the sample is not equivalent. In the former case the voltage contacts sense only a few copper-oxide layers at the surface, whereas an averaging over the large collection of bulk layers is sensed in the latter case. In this work, we use the two different voltage-contact configurations to probe and differentiate between the transport properties of the ab -plane surface and the bulk.

Figure 2.4: Schematic contact configurations for the resistivity measurement.

Current I is applied through the cross-sectional area A of the sample. Voltage contacts spaced at a distance L are placed on the top of the sample (left panel) to measure the voltage drop V_s on the surface, or on the side of the sample (right panel) to measure the voltage drop V_{ab} in the bulk. The surface and bulk resistivities are calculated as $\rho_s = -V_s/I \times A/L$ and $\rho_{ab} = -V_{ab}/I \times A/L$, respectively.

Fig. 2.4 shows the schematics of the two voltage-contact configurations for electrical resistivity and I-V characteristics measurements. Electrical contacts on samples were made with silver paste DuPont 6838 baked in high purity O_2 -flow environment at 450 °C for 10 minutes. Low contact resistance $< 0.5 \Omega$ is typically achieved which significantly reduces the measurement noise. For electrical transport measurements, the sample is mounted on a sapphire plate with GE varnish. The entire set up is then heat sunk to the sample stage to ensure temperature stability. Excitation currents typically 0.1 – 5 mA are used for resistivity measurements. The low current ensures the validity of Ohm's law. A much broader range of currents, 0.1 – 100 mA, is used to probe the non-linear regime of the IV characteristics. A typically small but unavoidable offset in the IV curve can be removed by averaging the signal between positive and negative bias.

Figure 2.5: Schematic contact configurations for the thermopower measurement. One end of the sample is thermally anchored to the sample stage at temperature T . Heating power of typically ~ 1 mW was generated by a $1k\Omega$ film heater and applied to the other end of the sample. Voltage contacts spaced at a distance L were placed on the top of the sample (left panel) to measure the voltage drop V_s on the surface, or on the side of the sample (right panel) to measure the voltage drop V_{ab} in the bulk. Temperature difference ΔT between the voltage contacts was measured by a pair of type-E differential thermocouple wires of diameter $25 \mu m$. The surface and bulk thermopowers were calculated as $S_s = -V_s/\Delta T$ and $S_{ab} = -V_{ab}/\Delta T$, respectively.

The thermopower is the electric field that develops along the longitudinal directions in response to an applied temperature gradient. When a magnetic field

is applied along the vertical direction, the electric field that develops along the transverse direction is known as the Nernst effect. A detailed introduction to the Nernst effect in high- T_c cuprates is given in chapter 4.

Figure 2.6: Schematic contact configuration for the Nernst effect measurement.

$H||\hat{z}$ was applied along the crystal c-axis. Heat was applied with the same heating configuration used for thermopower measurement. Voltage contacts spaced at a distance $W||\hat{y}$ were placed on the top of the sample (left panel) to measure the voltage drop V_s on the surface, or on the side of the sample (right panel) to measure the voltage drop V_{ab} in the bulk. Temperature difference ΔT was measured by a pair of type-E differential thermocouple wires spaced at $L||\hat{x}$ on the same side with the voltage contacts. The surface and bulk Nernst coefficients are calculated as $\nu_s = V_s/W \times L/\Delta T \times 1/H$ and $\nu_{ab} = V_{ab}/W \times L/\Delta T \times 1/H$, respectively. The sign of ν_s and ν_{ab} is defined by the vortex-flow convention for the Nernst effect. To remove the unavoidable pick-up of thermopower (field-symmetric) due to misalignment of voltage contacts, H was applied in both directions so that only the field-antisymmetric part of the data is taken.

The contact configurations for the two measurements are shown in Fig. 2.5 and Fig. 2.6, respectively. The contacts were made with the same annealing procedure for electrical transport. One end of the sample is glued with silver paste DuPont 6838 to a sapphire block that is in turn mounted on the sample stage. To achieve good thermal contact, the silver paste is further heat treated using the same process for electrodes. A Cernox sensor is mounted on the sapphire to monitor the base temperature of the sample. A 1k film heater is attached to the other end of the sample to generate a temperature gradient, which is measured by a pair of type-E thermocouple wires ($\phi = 25 \mu\text{m}$). The resistance

of the 1k heater remains constant over a broad range of magnetic fields. Fine gauge silver and chromel wires ($\phi = 25 \mu\text{m}$) are used as leads from the sample stage to the voltage contacts and heater, respectively. Typically in our experiments, low-noise dc current $\sim 0.1\text{--}1 \text{ mA}$ is supplied to the $1\text{k}\Omega$ heater to generate a temperature gradient of $\sim 0.1 \text{ K/mm}$.

Thermocouple

We use *differential* thermocouple to measure the temperature difference ΔT across the sample in a thermoelectric transport measurement. Type-E thermocouple, which is formed by constantan and chromel wires, is used for its relatively higher sensitivity to a temperature gradient compared to other types of thermocouple. The corresponding Seebeck coefficient S_E is the difference in the thermopower of the two metals and can be expressed as (in units of $\mu\text{V/K}$) [89–91]

$$S_E = \sum_{i=0}^{12} (i+1) C_i t^i \quad (2.1)$$

where t is the temperature in Celsius ($^{\circ}\text{C}$), and parameters C_i the fitting coefficients whose values are listed in Tab. 2.1. Fig. 2.7 plots S_E over the temperature range $0 - 300 \text{ K}$. The large values of S_E above the liquid Helium temperature ($\sim \mu\text{V/K}$) makes it the ideal choice for our measurements.

The thermocouple wires are joined directly with resistance spot welding. This avoids adding other metal to the joint, for example due to soldering or cold gluing with silver paste. Chromel and Constantan wires were laid to cross on a copper stage which was connected to the positive electrode of a spot welder Orion PA230. A thick copper wire ($\phi = 1 \text{ mm}$) was connected to the negative electrode as the welder tip. The tip has a rounded shape that is made by sand paper polishing. Successful welding is made when the tip presses precisely on

Figure 2.7: Temperature dependence of the Seebeck coefficient of type-E thermocouple, S_E . Inset shows the schematic of a differential thermocouple formed by metal wires A and B. The Seebeck coefficient of the thermocouple is the difference in the thermopower of the two metals. Let T_1 and T_2 be the temperature sensed by the two A-B junctions, and T_0 the base temperature which in our setup is the same as the sample temperature. A thermoelectric voltage $V = S_E \Delta T$, where $\Delta T = T_1 - T_2$ will develop across the thermocouple and measured by a voltmeter.

the wires joint, which requires some trial-and-error efforts. Ohmic contact of the joint in cryogenic environment is confirmed by I-V curve measurement at liquid Nitrogen temperature.

Helium Recovery

Due to the expensive cost of liquid Helium, it is necessary to recover the Helium boil-off from experiments. It is also important to ensure unperturbed supply of liquid Helium over a few months. Measurements performed with high magnetic fields, such as the Nernst effect, often require a long experiment time and therefore need to be supported by the Helium recovery system.

We use a Helium reliquefier Cryomech PT410 to provide immediate recovery

C_i	$t \leq 0$	$t \geq 0$
C_0	58.665508708	58.665508710
C_1	0.045410977124	4.5032275582e-2
C_2	-0.00077998048686	2.8908407212e-5
C_3	-2.5800160843e-5	-3.3056896652e-7
C_4	-5.9452583057e-7	6.5024403270e-10
C_5	-9.3214058667e-9	-1.9197495504e-13
C_6	-1.0287605534e-10	-1.2536600497e-15
C_7	-8.0370123621e-13	2.1489217569e-18
C_8	-4.3979497391e-15	-1.4388041782e-21
C_9	-1.6414776355e-17	3.5960899481e-25
C_{10}	-3.9673619516e-20	0
C_{11}	-5.5827328721e-23	0
C_{12}	-3.4657842013e-26	0

Table 2.1: Parameters C_i for the Seebeck coefficient of Type-E thermocouple. Taken from Ref. [91].

for the magnet (Fig. 2.3). The PT410 can produce 21 liters of liquid Helium a day. A more advanced Cryomech LHeP18 liquid Helium plant is also used. In a typical operation, the Helium boil-off is first collected in the gas bag. When the latter reaches its maximum capacity which is nearly 8.5 m^3 , a laser-based automation mechanism switches on the compressor in order to transfer the gas into the high pressure cylinders. The cylinders constantly supply Helium gas at 5 atm to the pulse-tube cryo-refrigerator PT410 through gas purifier. The end product is liquid Helium of 99.99% purity in the storage dewar.

Figure 2.8: Photograph of the Cryomech liquid Helium plant LHeP18 in our laboratory. (a) PT410 mounted on a storage dewar, (b) PT410 controller, (c) gas purifier (d) chiller water, (e) high pressure cylinders, (f) compressor, (g) Gas bag.

2.2.2 Homebuilt Probes

Designs and Fabrications

A transport probe is specially designed, built, and optimized for measurements that require magnetic field. We name this the “Nernst probe”. The probe is equipped with a Helium pot made of oxygen-free-high-conductivity (OFHC) copper, which can be continuously fed with liquid Helium from outside the probe. Typically, the liquid Helium comes from the main bath contained in the magnet dewar. The Helium pot is the cold finger of the probe. It has a base temperature of 4.3 K, which can be further brought down to ~ 2 K when pumped. The sample space is enclosed in a vacuum can made of brass, and is evacuated to a high vacuum level ($\lesssim 1 \times 10^{-6}$ mbar).

Twisted pairs of OFHC copper wires ($\phi = 50 \mu\text{m}$) are used as sample leads for voltage measurement and current supply. The twisting of ~ 1 pitch/mm mini-

mizes interference and pickup of rf noise among the wires. On the probe head, the sample leads are mechanically clamped to the signal cables from nanovoltmeters. Soldering is not used at room temperature to avoid thermal emf that commonly occurs at the joint of two dissimilar metals. A “nanovolt connector box” is specially designed to provide rf shielding and mechanical protection for

Figure 2.9: Schematics of the Nernst probe. Left panel shows the homebuilt probe. A Helium pot is incorporated which serves as the cold finger of the cryostat. The sample stage is attached to it through a thermal link composed of G10 spacers and a OFHC copper block which is known as the pre-sample stage. The entire setup is enclosed in a vacuum can. On the top of the probe are pump ports for the sample space and Helium pot, wire feedthrough, and the nanovolt connector box. Right panel shows a magnified view of the sample stage. The black and red lines represent the leads to temperature sensors and heaters. The blue line represents the leads to the sample and thermocouple. These wires are heat sunk on the extruded wall of the sample stage before approaching the sample and sensor. Black arrow indicates the location where the sample is mounted. Blue arrow indicates the locations of BeO chips to which the leads are soldered. The sample is enclosed in a thin-walled thermal radiation shield.

the joints. Twisted pairs of phosphor bronze wires ($\phi = 50 \mu\text{m}$) are used as leads for temperature sensors and heaters.

Inside the probe, *all* the leads are heat sunk to copper bobbins which are mechanically clamped to the 4K flange, and subsequently to the Helium pot. Further heat-sinking takes place at the sample stage which is also made of OFHC copper. All the leads that go into the sample stage are first wound and heat sunk around the thin-walled extruded shoulder (1.0 mm thickness) of the stage. After that, they are further heat sunk to beryllium oxide (BeO) chips mounted on the sample stage. The BeO chips thermally anchor the lead terminals to a common point, namely the stage temperature, thus minimizing thermal emf across the soldered joints. These multiple steps of heat sinking ensure the lowest attainable base temperature and thermal noise for the measurements.

Figure 2.10: Photographs of the Nernst probe. (a) the probe with its vacuum can attached, (b) a typical configuration for sample mounting, (c) the thin-walled ($\phi = 0.5 \text{ mm}$) thermal radiation shield, (d) the sample stage with a $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ crystal mounted for Nernst effect measurements.

The sample may develop a non-uniform temperature profile due to heat exchange

between the surroundings, such as the vacuum can which is held at 4.2 K. This causes background thermal emf which strongly affects the measurement accuracy. To suppress the exchange gas, the sample space is pumped to a high vacuum level ($< 1 \times 10^{-6}$ mbar). Furthermore, the sample is enclosed in a thermal radiation shield which is a thin-walled ($\phi = 0.5$ mm) OFHC copper can thermally anchored to the stage temperature. With these implementations, the background thermal emf is reduced to a marginal level, and eventually removed through differential measurements. Specifically, we take the difference in the voltage drop $\Delta V = V_1 - V_0$ as the raw signal, where V_0 and V_1 are respectively the voltage drops measured before and after the excitation current or temperature gradient is applied. Typically, a measurement noise level $< \pm 3$ nV is achieved. An example of raw data taken in Nernst measurement is shown in Fig. 2.11, which demonstrates the low noise condition.

Figure 2.11: The measured Nernst voltage as a function of time, taken during a temperature step. The signal noise is 5 nV, which is within the range of ± 3 nV.

Figure 2.12: Schematics of the zero-field probe. Left panel shows the home-built probe. The probe has a sliding mechanism which allows a gradual insertion into Helium dewars. It is made sufficiently long to access the bottom of standard storage dewars. On the top of the probe are pump port for the sample space, wire feedthrough, and the nanovolt connector box. The sample space is enclosed in a vacuum can. Right panel shows the magnified view of the sample stage. It is attached to the cold finger through a G10 spacer. The black and red lines represent the leads to temperature sensors and heaters. The blue line represents the leads to sample and thermocouple. These wires are heat sunk on the cold finger and the extruded wall of the sample stage. Black arrow indicates the location where the sample is mounted. Blue arrow indicates the locations of BeO chips to which the leads are soldered. The sample is enclosed in a thin-walled thermal radiation shield.

The sample stage is attached to the Helium pot through a thermal link which is composed of two G10 spacers bound together through a “pre-sample stage” made of OFHC copper. G10 glass-epoxy is a poor thermal conductor. This property enables heating the sample stage to high temperatures without delivering much heat to the cold finger, thus minimizing the Helium boil-off. Their lengths are chosen to position the sample to the center of the magnet solenoid. A set of cernox sensor and heater is mounted on the pre-sample stage to monitor and control its temperature. Optionally, the pre-sample stage can be enclosed in a thermal radiation shield. A broad range of temperatures, typically 5 – 300 K, needs to be accessed by the sample stage in transport experiments. To achieve a fast response to temperature changes, the thermal mass of the stage is minimized with a shape that is specially designed to optimize the ratio of surface area to volume. In a typical run, the sample stage is first stabilized at the desired temperature T with a stability ~ 1 mK. A $30\ \Omega$ heater made of twisted manganin wire provides heating which is constantly monitored and regulated by a temperature controller Lakeshore 336.

Figure 2.13: Schematics of the zero-field probe. Left panel shows the home-built probe. The probe has a sliding mechanism which allows a gradual insertion into Helium dewars. It is made sufficiently long to access the bottom of standard storage dewars. On the top of the probe are pump port for the sample space, wire feedthrough, and the nanovolt connector box. The sample space is enclosed in a vacuum can. Right panel shows the magnified view of the sample stage. It is attached to the cold finger through a G10 spacer. The black and red lines represent the leads to temperature sensors and heaters. The blue line represents the leads to sample and thermocouple. These wires are heat sunk on the cold finger and the extruded wall of the sample stage. Black arrow indicates the location where the sample is mounted. Blue arrow indicates the locations of BeO chips to which the leads are soldered. The sample is enclosed in a thin-walled thermal radiation shield.

In addition to the Nernst probe, we built a separate transport probe for measurements that do not require magnetic fields, hence the name “zero-field probe”. The probe was designed to be compatible with standard storage dewars. For this purpose, the sample space is made smaller than that of the Nernst probe. Furthermore, it is made much longer than the Nernst probe, in order to reach the bottom of most dewars.

The cold finger of the probe is a OFHC copper block attached to the 4K flange. The wiring is implemented in a way similar to the Nernst probe. Twisted pairs of OFHC copper wires and phosphor bronze wires are used as leads to the sample and thermometry, respectively. A “nanovolt connector box” is made for the sample leads. Inside the sample space, the leads are heat sunk at multiple places. Measurement noise level $< \pm 3$ nV is typically achieved.

Testing of Apparatuses

The probes were tested on samples of high- T_c cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). The temperature dependence of in-plane resistivity (ρ_{ab}) and thermopower (S_{ab}) of the material are measured and shown in Fig. 2.14 and Fig. 2.15, respectively. Bulk $T_c = 27$ K is consistently observed in the two transport measurements. At high temperatures, ρ_{ab} shows a T -linear dependence which is commonly observed in underdoped and optimally doped high- T_c cuprates [92]. Notably, this behavior has been taken as evidence for the deviation of the systems from conventional Fermi-liquid theory [93]. Our results are consistent with the data reported by Y. Nakaruma and S. Uchida [94].

It is worth noting that in the thermopower measurement, the quantity measured in the experiment is $S'_{ab} = S_{ab} - S_{Ag}$, where S_{Ag} is the thermopower of silver [95]. The pickup of S_{Ag} is due to our use of Ag wires as the leads to the sample. In response to the temperature gradient on the sample, the Ag wires develop a

Figure 2.14: Temperature dependence of the ρ_{ab} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). Solid line is a fit to the T -linear dependence commonly observed in underdoped and optimally doped high- T_c cuprates. The data was measured with the zero-field probe.

thermoelectric signal which adds to the raw signal measured in the experiment. Therefore, S_{Ag} needs to be removed in order to obtain the absolute thermopower of the sample, as demonstrated in the inset of Fig. 2.15.

The Nernst signal (e_y) was measured as a function of H at 22 K and 40 K, respectively, as shown in Fig. 2.16. In the superconducting state, the flow of vortices is the main source of Nernst signal [96]. Below T_c , however, the vortices are pinned and $e_y(H)$ is suppressed. The applied magnetic field needs to exceed a threshold value H_m in order to re-activate the vortex flow and produce a finite Nernst signal. The vortex pinning thus causes a non-linear H dependence in $e_y(H)$, which is seen in our data at $T = 22$ K. For $T = 40$ K, a H -linear dependence is observed which has been controversially attributed to various sources including the excitations of vortices above T_c [97, 98] and exotic quasiparticle

Figure 2.15: Temperature dependence of the S_{ab} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). The data was measured with the Nernst probe. Insets show the quantity $S'_{ab} = S_{ab} - S_{Ag}$ measured in the experiment. Solid line shows the thermopower of silver, S_{Ag} , which is reproduced from Ref. [95].

contributions [99, 100]. Our results are consistent with the data reported by Xu and co-workers [97].

Note that unlike in the case of thermopower measurement, lead wires do not contribute a thermoelectric signal to $e_y(H)$ since the latter is taken as the field-antisymmetric part of the raw signal. Specifically,

$$e_y(H) = \frac{e_y(+H) - e_y(-H)}{2} \quad (2.2)$$

where $e_y(+H)$ and $e_y(-H)$ are the data taken with positive and negative magnetic fields, respectively (Fig. 2.6). This field-antisymmetrization effectively removes the pickup of thermopower of sample and lead wires which commonly appears in the raw signal due to voltage-contact misalignment.

Figure 2.16: Field dependence of the e_y of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). The T_c of this material is 27 K. Filled and open circles represent data for $T = 22$ K and $T = 40$ K, respectively. The dashed line is a fit to the H -linear dependence commonly observed in high- T_c cuprates at temperatures above T_c . The data were measured with the Nernst probe.

The results reported here demonstrate the high resolution and reliability that we achieve in transport measurements using the specially designed homebuilt probes. In particular, we observed several unique features in high- T_c cuprates. These experimental capabilities enabled us to perform systematic investigations on the electronic properties of the striped cuprate $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ presented in chapters 3 and 4.

2.2.3 Quantum Design PPMS

In this work, we also use commercial Quantum Design PPMS (Physical Property Measurement System) for electrical transport measurements (Fig. 2.17). The system allows temperature control over the range 1.9 – 400K, and is equipped

with a 14 T superconducting magnet. A Helium reliquefier (Cryomech PT410) is installed on the PPMS dewar to recover the Helium boil-off. Nearly zero consumption of liquid Helium is achieved, which greatly reduces the experiment cost.

Figure 2.17: Photograph of the PPMS 6000 facility in the CryoFace laboratory. (a) Cryomech PT410 Helium reliquefier (b) PPMS Dewar (c) Magnet power supply (d) Instrument rack (e) Helium gas supply (f) User interface

AC Transport Measurements

The "ACT option" of PPMS is used for resistivity and I-V characteristics. In a typical run, the sample is glued to a sapphire block mounted on the sample puck (Fig. 2.18). Fine Ag wires are attached to the electrical contacts of the sample with silver paste DuPont 4929N which cures at room temperature. The other ends of the Ag wires are soldered to the contact pads of the sample puck.

The sample puck is transferred to the PPMS probe and installed at the bottom of the sample chamber where mechanical and electrical connections are made. The sample chamber is cooled by the enclosing cooling annulus that is constantly

Figure 2.18: Schematics of the ACT sample puck. Left and right panels show the top and side views of the puck, respectively. Taken from Quantum Design.

filled with Helium vapor drawn from the liquid-Helium bath. The chamber pressure is typically a few Torr. Radiation baffles are used to block the heat radiation from the top of the chamber.

A set of heater and thermometers is mounted at the base of the sample chamber, which stabilizes the sample stage to the desired temperature. Thermal isolation between the cooling annulus and the liquid-Helium bath is achieved with the inclusion of an evacuated chamber filled with super-insulation. The temperature range of 1.9 – 4.2 K can be readily accessed. The cooling annulus is filled with liquid Helium that is later pumped to achieve the desired temperature (pot-fill mode). Alternatively, a secondary impedance tube that is delicately made to provide stronger restriction to the gas flow is used in the continuous low-temperature control mode (CLTC).

AC frequency 33 Hz is used for sample excitations. The current amplitude is typically 0.05-5 mA for resistivity and Hall effect measurements, and 0.1 – 100 mA for I-V measurements. Due to Joule heating generated by the excitation current, the data acquisition is taken after the sample is stabilized at the temperature set-point. This is done by enforcing a 5 second wait after the stage temperature becomes stable. A signal integration time of 5 seconds is chosen. A measurement noise level better than 5 nV is typically achieved.

2.3 Magnetization Measurements

This section introduces the principles of Josephson effect and DC SQUID. The use of commercial Quantum Design MPMS for magnetization measurements is also described.

2.3.1 Josephson Effect

The Josephson junction is a weak link between two bulk superconductors. That Cooper pairs can *tunnel* across the junction without dissipation, was first predicted in 1962 by B. D. Josephson [101]. The effect was experimentally verified soon by Anderson and Rowell [102]. In general, the weak link can be a thin insulating layer, a normal metal layer made weakly superconductive by the so-called proximity effect, or a narrow constriction in the otherwise continuous superconducting material [103]. For superconductors which have short coherence length, such as high- T_c copper-oxides, the weak links can be formed at the grain boundaries of polycrystals.

The supercurrent across the junction is given by

$$I = I_c \sin \theta \quad (2.3)$$

where I_c is the critical current that the junction can support, and θ is the difference in the phase of the order parameters in the two superconductors. When a contact voltage V is maintained across the junction, the phase difference will *oscillate* according to

$$\frac{d\theta}{dt} = \frac{2eV}{\hbar} \quad (2.4)$$

and consequently, the current oscillates at $2eV/\hbar$.

2.3.2 DC SQUID

Consider a superconducting loop. Since the superconducting phase can be described by a *single*-valued complex superconducting order parameter $\Psi = \Psi_0 e^{i\varphi}$, the phase φ must change by integral multiples of 2π in making a complete loop such that

$$\oint \nabla \varphi \cdot ds = 2\pi n \quad (2.5)$$

where n is integer. This boundary condition leads to flux quantization effect where magnetic flux that threads the loop must be expressed as

$$\Phi = n\Phi_0 \quad (2.6)$$

where $\Phi_0 = 2.07 \times 10^{-15}$ weber is the flux quantum.

The DC SQUID (superconducting quantum interference device) contains a superconducting loop with two Josephson junctions in parallel (Fig. 2.19). Due to the presence of weak links, the magnetic flux is *no* longer quantized and can take on any value. Then, Eqn. 2.5 becomes

$$\oint \nabla \varphi \cdot ds = 2\pi n = \theta_1 + \theta_2 + 2\pi \frac{\Phi}{\Phi_0} \quad (2.7)$$

where θ_1 and θ are the phase differences at the two junctions taken in the same direction around the loop. The current that flows across the device is given by

$$I = I_1 \sin \theta_1 + I_2 \sin \theta_2 \quad (2.8)$$

with I_1 and I_2 being the critical current of each junction, which in practice

$I_1 = I_2 = I_0$. Substituting 2.7 into 2.8, one arrives at

$$I = I_0 (\sin \theta_1 + \sin (\theta_1 - 2\pi\Phi/\Phi_0)) \quad (2.9)$$

The maximum zero-voltage current, i.e. the critical current, can be determined by maximizing 2.9 with respect to θ_1 , which gives

$$I_c = 2I_0 |\cos \pi\Phi/\Phi_0| \quad (2.10)$$

Eqn. 2.10 shows that I_c is a periodic function of Φ/Φ_0 . In a SQUID measurement, the device is biased at a constant current $I > I_c$. This generates a finite voltage V across the device which has the same periodicity as I_c with respect to Φ/Φ_0 . As a result, the changes in $\delta\Phi$ can be determined from the measured δV . Note that due to the presence of the *second* junction, the device is not shorted by the otherwise superconducting path. The voltage can be directly measured by DC method, hence the name DC SQUID. In the configuration of RF SQUID, the superconducting loop consists of only one junction. The voltage can only be measured by coupling the loop to a RF bias tank circuit.

2.3.3 Quantum Design MPMS

In this work, we use a Quantum Design MPMS for magnetization measurements. The sample is securely mounted in a plastic straw, and moved through the *pickup coils*. The pickup coils are configured as a second-order gradiometer, where the signals detected by the coils are balanced against each other such that only the second differential of the magnetic field is detected. This eliminates the detection

of externally applied magnetic field whose changes are uniform throughout the pickup coils. When a magnetized sample is placed in the coils, it acts like a

Figure 2.19: Schematic of DC SQUID. Left panel shows the device configuration. Two weak links ($\times$) form a parallel circuit. Magnetic flux Φ threads the loop. A bias current $I > I_c$ is maintained across the device, which produces a finite voltage V . Right panel shows that V is a periodic function of Φ/Φ_0 . This property enables the determination of Φ from the experimentally measured V .

magnetic dipole, provided the sample dimension is much smaller than that of the pickup coils. Signals detected by the pickup coils are *coupled* into a DC SQUID sensor through a superconducting transformer.

We usually center the sample with respect to the pickup coils at 10 K. To eliminate any remnant field in the superconducting magnet, the magnetic field is typically swept between positive and negative values on decreasing magnitude. Raw signals are matched up against the theoretical curve for a dipole to determine the magnetization of the sample. The data acquisition is fully automated by the system software.

Fig. 2.21 shows the temperature dependence of the magnetization of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). The onset of diamagnetic response (Meissner effect) at 27 K is consistent with the superconducting transition seen in the resistivity and thermopower measurements (Fig. 2.14 and Fig. 2.15).

Figure 2.20: Schematic of MPMS measurements. Left panel shows that the sample is scanned through the pickup coils which are configured as a second-order gradiometer. The input coils (not shown) are tightly coupled to the DC SQUID sensor. Right panel shows the SQUID response as a function of sample position, which is fitted by the theoretical curve for a dipole moment. Taken from Quantum Design.

Figure 2.21: Temperature dependence of the magnetization of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.105$). The data was measured with Quantum Design MPMS.

3 Surface-Enhanced Superconductivity in a High- T_c Cuprate

Surfaces of materials often possess properties which are distinctly different from their bulk [104, 105]. The atomic structure can develop intricate new patterns due to surface reconstruction [106] and the electronic properties can be very distinct, as most dramatically manifested in topological insulators [107]. However, more subtle collective phenomena such as superconductivity are not as strongly affected by the presence of surfaces.

In this chapter, we present an unprecedented finding of enhanced superconductivity at the ab-plane surface of high- T_c cuprate $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO- x). Electrical and thermoelectric transport measurements detect a superconducting surface below a transition temperature T_{cs} which is considerably higher than the bulk T_c . Systematic investigations over a range of charge carrier doping (x) reveal a subtle coincidence of the effect with an electronic phase known for stripes [17, 47, 49–51]. Notably, for $x = 0.12$, T_{cs} reaches 36 K, exceeding even the highest reported bulk T_c in this material for any doping [17]. Possible scenarios for the novel effect are discussed.

3.1 Higher T_{cs} at the Surface

This section demonstrates that the surface-enhanced T_{cs} is consistently observed in a range of transport and magnetization measurements on LBCO samples. Despite a difference in the superconducting transition temperatures, in the normal state, the surface and the bulk have common transport properties.

3.1.1 Transport Measurements

High quality single crystals of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO- x) over the composition range $0.076 < x < 0.139$ were grown with the newly developed laser-diode-heated floating zone (LDFZ) method which enabled exceptionally high degree of homogeneity [81]. Laue and x-ray diffraction indicated single crystallinity and absence of impurity phases. The samples were cut into bar shape of typical dimensions 3.0 mm x 0.5 mm x 0.5 mm, with the last dimension along the crystallographic c-axis. Distinction between crystal a- and b-axes was omitted as the samples were not detwinned. These materials have a strongly layered structure with copper-oxide planes stacked along the c-axis. Transport properties along the surface and the bulk planes can be probed and differentiated with voltage contacts placed on the crystal ab or ac faces, respectively, as described in chapter 2. In either configuration, electrical or heat current is applied through the entire bc faces. Electrical resistivity and thermopower measurements were performed over a wide range of temperature and magnetic fields. Throughout this work, the subscripts s and ab are used to denote surface and bulk properties, respectively.

Fig.3.1a-e show the temperature dependence of ρ_s and ρ_{ab} for various x . For LBCO-0.076 and LBCO-0.092, ρ_s and ρ_{ab} undergo superconducting transitions at a common T_c , which are 22 K and 30 K for the two compositions, respectively.

Figure 3.1: Observation of surface-enhanced superconductivity by in-plane transport measurements. a-e, Temperature dependence of ρ_s and ρ_{ab} for various compositions. For LBCO-0.076 and LBCO-0.092, ρ_s and ρ_{ab} drop to zero at a unique T_c . For LBCO-0.115, LBCO-0.120, and LBCO-0.139, ρ_s and ρ_{ab} drop to zero at T_{cs} and T_c , respectively. The fact that $T_{cs} > T_c$ indicates the occurrence of surface-enhanced superconductivity. Insets of c-e show magnified views of ρ_s and ρ_{ab} measured with different currents near the superconducting transitions. f, Temperature dependence of S_s and S_{ab} for LBCO-0.120. S_s and S_{ab} drop to zero at $T_{cs} = 36$ K and $T_c = 22$ K respectively, consistent with the results of resistivity measurement. Inset shows magnified view of S_s and S_{ab} near the superconducting transitions indicated by blue and red arrows, respectively. The green arrows in c-f indicate the low-temperature-tetragonal (LTT) structural transition at T_d .

Surface enhancement on superconductivity is absent or too weak to be detected in these samples. For LBCO-0.115, LBCO-0.120, and LBCO-0.139, a kink is observed in both ρ_s and ρ_{ab} at the low-temperature-tetragonal (LTT) structural transition temperature T_d [17]. The striking observation here is that ρ_s and ρ_{ab} drop to zero at two different critical temperatures namely, T_{cs} and T_c , with the former significantly higher than the latter. In particular, for LBCO-0.120, $T_{cs} = 36$ K which is 64 % higher than $T_c = 22$ K. Fig. 3.1f shows the temperature dependence of surface (S_s) and bulk (S_{ab}) thermopower for LBCO-0.120. At high temperatures, the two curves overlap with a rapid drop at T_d . As the temperature decreases further, S_s drops to zero at $T_{cs} = 36$ K, whereas S_{ab} crosses from positive to negative before it eventually becomes zero at $T_c = 22$ K. The zero-crossing of S_{ab} has been recently attributed to electronic reconstruction which produces charge carriers of different signs at low temperatures [108, 109]. Both electrical resistivity and thermopower consistently point to an enhanced superconductivity at the surface. The effect was also observed on the opposite side of the crystals.

Scaling of Normal-state Resistivity

We note that S_s and S_{ab} overlap at high temperatures. Below 40 K which is slightly above T_{cs} , S_s deviates from S_{ab} due to the onset of surface-enhanced superconductivity. On the other hand, the normal-state ρ_s and ρ_{ab} cannot be simply scaled by a constant factor. Here, we investigate if the two quantities can be described by a common normal-state curve as in the case of thermopower. Such analysis will add credence to the high quality of the samples studied here, which is important, for example, to rule out inhomogeneity as the origin of T_{cs} as will be discussed in sec. 3.3.2.

For a homogeneous sample, the normal-state resistivity should be uniform through-

out the sample. Therefore, the surface resistivity should satisfy

$$\rho_s^n = A\rho_{ab} \quad (3.1)$$

where the superscript denotes normal-state property, $A \approx 1$ is a scaling factor that does not change with temperature.

Figure 3.2: Scaling of ρ_s and ρ_{ab} . (a)-(e) ρ_s for various composition are fitted by $\rho_s^{\text{obs}} = A\rho_{ab} + B\rho_c$. Also shown are the temperature dependence of ρ_{ab} and ρ_s (inset). (f) Fitting coefficients A and B used in (a)-(e).

We further note that in reality, the surface may not be perfectly parallel to the ab-plane. This could happen, for instance, due to a small but unavoidable misalignment in the cutting of samples. Subsequent surface polishing may also modify the alignment. Due to the strong anisotropy in resistivity ($\rho_c/\rho_{ab} \sim 10^{-3}$) as shown in Fig. 3.2 for all compositions studied here, the small misalignment cause a sizable pickup of ρ_c when measuring ρ_s . Note that in the case of thermopower measurement, the misalignment causes much less problems since the thermal property is essentially isotropic [94]. Therefore, in the normal state, the observed values of surface resistivity, ρ_s^{obs} , should be described by

$$\begin{aligned}\rho_s^{\text{obs}} &= \rho_s^n + B\rho_c \\ &= A\rho_{ab} + B\rho_c\end{aligned}\tag{3.2}$$

where $B \gtrless 0$ is the pickup coefficient which does not depend on temperature.

Fig. 3.2 shows that for all our samples, ρ_s can be fit by ρ_s^{obs} over a wide range of temperature. At low temperatures, the onset of surface superconducting fluctuations makes the surface more conductive than the normal-state counterpart, i.e. $\rho_s^n < A\rho_{ab}$. Furthermore, proximity effect [110, 111] shorts c-axis resistivity within the surface layer which consists of several copper-oxide planes. As a result, ρ_s deviates downward from ρ_s^{obs} and eventually vanishes at T_{cs} . Our data also show that ρ_c remains finite above T_c despite the onset of surface-enhanced superconductivity. Again, this confirms that T_{cs} is observed only at the surface.

We note that for $x = 0.115$ (Fig. 3.2c), in run 1, a large pickup coefficient $B = 14.5 \times 10^{-4}$ causes a strong deviation of ρ_s from ρ_{ab} . In run 2, however, measurement on the re-polished surface contains a smaller ρ_c pickup with $B = 3 \times 10^{-4}$. The important point is that while polishing modifies the surface alignment and hence the degree of ρ_c pickup, it does not affect T_{cs} . For $x = 0.139$, where surface-enhanced T_{cs} is also observed, the ρ_c pickup is in fact zero.

Specifically, an excellent scaling $\rho_s = 1.6 \times \rho_{ab}$ is observed in the normal state. These observations suggest that the pickup is a side effect due to imperfect experimental conditions, which can in principle be removed, and are not relevant to the surface enhancement in T_{cs} .

Thus the seemingly absent scaling between ρ_s and ρ_{ab} is due to a small but unavoidable pickup of ρ_c in the former. A scaling does exist for the two quantities at temperatures higher than T_{cs} . Our results indicate that the surface and the bulk have *common* normal-state transport properties.

Magneto-Transport Measurements

Magneto-resistivity measurements on LBCO-0.12 with magnetic fields (H) applied along the c-axis reveal that superconductivity at the surface is more robust than in the bulk (Fig. 3.3).

Upon increasing H , both T_{cs} and T_c decrease; however, T_{cs}/T_c which characterizes the relative enhancement is found to increase. At the highest applied magnetic field ($H = 14$ T), both ρ_s and ρ_{ab} show insulating behavior ($d\rho/dT < 0$) before the onset of superconductivity, characteristic of underdoped lanthanum-based high- T_c cuprates [112].

Fig. 3.4 shows the magneto-thermopower of LBCO-0.12. The variations of T_{cs} and T_c with magnetic field are consistent with the magneto-resistivity measurements. The application of strong magnetic fields restores the normal state, which makes the overlap of S_s and S_{ab} to persist to even lower temperatures. For example, in the case of $H = 14$ T, the overlap persists down to ~ 17 K.

We also measured Nernst effect which is an effective probe of superconducting vortices. In the mixed state of type-2 superconductors, vortices are generated by a magnetic field applied along the c-axis. The flow of vortices driven by a temperature gradient generates an electric field along the traverse direction, and

Figure 3.3: Temperature dependence of ρ_s and ρ_{ab} measured in various magnetic fields along the c-axis. Inset shows T_{cs} , T_c , and T_{cs}/T_c as a function of magnetic field, indicating that superconductivity at the surface is more robust with respect to applied magnetic field than in the bulk.

is measured as the Nernst signal [97, 98, 113–116].

Fig. 3.5 presents the temperature dependence of surface (ν_s) and bulk Nernst coefficient (ν_{ab}) measured in $H = 1$ T. At high temperatures, the two quantities overlap which is consistent with the previous finding of a common normal-state resistivity and thermopower for the surface and bulk. However, the two quantities diverge below 45 K due to the onset of superconducting fluctuations.

The flow of vortices is typically optimal near the superconducting transition. In our case, the vortex-flow causes a pronounced peak in ν_s and ν_{ab} near $T_{cs} = 36$ K and $T_c = 22$ K, respectively. Below the transition temperatures, ν_s and ν_{ab} are suppressed and eventually vanish due to the pinning of vortices. A minimum H was required to reactivate the vortex-flow to attain a finite Nernst signal. The fact that vortex pinning at the surface occurs just below T_{cs} provides another

Figure 3.4: Temperature dependence of S_s and S_{ab} measured in various magnetic fields along the c-axis. At low temperatures, the overlap of the two quantities under strong magnetic fields suggests a common normal state from which the surface-enhanced superconductivity emerges.

evidence for enhanced superconductivity.

3.1.2 Magnetization Measurements

The surface-enhanced superconductivity should show diamagnetic response to an applied magnetic field. Fig. 3.6 shows the magnetization data of LBCO-0.12 measured with $H = 20$ Oe applied along the c-axis, under field-cooling (FC) and zero-field-cooling (ZFC) conditions. The onset of diamagnetism is observed slightly above $T_{cs} = 36$ K, consistent with a screening by the surface. In particular, the divergence between FC and ZFC data below T_{cs} points to the trapping of vortices in the FC measurement run. Thus the magnetization data supports the conclusion of surface-enhanced superconductivity.

Figure 3.5: Temperature dependence of ν_s and ν_{ab} . The measurements were performed with $H = 1$ T. The two quantities deviate below 45 K due to the onset of superconducting fluctuations. Pronounced peaks in the two quantities are due to the optimal vortex-flow near the superconducting transition temperatures.

3.2 Surface Confinement

This section presents further experimental results on LBCO-0.12 where the surface enhancement is most pronounced. Various parts of the same sample were probed by a set of “resistance tomography” measurements, which indicates that the enhanced T_{cs} is only observed near the surface. Surface I-V characteristics and ρ_s are well fitted by the Berezinskii-Kosterlitz-Thouless (BKT) transition which describes 2D superfluid systems. On the other hand, the bulk remains resistive and “sandwiched” by the superconducting surfaces over the temperature range $T_c < T < T_{cs}$, and becomes superconducting only below T_c . Model calculation shows that the superconducting surface does not short the resistive bulk, due to the large c-axis and current-contact resistances. When voltage contacts

Figure 3.6: Temperature dependence of DC magnetization of LBCO-0.120 in field-cooling (FC) and zero-field-cooling (ZFC) conditions. $-M/H$ was plotted in semi-log scale. The measurements were performed with a magnetic field $H = 20$ Oe applied along the c -axis. Courtesy of Dr Anjan Soumyanarayanan (Laboratory for Physics of Novel Electronics; Prof. Christos Panagopoulos' group)

were placed over the crystal ac and ab faces simultaneously, a contribution from both the surface and the bulk was observed. For instance, the measured resistance showed a partial drop at T_{cs} prior to the full superconducting transition at T_c . Our results thus indicate that the enhanced-superconductivity is confined to the surface.

3.2.1 Resistance Tomography

We design and perform a novel method which we name “resistance tomography”. The basic idea is to measure the resistances of different regions of the sample and check for consistency. Four contacts numbered $i = 1, 2, 3$, and 4 were

placed with silver paste on the sides or top of the sample for bulk and surface measurements, respectively (Fig. 3.7). We measured the resistance across two contacts i and j , defined as $R_{ij} = V_{ij}/I_{ij}$ and $R_{s(ij)} = V_{ij}/I_{ij}$ for the bulk and the surface configurations, respectively, by applying current I_{ij} and sensing the voltage drop V_{ij} strictly through the same pair of contacts. In this setting, R_{ij} and $R_{s(ij)}$ contain two terms, namely the resistance of the local region sensed by the current path, and the contact resistances which as we shall show shortly, can be removed.

Figure 3.7: Schematic contact configurations for “resistance tomography” experiments on LBCO-0.120. Four contacts numbered $i = 1, 2, 3$, and 4 were placed on the sides or top of the sample for **(a)** the bulk and **(b)** the surface measurements, respectively. In each configuration, current I_{ij} was applied through two contacts i and j and the corresponding voltage drop V_{ij} was measured, for all six combinations of $\{i, j\}$. The regional resistance across any two contacts is defined as $R_{ij} = V_{ij}/I_{ij}$ for the bulk measurements, and $R_{s(ij)} = V_{ij}/I_{ij}$ for the surface measurements.

Fig. 3.8a-b show the temperature dependence of R_{ij} and $R_{s(ij)}$ for all six combinations of $\{i, j\}$. R_{ij} and $R_{s(ij)}$ show a rapid drop at the respective T_c and T_{cs} due to the *two distinct* superconducting transitions. At lower temperatures, both R_{ij} and $R_{s(ij)}$ are dominated by the contact resistances which show semiconducting-like temperature dependence. The results indicate that the bulk and surface-enhanced superconductivities are consistently observed in different local regions of the bulk and surface, respectively. It is also important to note that T_{cs} is observed exclusively in the surface measurements, thus confirming the confinement of surface-enhanced superconductivity to a thin surface layer.

Figure 3.8: Resistance tomography of LBCO-0.120. a-b, Bulk R_{ij} and surface $R_{s(ij)}$ as defined in the supplementary text, are rescaled to demonstrate the general trends. Both sets of R_{ij} and $R_{s(ij)}$ show rapid drops at the respective T_c and T_{cs} , consistent with the *two distinct* superconducting transitions. At lower temperatures, semiconducting-like contact resistances dominate. The applied current was 1 mA in each measurement run. c-d, $R_{ij,kl} = R_{ij} + R_{kl}$ and $R_{s(ij,kl)} = R_{s(ij)} + R_{s(kl)}$ are calculated. The overlapped part below the respective T_c and T_{cs} is the sum of all the contact resistances for each configuration. e-f, The differential values of $\Delta R_{ij,kl}$ and $\Delta R_{s(ij,kl)}$ are calculated in order to cancel out the contact resistances. $R_{14,23} - R_{13,24}$ and $R_{s(14,23)} - R_{s(13,24)}$ are omitted due to their relatively small values. Clearly, $\Delta R_{ij,kl}$ and $\Delta R_{s(ij,kl)}$ can be rescaled to R_{ab} and R_s , respectively, which are the bulk and surface resistances measured by the standard four-terminal method.

Next, we remove the contact resistances for a more rigorous test of sample homogeneity. We calculate the combination $R_{ij,kl} = R_{ij} + R_{kl}$ and $R_{s(ij,kl)} = R_{s(ij)} + R_{s(kl)}$ (Fig. 3.8c-d). Note that the sum of all the contact resistances is reproducible over measurement runs, as seen in both sets of $R_{ij,kl}$ and $R_{s(ij,kl)}$ overlapping below the superconducting transition temperatures. This fact enabled us to cancel out the contact resistance, by calculating $\Delta R_{ij,kl}$ and $\Delta R_{s(ij,kl)}$ which are the differences between two combinations (e.g. $R_{14,23} - R_{12,34}$). Fig. 3.8e-f show the main results where $\Delta R_{ij,kl}$ and $\Delta R_{s(ij,kl)}$ are rescaled to the bulk and surface resistances measured by the standard four-terminal method, R_{ab} and R_s , respectively. The excellent scaling observed here, indicates consistency in the resistance measured in different parts of the sample. This confirms the sample homogeneity within the bulk and the surface.

3.2.2 Berezinskii-Kosterlitz-Thouless Transitions

Two-dimensional (2D) superconductivity can be described by Berezinskii-Kosterlitz-Thouless (BKT) transition [117–120]. Near the transition, the I-V curves are expected to obey $V \propto I^\alpha$ with $\alpha = 3$ at T_{BKT} , and the resistivity follows the temperature dependence $\rho \propto \exp(-b/t)$, where b is material parameter, and $t = T/T_{BKT} - 1$.

It is instructive to check if the surface-enhanced superconductivity is consistent with a 2D-like transition. We analyze the surface I-V curves and ρ_s of LBCO-0.120, both of which were measured using the same surface voltage-contact configuration. Fig. 3.9 presents our results which are well fitted by the BKT transition with $T_{BKT} = 36.6$ K and $b = 0.996$. The fits support 2D-like characteristics of the surface-enhanced superconductivity. Interestingly, BKT behavior is also observed in the bulk, as shown in Fig. 3.10. However, the bulk parameters $T_{BKT} = 21.5$ K and $b = 3.313$ are considerably different from the surface values,

pointing to a distinction between the surface and the bulk.

Figure 3.9: Surface I-V characteristics and ρ_s of LBCO-0.120 fitted by the BKT transition. **a**, Surface I-V curves on a logarithmic scale, measured with the ρ_s contact configuration at different temperatures near T_{cs} . The solid lines are fits to the power law $V \propto I^\alpha$. **b**, The exponent α as a function of temperature, reaching a value of 3 at $T_{BKT} \approx 36.5$ K. **c**, Near the superconducting transition, ρ_s is well fitted by $\rho \propto \exp(-b/t)$ (solid line) with $b = 0.996$ and $T_{BKT} = 36.6$ K.

3.2.3 Resistor Network Model

Here we explicitly consider a resistor network model to analyze resistivity measurements in the presence of superconducting surface layer. As we shall show, surface superconductivity is ineffective in fully shunting the current from the bulk. This explains the coexistence of the superconducting surface with the normal-state bulk over the temperature range $T_c < T < T_{cs}$.

Since the sample can be viewed as repetition of the ac-plane along the b-axis, it suffices to consider the current flow in the ac-plane which essentially captures the shunting effect of the surface. The ac-plane can be described as an anisotropic resistive plane with dimensions L_x and L_y along the x and y directions, respec-

Figure 3.10: Bulk I-V characteristics and ρ_{ab} of LBCO-0.120 fitted by the BKT transition. **a**, Bulk I-V curves on a logarithmic scale, measured with the ρ_s contact configuration at different temperatures near T_c . The solid lines are fits to the power law $V \propto I^\alpha$. **b**, The exponent α as a function of temperature, reaching a value of 3 at $T_{BKT} \approx 21.3$ K. **c**, Near the superconducting transition, ρ_{ab} is well fitted by $\rho \propto \exp(-b/t)$ (solid line) with $b = 3.313$ and $T_{BKT} = 21.5$ K.

tively, where the x and y directions are set parallel to the a- and c-axes of the sample. In the absence of magnetic field, the current density $\hat{J}$ and electric field $\hat{E}$ are related by a diagonal conductivity tensor $\sigma = \begin{bmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{bmatrix}$ such that

$$\hat{J} = \sigma \hat{E} = \hat{x} \sigma_{xx} E_x + \hat{y} \sigma_{yy} E_y \quad (3.3)$$

Substitute $\sigma_{xx} = \sigma_{ab}$, $\sigma_{yy} = \sigma_c$, and $\hat{E} = -\nabla \phi$ into the equation, we get

$$\hat{J} = -\hat{x} \sigma_{ab} \partial_x \phi + \hat{y} \sigma_c \partial_y \phi \quad (3.4)$$

Since there is no charge accumulation, $\nabla \cdot \hat{J} = 0$,

$$\Rightarrow \sigma_{ab} \partial_x^2 \phi + \sigma_c \partial_y^2 \phi = 0 \quad (3.5)$$

Defining $\tilde{y} = y\sqrt{\sigma_{ab}/\sigma_c}$, we get

$$\partial_x^2 \phi + \partial_{\tilde{y}}^2 \phi = 0 \quad (3.6)$$

Thus we have mapped the system into an isotropic resistive plane with the new dimensions $L_x \times L_{\tilde{y}}$, where $L_{\tilde{y}} = \sqrt{\sigma_{ab}/\sigma_c} L_y$.

To perform numerical analysis, we discretise the isotropic resistive plane into a rectangular mesh of $N_x \times N_y$ sites, where $N_x \propto L_x$ and $N_y \propto L_{\tilde{y}}$ (Fig. 3.11). The sites are interconnected through resistors R , except for those at the top and bottom boundaries (i.e. the surfaces), which are connected to the inner sites through R but are horizontally interconnected through resistors R_s . R_s represents the surface layer and is set to zero at temperatures below T_{cs} . In addition, we model the current contacts as contact resistors R_c connected to the sites on the left and right boundaries.

Figure 3.11: Schematic of the rectangular resistor network. $N_x = 6$ and $N_y = 5$ were chosen for illustration purpose. In the numerical calculation, the boundary voltage $V_L > V_R$ are kept constant along the y direction.

The current I_0 is applied between the boundaries through the resistive contacts. Numerically this is implemented by setting the voltage at the left and right boundary sites, to V_L and V_R , respectively, constant along the y direction. For every site i the voltage V_i satisfies Kirchoff's current law $\sum_j \frac{V_i - V_j}{R_{ij}} = 0$, where $\{j\}$ are the neighboring sites connected to site i . Thus, we have a system of linear equations for voltage $\{V_i\}$ which can be solved numerically as described elsewhere [121, 122]. The current flow between two adjacent sites i and j can be determined as $I_{ij} = (V_j - V_i)/R_{ij}$, where $R_{ij} = R$ for the bulk and $R_{ij} = R_s$ for the surface.

Here, we are mainly interested in the current flow at the top surface. Let $n_x^{(s)} = 1, 2, 3 \dots N_x$ and $V(n_x^{(s)})$ denote the coordinates and voltage of the surface sites. The surface current at site $n_x^{(s)}$ is determined as

$$\Delta I_s(n_x^{(s)}) = \frac{V(n_x^{(s)} + 1) - V(n_x^{(s)})}{R_s} \quad (3.7)$$

which equals the amount of current flowing from site $n_x^{(s)}$ to site $n_x^{(s)} + 1$ in the limit $R_s \rightarrow 0$.

In our calculation, we set $\sigma_{ab}/\sigma_c = 10^4$ which is a reasonable value for LBCO-0.12 at temperatures near T_{cs} (Fig. 3.2d), and $L_x : L_y = 6 : 1$ due to the sample dimension $a \times c = 3.0 \text{ mm} \times 0.5 \text{ mm}$ typically used in this work. Based on these values, we derive the mesh aspect ratio

$$N_x : N_y = L_x : L_{\tilde{y}} = L_x : \sqrt{\sigma_{ab}/\sigma_c} L_y \approx 1 : 17 \quad (3.8)$$

In addition, we have $R_c \gtrsim R \times N_x$ since the contact resistance is typically slightly higher than the sample resistance (e.g. the resistance tomography results in Fig. 3.8a). This sets the resistor ratio $R_s : R : R_c \approx 0 : 1 : N_x$ for our numerical analysis.

Figure 3.12: Surface current ΔI_s as a function of site position $n_x^{(s)}$. **a**, For $R_c = 3N_x$, ΔI_s is consistently reproduced over $N_x=50, 100, 200$, with the peak value reaching 2.3 % of the applied current I_0 . **b**, For $N_x = 100$, $\Delta I_s/I_0$ is slightly suppressed on increasing R_c , resulting in a change of 0.35 % in the peak value between the cases of $R_c = N_x$ and $R_c = 10N_x$.

Following the physical constraints described in the previous paragraph, we set $N_y = 17N_x$, $R_s = 0.0001$, $R = 1$, $V_L = 1$, and $V_R = 0$, with N_x and R_c being the variable parameters in the calculations. Fig. 3.12 shows the numerical results of ΔI_s for $N_x=50, 100, 200$ and $R_c=3N_x$. The surface current ΔI_s exhibits approximately a parabolic curve along the surface, with the peak value at the center, which is equal to 2.3% of the total applied current I_0 . It is important to note that the curve of ΔI is consistently reproduced for different values of N_x . This indicates that numerical error due to finite mesh size is insignificant in our calculation. On the other hand, we note that a larger value of R_c results in slightly lower values of ΔI_s , as shown in Fig. 3.12b for $R_c = N_x, 3N_x, 10N_x$ and $N_x = 100$. The peak value changes by 0.35% when the setting goes from $R_c = N_x$ to $R_c = 10N_x$. That is because in the limit of very high contact resistance the current injection becomes completely uniform through the contact cross-section, while for lower R_c , there is somewhat higher injection into the surface. In the limit of high contact resistance, the fraction of the current deflected to the surface scales as $L_x/L_{\bar{y}}$.

Fig. 3.13 shows the current flow in the bulk for illustration purpose. The local

Figure 3.13: The local current in the bulk ΔI plotted as a vector mesh. Here $N_x \times N_y = 20 \times 40$ is chosen for illustration purpose. The green arrows depict the local trends of the current flow in regions close to the surface.

current ΔI is plotted as vector, with the x and y components determined as

$$\Delta I_x(n_x, n_y) = \frac{V(n_x + 1, n_y) - V(n_x, n_y)}{R} \quad (3.9)$$

$$\Delta I_y(n_x, n_y) = \frac{V(n_x, n_y + 1) - V(n_x, n_y)}{R} \quad (3.10)$$

where (n_x, n_y) denote the site coordinate. We note that only regions close to the surface are affected by the latter. This indicates that the superconducting surface is ineffective at shunting the bulk current, consistent with the results of ΔI_s where less than 2.5% of the applied current I_0 actually reaches the surface.

3.2.4 Mixture of Surface and Bulk Signals

In the measurements reported in the preceding sections, the voltage contacts were confined to either the top or the side of the sample. This ensured the surface and bulk were probed selectively enabling differentiation of the respective electronic transport. In the test case where the voltage contacts covered both

the top and side of the sample, a combination of surface and bulk signals was measured.

Fig. 3.14 shows an example of a resistivity measurement where the contribution from ρ_s and ρ_{ab} was observed in LBCO-0.120, as indicated by the partial drop at T_{cs} and the bulk superconducting transition at T_c . The partial drop is due to the surface superconducting transition which is sensed by the voltage contacts covering both the top and the side. While one may expect the superconducting surface to short out the applied current, the shorting is prevented by the large c-axis and current-contact resistances as demonstrated in the section of “Resistor Network Model”.

Figure 3.14: Mixture of ρ_s and ρ_{ab} in LBCO-0.120. The voltage contacts covered both the top and side of the sample (inset). The measured resistivity showed a partial drop at T_{cs} and eventually a complete one at T_c . The former is due to a pick-up of surface superconductivity.

3.3 Possible Scenarios

The phase diagram of LBCO (Fig. 3.15) is known to show a strong suppression of bulk superconductivity over the composition range $0.095 < x < 0.155$, with the strongest effect at $x = 1/8$ where T_c is approximately 5 K [17,59]. This effect is known as the “1/8 anomaly” and has been attributed to the stabilization of stripe order, which is the segregation of charge carriers (holes) into hole-rich unidirectional charge stripes, forming antiphase boundaries between hole-poor antiferromagnetically ordered spin domains [17,47,49–51]. Surprisingly, this is exactly

Figure 3.15: Phase diagram of LBCO single crystals. T_{cs} and T_c as a function of x from this work (solid circles). The dashed lines are drawn as a guide to the eye. Around $x = 1/8$, the material exhibits the “1/8-anomaly” where bulk superconductivity is suppressed. Surface enhancement of superconductivity was found in this 1/8-anomaly region. Also shown is a schematic illustrating the successive evolution of the sample as it is cooled to lower temperatures: first a fully resistive state for $T > T_{cs}$, then a resistive bulk “sandwiched” by superconducting surfaces for $T_c < T < T_{cs}$, and finally a fully superconducting state for $T < T_c$.

the region where we observed surface-enhanced T_{cs} for $x = 0.115$, 0.12 and 0.139 . For $x = 0.076$ and 0.092 , where the stripes are fluctuating [49, 51], the effect was not observed. The coincidence of the two phenomenon suggests a subtle relation, which we will discuss in this section.

3.3.1 The Stripe Order

Stabilization Effect

It is known that static stripes destroy the long-range order of superconductivity. When carriers are tied up in the stripes they cannot effectively participate in superconductivity, which results in a weaker phase coherency. For the suppression to be effective, however, low-temperature-tetragonal (LTT) structure is required to stabilize the fluctuating stripes [49, 56–58].

Indeed, reports suggest that suppression of the LTT structural transition by hydrostatic pressure or strain enhances the T_c of LBCO [123, 124]. Since surface represents an abrupt structural termination, it is possible that the crystal structure near the surface differs significantly from the bulk [104–106]. A well known example of surface reconstruction is the development of 7×7 structure on the (111) surface of Si [106]. Thus, perhaps the ab-plane surface does not transform into the LTT structure. Without the stabilization effect of the LTT structure, stripes at the surface become dynamic [49] and superconductivity is enhanced [73].

Testing this scenario would require surface-sensitive probes such as X-ray or neutron scattering to examine the surface structure. Another useful technique for this purpose is the low-energy electron diffraction (LEED) experiment, which has long been used to determine the surface structure of single-crystalline materials [104]. In either scenario, it is clear that the thickness of the surface layer

hosting superconductivity cannot be large, or else the bulk structural transition at T_d that we observe in the surface measurements would not be visible.

Proximity Effect

The bilayer systems of high- T_c cuprates are known for their ability to achieve a *higher* T_c than the parent materials [125–127]. In their pioneering work, Bozovic and co-workers synthesized a composite film consisting of a 15-unit-cell thick layer of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, covered with a 5-unit-cell layer of $\text{La}_2\text{CuO}_{4+\delta}$, as grown, on LaSrAlO_4 substrates [125]. Growth of atomically smooth layers in the experiment was achieved with an atomic-layer-by-layer molecular beam epitaxy (ALL-MBE) system. The $R(T)$ curve shows a sharp transition which drops to zero at $T_c = 51.5$ K, considerably higher than the maximum $T_c^{\text{max}} \sim 40$ K of single-phase $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (crystals or thin films) over the entire doping range. The enhanced T_c was later shown to be confined to the interface of the LSCO-LCO bilayer, with a thickness of approximately 1 unit cell [126].

Similar enhancement was observed in other LSCO bilayers grown on (100) SrTiO_3 substrates by pulsed laser deposition [127]. The layer on the substrate was a 90 nm-thick slab of underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which was in turn covered by an overdoped $\text{La}_{1.65}\text{Sr}_{0.35}\text{CuO}_4$ layer of 10 nm thick. The T_c of the bilayers was found to be higher than that of the bare underdoped layer of the same composition. Interestingly, the strongest enhancement occurs for $x = 0.12$.

Kivelson proposed that T_c enhancement could be achieved by coupling a material with high pairing scale to another material with large superfluid phase stiffness [128]. In the case of cuprates, the proximity effect could enhance the phase coherence in the underdoped system, and bring it to a higher T_c implied by the large pairing energy of underdoped regime. Notably, this theoretical proposal has been used to explain the T_c enhancement in LSCO bilayers [127].

We consider a similar effect for our observations. In addition to the structural change scenario, the electronic structure at the surface can also be different than in the bulk [104,105]. Since the stripe order strengthens pairing correlations but reduces phase stiffness, a different degree of stripe stabilization in the two regions may lead to an *effectively* bilayer system. This may happen, for example, if the surface does not develop the LTT structure that stabilizes the stripes. If it so happens that the phase stiffness is higher at the surface, then proximity coupling to the underdoped bulk of stronger pairing correlations could lead to enhanced values of T_{cs} [128].

LSCO-0.105

The 1/8-anomaly has also been reported for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO- x) [129,130]. However, the effect is less pronounced than the LBCO family due to the absence of LTT structure which stabilizes stripes [60,86,130]. Here, we measured ρ_s and ρ_{ab} of LSCO-0.105. The result is presented in Fig. 3.16. In the normal state, the two curves show similar curvature in temperature dependence. ρ_{ab} is slightly higher than ρ_s , possibly due to a larger degree of ρ_c pickup. The important observation is that, clearly, the surface result indicates $T_{cs} = 33$ K which is significantly higher than the bulk $T_c = 27$ K. This observation adds credence to the role of stripe order in our results.

3.3.2 What Doesn't Cause the Effect?

Chemical Inhomogeneity

The observations of two superconducting transitions may at first be attributed to inhomogeneity across the sample. For instance, the surface may have an effective concentration of Ba ions, x_s , different from its bulk counterpart x . Since bulk T_c correlates with x , this could lead to the enhanced T_{cs} . However,

Figure 3.16: Temperature dependence of ρ_s and ρ_{ab} of LSCO-0.105. Surface $T_{cs} = 33$ K and bulk $T_c = 27$ K are clearly resolved. Inset shows the magnified view near the superconducting transitions.

earlier investigation on the bulk superconductivity of LBCO revealed that the maximum $T_c^{\max} = 32$ K is reached for $x = 0.095$ [17]. The fact that surface T_{cs} of LBCO-0.115, LBCO-0.120, and LBCO-0.139 are higher than bulk $T_c^{\max}$ cannot be explained by an effective x_s . Also, if the enhanced values of T_{cs} were linked to such sample imperfection, it should be modified when the original surface is removed or heat treated. However, polishing, or annealing the surface up to 900 °C had no effect on the surface properties. In fact, the novel effect was reproducibly observed in a sample despite several times of surface polishing over a period of approximately two years.

Sample homogeneity in our work is further confirmed by the overlap of normal-state transport properties between the surface and the bulk. Thermopower (Fig. 3.4) and Nernst coefficient (Fig. 3.5) of the two regions show an excellent overlap prior to the onsets of the superconducting phases. When superconduct-

tivity is suppressed and the normal state recovered by strong magnetic field, the overlap of thermopower persists to even lower temperatures (Fig. 3.4). For resistivity measurements, with the unavoidable pickup of ρ_c taken into account, excellent scaling is observed between ρ_s and ρ_{ab} at temperatures higher than T_{cs} (Fig. 3.2). Scaling is also observed in resistance measured across different parts of the sample (Fig. 3.8). These results rule out macroscopic inhomogeneity.

Oxygen Deficiency

Oxygen can be removed from LBCO. A successful method was reported by Takayama-Muromachi and co-workers through the following process [131]. First, the sample is annealed at a very high temperature ($T \gtrsim 900$ K) in Ar-O₂ gas environment with a low partial pressure of oxygen, $PO_2 = 1 \times 10^{-3}$ atm. The annealing process takes about 5-12 hours. After that, the furnace glass tube that contains the sample is removed and immediately dipped into liquid LN₂. Importantly, the Ar-O₂ gas flow is maintained during the quenching process to prevent recovery of the sample oxidation.

We note that surface-enhanced superconductivity could not be due to oxygen deficiency. This is because the O₂-flow environment and annealing temperature (450 °C) used in our procedure is different from the aforementioned complicated process. In particular, the high values of surface T_{cs} , e.g. 36 K for LBCO-0.12, cannot be explained by oxygen deficiency, since the latter can mostly elevate the T_c to ~20 K.

Other Possibilities

We wish to point out what the observed effect is not. It is well known that in a magnetic field applied parallel to the sample surface, superconductivity first nucleates within the surface layer of thickness of the order of superconducting

coherence length [132]. However, we find superconductivity at the surface to be enhanced relative to the bulk even in zero magnetic field. It has also been proposed that superconductivity near surfaces can be enhanced due to modification of the electronic wavefunction by the scattering off the surface [133]. However, this effect is not expected to have a strong dependence on the sample doping, which we observe here. In addition, the strong anticorrelation between T_c and T_{cs} is not expected within this scenario.

3.4 Concluding Remarks

Extensive experimental and theoretical investigations on high- T_c cuprates since their discovery in 1986 have revealed that superconductivity in these materials occurs in close proximity to a variety of charge and spin ordered states. In the underdoped cuprates, whose composition is near the antiferromagnetic Mott insulator, the onset of global superconducting phase coherence is likely suppressed due to small superfluid stiffness [36, 134]. That is despite the fact that the interactions, which drive both superconductivity and other orderings, are stronger in this composition range than at optimal doping. Indeed, many attempts to increase the superconducting transition temperature have been undertaken, including those by spatially bringing together the strongly correlated physics of low-doping with the large superfluid density of highly doped cuprates [126–128]. It has also been found that application of strain to suppress the static charge and spin orders enhances superconductivity [135, 136]. Here we demonstrate that, surprisingly, the free surfaces of cuprates are capable of tilting the balance in favor of superconductivity.

That surface may enhance the superconducting order in cuprates has been discussed several times in the literature. Based on a BCS-like weak-coupling model, Giamarchi and co-workers proposed that the extremely short coherence length

of these materials may cause a $\sim 20\%$ enhancement on the superconducting gap near the surface, which persists over tens of inter-atomic distance into the bulk [133]. They further suggested that the effect could be more pronounced if strong-coupling interactions were taken into consideration. Another notable work is due to Jacobi and co-workers who performed high-resolution-electron-energy-loss spectroscopy (HREELS) on polycrystalline samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [137]. In the experiment, the loss intensity of inelastic scattering is inversely proportional to the ac conductivity of the sample, $\sigma(\omega)$, under certain approximations. Intriguingly, they found that the loss intensity shows a drastic drop below 200 K which is far above the bulk $T_c = 83$ K. Since the technique probes only a few copper-oxide layers at the surface, the observations have been attributed to an enhancement on the surface conductivity prior to the bulk superconducting transition. Despite these efforts, we note that the detection of an enhanced T_{cs} at the surface had not been conclusive.

Surface-enhanced superconductivity was not observed in earlier transport measurements on LBCO [84, 138–140]. A partial drop in ρ_{ab} at a temperature above T_c has been reported for LBCO near $x = 1/8$ and attributed to the onset of superconducting fluctuations [138]. Notably, this behavior was absent in other works [84, 139, 140]. The discrepancy may be due to differences in the contact configuration. For example, the partial drop in ρ_{ab} could be due to a contribution from the surface when the voltage contacts cover both the top and side of the sample (Fig. 3.14). On the other hand, confining the voltage contacts to the side of the sample removes the partial drop, and measures purely ρ_{ab} as demonstrated in this work. It is the careful probing of the surface and bulk regions separately by different contact configurations which enabled us to differentiate between the electronic transport through the surface and the bulk, and allowed us to observe the surface-enhanced T_{cs} in addition to the bulk T_c .

Several surface-sensitive experiments can be performed to investigate the origin

of this surface effect. As discussed in section 3.3.1, x-ray or neutron scattering can be used to examine the crystal structure of the surface. To probe the electronic structure of the surface, angle-resolved photoemission spectroscopy (ARPES) is one of the ideal choices. It is highly surface sensitive and importantly, able to measure the superconducting gap as a function of momentum k . Interestingly, reported ARPES data of LBCO reveals an d -wave gap whose magnitude peaks at $x = 1/8$, even though the bulk T_c is the lowest at that point [141]. This led the authors to question on the origin of the observed d -wave gap in the absence of bulk superconductivity. Here, our finding suggests that the superconducting gap could be of surface origin.

We have demonstrated the very first experimental observation of surface-enhanced superconductivity in bulk material. This was achieved by probing the electrical and thermoelectric transport properties of the surface, which shows superconducting characteristics including the T_{cs} strongly enhanced relative to the bulk counterpart. The effect was observed in samples where other peculiar electronic orders are present, pointing to an origin possibly linked to the strong correlations in these materials. Our finding presents a fundamentally new surface effect on superconductivity. Further investigations on its mechanism, occurrence in other materials, and attainable values of T_{cs} , may lead to a hitherto unexplored paradigm for surface electronic properties. More than 25 years ago, the discovery of LBCO by Bednorz and Muller [7] led to an explosion of research activities on high- T_c superconductors that continues to the present day. Clearly, this particular material remains a “treasure box” of novel properties, constantly inspiring the imagination of researchers towards a deeper understanding of superconductivity in strongly correlated systems

4 Nernst Effect Studies of Striped Superconductors

As described in chapter 1, the onset of stripe order at low temperatures suppresses bulk superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO- x). However, the mechanism responsible for this effect is not fully understood and remains an active research topic for high- T_c cuprates.

From an experimental perspective, it is instructive to investigate the quasi-particle transport and superconducting fluctuations in the stripe phase. This motivated us to measure the Nernst effect on the $x = 0.12$ sample previously characterized in chapter 3, where the suppression on bulk T_c is found to be the most pronounced among other compositions available to us. Several unusual features are identified in both the measurements performed with a finite and zero magnetic field, respectively. We discuss possible origins for the observations.

4.1 Sources of Nernst Signal

In this section, we discuss the contributions of quasiparticles and superconducting (SC) fluctuations to the Nernst effect. Note that the SC fluctuations are classified by phase-fluctuations or amplitude-fluctuations. The flow of superconducting vortices, and short-life Cooper pairs, are responsible for these two cases, respectively.

Consider a sample subject to a longitudinal temperature gradient $(-\nabla_x T)$, and a magnetic field along the vertical direction (H_z) . The generation of a transverse electric field (E_y) is known as the Nernst effect.

Starting with the transport equation

$$j = \sigma \cdot E + \alpha \cdot (-\nabla T) \quad (4.1)$$

where σ and α are the two-dimensional electrical and Peltier conductivity tensors, respectively. The components of j are therefore

$$\begin{aligned} j_x &= \sigma E_x + \sigma_{xy} E_y + \alpha(-\nabla_x T) + \alpha_{xy}(-\nabla_y T) \\ j_y &= \sigma E_y + \sigma_{yx} E_x + \alpha(-\nabla_y T) + \alpha_{yx}(-\nabla_x T) \end{aligned} \quad (4.2)$$

where $\sigma = \sigma_{xx} = \sigma_{yy}$ and $\alpha = \alpha_{xx} = \alpha_{yy}$ are the diagonal elements of the tensors. The experimental conditions of Nernst measurement require that $\nabla_y T = 0$ and $j = 0$. This leads to

$$\begin{aligned} 0 &= \sigma E_x + \sigma_{xy} E_y + \alpha(-\nabla_x T) \\ 0 &= \sigma E_y + \sigma_{yx} E_x + \alpha_{yx}(-\nabla_x T) \end{aligned} \quad (4.3)$$

The Nernst coefficient is defined as

$$\begin{aligned} e_y &= \frac{E_y}{-\nabla T} \\ &= \frac{\alpha_{xy}\sigma - \alpha\sigma_{xy}}{\sigma^2 + \sigma_{xy}^2} \end{aligned} \quad (4.4)$$

Eqn. 4.4 is the master equation for Nernst effect which express e_y in terms of conductivity tensor elements.

One can relates e_y to other experimentally measurable transport quantities. Recall that thermopower $S = E_x/(-\nabla_x T) = \alpha/\sigma$, and Hall angle $\tan \theta_H =$

σ_{xy}/σ . Therefore, we can rewrite Eqn. 4.4 as

$$\begin{aligned}
 e_y &= \frac{\alpha_{xy}\sigma - \alpha\sigma_{xy}}{\sigma^2(1 + (\sigma_{xy}/\sigma)^2)} \\
 &= \frac{\alpha_{xy}}{\sigma} - \frac{\alpha\sigma_{xy}}{\sigma^2} \\
 &= \frac{\alpha_{xy}}{\sigma} - S \tan \theta_H
 \end{aligned} \tag{4.5}$$

Since S , $\tan \theta_H$, and σ can be directly measured in experiments, it turns out that the *off-diagonal* Peltier component α_{xy} is effectively probed in the Nernst effect measurement.

4.1.1 Quasiparticle Contribution

In semi-classical Boltzmann transport theory, the Peltier conductivity is closely related to the electrical conductivity through [142]

$$\alpha = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{\partial \sigma}{\partial \epsilon} \right)_\mu \tag{4.6}$$

$$\alpha_{xy} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{\partial \sigma_{xy}}{\partial \epsilon} \right)_\mu \tag{4.7}$$

where μ is the chemical potential of the system. Substituting Eqns. 4.6 and 4.7 into Eqn. 4.4 and recall that $\sigma_{xy}/\sigma = \tan \theta_H$, we get

$$\begin{aligned}
 e_y &= \frac{\alpha_{xy}\sigma - \alpha\sigma_{xy}}{\sigma^2 + \sigma_{xy}^2} \\
 &= \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \sigma \left(\frac{\partial \sigma_{xy}}{\partial \epsilon} \right)_\mu - \sigma_{xy} \left(\frac{\partial \sigma}{\partial \epsilon} \right)_\mu \right\} \left(\frac{1}{\sigma^2 + \sigma_{xy}^2} \right) \\
 &= \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{\partial (\sigma_{xy}/\sigma)}{\partial \epsilon} \right)_\mu \\
 &= \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left(\frac{\partial \tan \theta_H}{\partial \epsilon} \right)_\mu
 \end{aligned} \tag{4.8}$$

which shows that e_y is linearly proportional to T , and the first derivative of Hall angle θ_H with respect to energy ϵ at the chemical potential.

One-band Metal

According to Eqn. 4.8, the Nernst signal is finite when the derivative of Hall angle is non-zero. To the first approximation,

$$\left(\frac{\partial \tan \theta_H}{\partial \epsilon} \right)_{\mu} = \frac{\tan \theta_H}{\epsilon_F} \quad (4.9)$$

where a linear dependence of energy in $\tan \theta$ is assumed near the Fermi level [142]. Then, Eqn. 4.8 is simplified to

$$e_y = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\tan \theta_H}{\epsilon_F} \quad (4.10)$$

For a one-band metal, $\tan \theta_H$ is related to the carrier mobility μ through

$$\tan \theta_H / B = \mu = \frac{e\tau}{m^*} \quad (4.11)$$

where τ is the scattering time, and m^* is the effective mass of the carriers. Thus

$$e_y = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\mu}{\epsilon_F} B \quad (4.12)$$

Eqn. 4.12 shows that the Nernst signal is strong when the electronic mobility is large and the Fermi energy is small.

In the special case where

$$\left(\frac{\partial \tan \theta_H}{\partial \epsilon} \right)_{\mu} = 0 \quad (4.13)$$

the Nernst signal will be negligible. This condition is known as the Sondheimer

cancellation and typically observed in conventional metals [143].

The cancellation is equivalent to the special case of Eqn. 4.4, where

$$\begin{aligned}\sigma E_x &= \alpha \nabla_x T \\ \sigma_{yx} E_x &= \alpha_{yx} \nabla_x T\end{aligned}\tag{4.14}$$

This corresponds to a balance in the longitudinal *and* the transverse components of the counter-flow currents $\alpha(-\nabla_x T)$ and σE_x .

Ambipolar Metal

In the proceeding section, the Sondheimer cancellation is derived only for a one-band metal. Consider an ambipolar metal with two conduction bands of opposite charge carrier signs. Eqn. 4.4 is then modified to [142]

$$e_y = \frac{(\alpha_{xy}^+ + \alpha_{xy}^-)(\sigma^+ + \sigma^-) - (\alpha^+ + \alpha^-)(\sigma_{xy}^+ + \sigma_{xy}^-)}{(\sigma^+ + \sigma^-)^2 + (\sigma_{xy}^+ + \sigma_{xy}^-)^2}\tag{4.15}$$

where the superscript designates the sign of the carriers. Here, the cancellation within each band (if any) does not imply a cancellation of the overall signal. For example, the ambipolar NbSe₂ is known for having a large Nernst signal [144].

4.1.2 Vortex Contribution

Superconductors are known to expel an externally applied magnetic field due to the Meissner effect. However, when the magnetic penetration depth λ is relatively large compared to the coherence superconducting length ξ , such that, $\lambda/\xi > 1/\sqrt{2}$, it becomes more energetically favorable for the magnetic field to penetrate the superconductor as flux quantum of $\phi_0 = h/2e$ [103]. These superconductors are known as type-2. An extreme example is the high- T_c copper-oxides which typically have a large $\lambda \sim 1000$ Å and a short coherence length

$\xi \sim 10$ Å. The flux quantum is also known as superconducting vortex [145]. The vortex has a normal-state core of size $\sim \xi$, and surrounded by circulating supercurrent (Fig. 4.1). At the core center, the superconducting order parameter $\psi(r)$ is suppressed to zero but its amplitude recovers over a length scale ξ . Conversely, the local magnetic flux density $B(r)$ is strongest at the core center and decays over the penetration depth length scale λ .

Figure 4.1: Schematic of a vortex in a type-2 superconductor. The order parameter $|\psi|$ and the local magnetic field B vary with their own characteristics length scales, ξ and λ , respectively.

A moving vortex causes phase slip, and generates a potential difference along the transverse direction

$$2eV = 2\pi\hbar\dot{n}_v \quad (4.16)$$

When a Cooper pair travels around the vortex core for a full circle, its phase θ jumps by 2π . According to Josephson, the phase slips generated by a moving vortex produce an electric field along the direction transverse to its motion [113]. The electric field is given by the simple expression

$$E = B \times v \quad (4.17)$$

where B is the external magnetic flux density, and v is the velocity of the vortex. In the Nernst effect measurement, the applied temperature gradient causes the vortices to move from the hotter to the colder ends. The transport occurs since the normal-state vortex core has a finite entropy relative to the superfluid background, which tends to diffuse away to colder regions to minimize the system entropy. The phase slips generated by thermally induced motion of these vortices therefore results in a traverse electric field known as the vortex-Nernst signal.

Figure 4.2: Vortex-Nernst effect in a type-2 superconductor. The externally applied field B_z generates vortices in the sample. A temperature gradient $-\nabla_x T$ drives these vortices to the cold end at velocity v . The electric field E_y generated along the transverse direction is detected as the vortex-Nernst signal.

Consider a simple scenario [114] where each vortex carries an entropy of S_ϕ . The entropy force exerted on it by the temperature gradient ∇T is $f_\phi = S_\phi(-\nabla T)$. In the steady state, this entropic force is balanced by the damping force $f_\eta = \eta v$, where η is the viscosity and v is the velocity of the vortex. The vortex-Nernst signal is given by

$$e_y = \frac{E}{-\nabla T} = B \times v = BS_\phi/\eta \quad (4.18)$$

The viscosity to flux-flow can be measured experimentally. Recall that in a flux-flow resistivity measurement, the Lorentz force $f_L = j \times \phi$ on the vortex

is balanced by the same damping force. So we have $j\phi_0 = \eta v$, which gives flux flow resistivity

$$\rho_H = E/j = B \times v/j = B \cdot \phi_0/\eta \quad (4.19)$$

combining the two equations, we derive the vortex-Nernst signal as

$$e_y = \frac{\rho_H \cdot S_\phi}{\phi_0} \quad (4.20)$$

Eqn. 4.20 relates the vortex-Nernst signal to the flux-flow resistivity and the entropy of each vortex core.

4.1.3 Cooper-Pair Contribution

A finite Nernst signal in superconductors can also result from fluctuations in the pairing amplitude. For example, Ussishkin, Sondhi and Huse (USH) calculated the contribution of Gaussian superconducting fluctuations (amplitude) on thermoelectric transport [146]. In their model, the thermal excitations of Cooper pairs above T_c has a finite lifetime that decreases with increasing temperature. Under an applied temperature gradient, the pairs that diffuse towards the cold end live longer than those flowing in the opposite direction, which causes a *net* flow in the former direction. In the presence of a magnetic field, the flow is deflected due to the Lorentz force which leads to a transverse electric field measured as the Nernst signal.

Based on the Lawrence-Doniach model, the USH theory predicts that in the *low-field* limit ($B \rightarrow 0$) the Nernst coefficient is

$$v_N = v_N^{sc} + v_N^n \quad (4.21)$$

where v_N^{sc} and v_N^n are respectively the Gaussian-fluctuation and the normal-state quasiparticle contributions. The Gaussian contribution is given by

$$v_N^{sc} = \frac{\alpha_{xy}^{sc}}{\sigma} \frac{1}{H} \quad (4.22)$$

where σ is the *total* electrical conductivity, and α_{xy}^{sc} is the transverse Peltier component of the short-lifetime Cooper pairs. For strongly-layered superconductors,

$$\alpha_{xy}^{sc} = \frac{k_B e \xi_{ab}^2}{6\pi\hbar l_B^2 s} \frac{1}{\sqrt{1 + (2\xi_c/s)^2}} \quad (4.23)$$

where ξ_{ab} and ξ_c are the coherence length along the ab-plane and c-axis, respectively, s is the inter-layer spacing, and $l_B = (\hbar/eB)^{1/2}$ is the magnetic length scale. Note that temperature dependence of α_{xy}^{sc} depends only on the coherence length $\xi_{ab} = \xi_{ab}^0 \sqrt{T_c/(T - T_c)}$ and the anisotropy $\gamma = \xi_c/\xi_{ab}$. A test of the Gaussian fluctuations is given by [147, 148]

$$\alpha_{xy}^{sc} \propto \frac{1}{T \ln(T/T_c)} \quad (4.24)$$

Near T_c , the quasiparticle contribution is negligible which gives the approximation $v_N \approx v_N^{sc}$. A fit of Eqn. 4.24 to $\alpha_{xy}^{sc} = v_N \sigma$ is considered an effective identification of Gaussian fluctuations, which has been verified in a range of materials including the high- T_c copper-oxides [100, 146, 149–151].

4.2 Nernst Effect in High- T_c Copper-Oxides

4.2.1 Discovery and Controversy

As described in sec. 4.1, superconducting fluctuations may occur in the phase or in the amplitude of the order parameter. In the former case, the amplitude of the superconducting order parameter $|\psi|$ remains finite above T_c . However, the thermally excited vortex excitations cause fluctuations in the phase θ , since each vortex represents a 2π phase singularity in the superfluid. In the case of amplitude fluctuations, while $|\psi|$ vanishes above T_c , amplitude fluctuations happen when $\langle\psi^2\rangle \neq 0$. Physically, this implies the presence of superfluid “droplets” of size ξ , the superconducting coherence length [103]. These droplets provide short-life Cooper pairs that affect the physical properties of the material, such as the phenomenon of paraconductivity above T_c .

Nernst effect measurements on high- T_c copper-oxides were initially focused on the flux-flow mechanism near T_c [96, 115, 116, 152, 153]. It received considerable attention after the observation of a signal that persists up to temperatures far above T_c in superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [97]. The effect has been interpreted as vortex excitations above T_c , and taken as evidence for *phase-fluctuating* superconductivity [98, 154]. Such an interpretation is further supported by the detection of diamagnetism near the onset of the Nernst signal [155–158]. Importantly, this effect was considered incompatible with the standard *Gaussian fluctuations* (in amplitude) of a superconducting order parameter, since the latter may not extend to such high temperatures.

Controversies arose, as according to some groups, Gaussian fluctuations could explain the previously observed Nernst effect [151, 159] and diamagnetism [160, 161] if the anisotropy and small conductivity near T_c of quasi-2D systems were treated correctly [146–148]. That the Nernst signal correlates to electrical con-

ductivity was indeed demonstrated in the Zn doping on YBCO films [151]. Furthermore, the “stripe order” (sec.1.3) was claimed to be another source for the Nernst signal [99,162]. In the striped superconductor $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{Sr}_x\text{CuO}_4$ (Eu-LSCO-1/8), two separate peaks in the Nernst coefficients were resolved and attributed *respectively* to the onset of stripe order at high temperature and bulk superconductivity near T_c . It was further suggested that the vortex-excitation mechanism [97,98] is not required to explain the high-temperature onset of the Nernst effect. Subsequent analysis showed that in Eu-LSCO-1/8, the superconducting component of the Nernst signal could be fit to the Gaussian fluctuations [100,146–148].

4.2.2 Zero-Field Nernst Effect

A recent transport study by Li *et al.* has detected a finite Nernst effect signal in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 1/8$) that onsets at the charge ordering temperature $T_{co} > T_c$ even in zero magnetic field [162]. The zero-field Nernst (ZFN) signal has been interpreted as evidence of vortex generation due to time-reversal-symmetry breaking (TRSB). According to this scenario, the vortices appear even at $H = 0$, and are predominantly along a certain direction to produce a finite e_N . The irreversibility field H_{irr} below which vortices can be trapped, vanishes at 20 K while e_N attains its maximum. This rules out the possibility of e_N being caused by field-induced vortices trapped in a non-equilibrium state, thus pointing to a *spontaneous* magnetism that leads to the ZFN signal.

Pair-density-wave (PDW) superconductivity has been proposed to explain the TRSB [163–165]. In the model, superconductivity develops on the electronic stripes. The stripe modulation direction is orthogonal between adjacent layers. The stripe system can be considered as a 3D discrete lattice of Josephson junctions, where the in-plane and out-of-plane lattice spacing are taken as the

inter-stripe and the inter-plane distances, respectively. Calculations show that it is energetically favorable to develop phase incoherence in the system. This is attained through the spontaneous current flow across the junctions, which in turn produces a finite magnetic field and leads to the TRSB. In the PDW scenario, therefore, vortices are induced by spontaneous magnetism below T_{co} . These vortices are suggested to produce the ZFN signal when a temperature gradient is applied.

According to some groups [166–168], the ZFN effect may also occur in a “gyrotropic” system where the inversion and mirror symmetries are broken. Consider a homogeneous medium which obeys time-reversal symmetry, the dielectric tensor satisfies the reciprocity relations $\epsilon_{ab}(\omega, k) = \epsilon_{ab}(\omega, -k)$. Any odd in k contribution to ϵ must be antisymmetric, that is

$$\epsilon_{ab}(\omega, k) = \epsilon_{ab}(\omega) + i\gamma_{abc}(\omega)k_m + \dots \quad (4.25)$$

where $\gamma_{abc}(\omega) = -\gamma_{abc}(\omega)$ is the first derivative of $\epsilon_{ab}(\omega, 0)$ with respect to the wave vector in the medium, k_m , and “...” refers to the higher order terms of k_m . $\gamma_{abc}(\omega)$ is called the gyrotropic tensor. A system is said to be gyrotropic when $\gamma_{abc}(\omega) \neq 0$. This leads to non-zero off-diagonal elements of the conductivity and Peltier tensors, σ_{xy} and α_{xy} , hence the ZFN signal [166].

Chiral charge order has been proposed to explain the gyrotropic order in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 1/8$) [166, 168]. Consider a tetragonal structure consisting of unidirectional stripes in the ab planes. The direction of stripes rotate by $\pi/2$ between neighboring planes. More importantly, the charge stripes are stacked in a chiral fashion along the c -axis with a period of four, causing a “handedness” in the system. This chiral state breaks inversion and mirror symmetries.

The possibility of a gyrotropic order is also supported by the observation of Kerr effect below the charge stripe ordering temperature T_{co} [167, 168]. In the

measurement, the polarization plane of the reflected light off the sample surface is measured. The rotation angle is given by [169]

$$\theta_K = -\text{Im} \left\{ \frac{\tilde{n}_L - \tilde{n}_R}{\tilde{n}_L \tilde{n}_R - 1} \right\} \quad (4.26)$$

where the complex refraction indices $\tilde{n}_{R,L}$ for right (R) and left (L) circularly polarized light are related to the complex optical conductivity σ by

$$\epsilon_{R,L} = \tilde{n}_{R,L}^2 = (n_{R,L} + i\kappa_{R,L})^2 = 1 + i \frac{4\pi\sigma_{R,L}}{\omega} \quad (4.27)$$

Therefore, a finite Kerr response occurs when

$$\tilde{n}_L \neq \tilde{n}_R \quad (4.28)$$

There are two situations where Eqn. 4.28 can be satisfied. In the first case, the occurrence of TRSB leads to

$$\sigma_{R,L} = \sigma_{xx} \pm i\sigma_{xy} \quad (4.29)$$

In the second case, the breaking of inversion and mirror symmetries by a gyrotropic order leads to $\gamma_{abc} \neq 0$.

Initially, the results were interpreted as TRSB. However, subsequent observations cast doubts on the standard interpretation. The sign of θ_K was found to be the same for opposite surfaces of the same sample, and could not be “trained” while cooling through T_{co} with strong magnetic field [167]. Furthermore, it shows odd response with respect to strain applied in the (110) direction [168]. These have been taken as the evidence for gyrotropic ordering [166, 168, 170].

The source of ZFN effect is still a subject of much debate. In either case, the symmetry breaking is to likely be associated with the *stripe order*, since the

onset of ZFN effect coincides with that of the charge stripes.

4.3 Data and Analysis

This section presents our results of Nernst effect measurements on LBCO-0.12. From the results in chapter 3, we know that the ab-plane surface and the bulk of this material develop two distinct superconducting orders. Here, we focus our measurements on the bulk for a more pronounced stripe order. This is supported by the fact that the bulk T_c is more suppressed than the surface counterpart. As a result, the effects of stripes on electronic transport and SC fluctuations can be readily identified and examined in the bulk measurements.

Figure 4.3: Schematic contact configuration for the Nernst effect measurements reported in this chapter. Reproduced from Fig. 2.6.

The experimental setup of our measurements is shown in Fig. 4.3. In a typical run, the magnetic field is applied along the crystal c-axis. Distinction between the crystal a- and b-axes was omitted as the samples were not detwinned. Temperature gradient ~ 0.1 K/mm is applied along the long axis of the sample, and voltage across the transverse direction is measured as the Nernst signal. To remove the unavoidable pick-up of thermopower (field-symmetric) due to misalignment of voltage contacts, H was applied in both directions so that only the field-antisymmetric part of the data is taken.

Before we proceed, we note that there are two conventions for the sign of Nernst signal (*Fig. 4.4*). In the first one, the electric field that develops along the y-axis in the presence of a temperature gradient along the x-axis and a magnetic field along the z-axis, is taken as positive for the Nernst effect. In the second one, the x-axis is defined by the heat-flow direction, i.e. $-\nabla_x T$ instead of temperature gradient $\nabla_x T$. It is also known as the *vortex convention* since a moving vortex will produce a positive signal $E_y = B \times v$, where v is the vortex velocity which follows the heat-flow direction. The vortex convention is used in this work.

Figure 4.4: Two sign conventions for Nernst effect. Left panel shows the traditional convention that has been used in the old literature. Right panel shows the vortex convention which has become widely used in the recent years. In this convention, vortex-flow that is driven by a temperature gradient will produce a positive signal.

Previous characterizations on LBCO-0.120 (chapter 3) revealed that the transition from low-temperature orthogonal (LTO) to low-temperature tetragonal (LTT) structures occurs at $T_d = 51$ K. Furthermore, the charge stripes and the bulk superconductivity onset at $T_{co} = 47$ K and $T_c = 22$ K, respectively.

The temperature dependence of Nernst coefficient $v_N = e_N/H$ at various applied magnetic fields H is shown in Fig. 4.5. At high temperatures, v_N is caused by quasiparticle transport which is weak, field-independent, and nearly T -independent due to the so-called Sondheimer cancellation [98]. Below the onset temperature $T_v \sim 110$ K, v_N shows upward deviation from the high-temperature

Figure 4.5: Temperature dependence of ν_N at various magnetic fields. $T_v \sim 110$ K indicates the deviation of ν_N from the quasiparticle background signal. Two peaks are observed which onsets respectively at T_1 and T_2 . Application of higher H suppresses the low-temperature peak but no effects on its high-temperature counterpart. T_B marks the onset temperature of field-dependence in ν_N . Inset: ν/T is plotted against T for precise determination of T_1 , T_B , and T_2 . Dashed lines show linear extrapolations from the regimes prior to T_1 and T_2 to the lower temperatures. T_1 and T_2 are taken as the point at which ν_N show upward kink from the linear extrapolations.

quasiparticle background. The origin of the high-temperature onset is still an open question, although several scenarios based on vortex excitations [97, 98], Gaussian fluctuations [146, 151], and stripe order [99, 100, 108] have been proposed.

At low temperatures, ν_N develops a field-dependence below $T_B = 45$ K. The suppression of ν_N by magnetic field indicates a sizable contribution from SC fluctuations [97, 98, 146, 151]. We observe *two* separate peaks in ν_N which are better resolved under the strongest applied magnetic field $H = 14$ T. On *decreasing* magnetic field, the high-temperature peak is not affected, but the low-

temperature peak grows in magnitude and shifts to higher temperature. The onset temperatures for the two peaks, $T_1 = 51$ K and $T_2 = 33$ K, are determined as the points at which v_N/T shows an upward kink with decreasing temperature (inset of Fig. 4.5).

The high-temperature peak has been attributed to quasiparticles [99, 100] and SC-fluctuations [162]. It is known that the LTT structural transition stabilizes the stripe order and thus affect the electronic properties [56–58]. For example, kinks in ρ_{ab} and S_{ab} are observed at structural transition temperature, T_d . It is thus reasonable that the same effect is also responsible for the v_N peak which onsets at $T_1 = T_d$. Another possible origin for the high-temperature peak is the superconducting phase fluctuations which persist up to $T_v \sim 100$ K [97, 98, 157, 162]. However, as we shall show shortly, Gaussian fluctuations onset at a much lower temperature than T_1 . Thus our results suggest that near T_c , v_N is dominated by quasiparticle signal.

The low-temperature peak shows a strong response to magnetic fields. At higher magnetic fields, its is suppressed and both T_2 and the peak position are shifted to lower temperatures. This observation, and the fact that it develops around T_c , suggest a superconducting origin. There has been a report that in striped superconductor, Gaussian fluctuations are responsible for v_N above T_c [99, 100]. In the $H \rightarrow 0$ limit, Gaussian theory [146–148] predicts that (Eqn. 4.24)

$$v_{sc}\sigma = \alpha_{xy}^{sc}/H \sim \frac{1}{T \ln(T/T_c)} \quad (4.30)$$

where σ is the normal-state resistivity.

Fig. 4.6 presents our fitting results for $H = 1$ T which represent the low-field limit. A linear relation between $1/(v_N\sigma T)$ and $\ln(T/T_c)$ is observed which persists up to $T_{gf} = 33$ K or $1.6T_c$. Thus Gaussian fluctuations onset at T_{gf} . Importantly, the onset of Gaussian fluctuations coincides with that of the low-

temperature v_N peak, i.e. $T_{gf} = T_2$. This indicates that the latter originates from Gaussian fluctuations.

Figure 4.6: Plot of $1/(v_N \sigma T)$ versus $\ln(T/T_c)$. Solid line is the fit to Gaussian theory which predicts a linear relation between the two quantities [147, 148]. $T_c = 23.3$ K is used in the fitting,. From the fitting, $T_{gf} = 33$ K is determined. $T_B = 45$ K is the onset temperature for the field-dependence of v_N .

We note that the field-dependence in v_N occurs at $T_B > T_{gf}$. As a check, we focus on the field-sweep measurements of e_N at various temperatures (Fig. 4.7). The results clearly show that e_N is nonlinear in H for $T < T_B = 45$ K. The nonlinear e_N has been commonly interpreted as the signature of superconducting fluctuations in high- T_c cuprates [97–100]. Our results suggest a non-Gaussian fluctuation regime over $T_{gf} < T < T_B$.

As a check for superconducting fluctuations, we consider the magnetization measurements on LBCO-0.12. Fig. 4.8 presents our data taken with $H = 20$ Oe in field-cooling (FC) and zero-field-cooling (ZFC) conditions. We observe a strong onset of diamagnetism just below T_B . Notably, this is the temperature regime

Figure 4.7: Field dependence of e_N at various temperatures. Non-linear curves are observed for $T < T_B = 45$ K which is commonly interpreted as the signature of SC fluctuations.

where the surface-enhanced superconductivity develops as discussed in the previous chapter. Difference between the FC and ZFC data becomes sizable as the temperature drops below T_{gf} . This is caused by the trapping of vortices in the FC run, which significantly reduces the diamagnetic response of the sample. Incidentally, at a much lower temperature $T_{3D} = 12$ K, the sample develops a stronger diamagnetic response possibly due to an enhancement on the phase coherency along the c-axis [138, 171].

Next, we present our results on the zero-field-Nernst (ZFN) effect. Typically, the Nernst coefficient measurement is influenced by unavoidable pickup of the longitudinal thermopower (S_{ab}) due to a slight misalignment of the contact leads. While field-dependent Nernst coefficient can be determined using measurements at fields $\pm H$, this is not possible for $H = 0$. Therefore, the true ZFN signal,

Figure 4.8: Temperature dependence of M/H . T_B is the onset temperature of field-dependent Nernst coefficient, T_{gf} the onset of Gaussian fluctuations, T_c the superconducting transition defined by zero resistivity, and T_{3D} the onset of superconducting phase coherency along the c -axis [138,171]. Courtesy of Dr Anjan Soumyanarayanan (Laboratory for Physics of Novel Electronics; Prof. Christos Panagopoulos' group).

e_{ZFN} , is obtained by removing the S_{ab} contribution from the observed Nernst signal e_y^{obs} according to

$$e_{ZFN} = e_y^{obs} - kS_{ab} \quad (4.31)$$

where k is a constant due to the contact misalignment.

Fig. 4.9 shows the temperature dependence of e_y^{obs} . S_{ab} is scaled by a factor $1/9.2$ and overlaid on e_y^{obs} . At high temperatures, the two curves overlap since e_y^{obs} is simply the pickup of thermopower due to slight contact misalignment. Below T_d , however, the two curves deviate due to the contribution of ZFN signal to e_y^{obs} . The difference between the two curves is taken as e_{ZFN} which is non-zero

Figure 4.9: Temperature dependence of the observed e_y^{obs} and S_{ab} of LBCO-0.12. S_{ab} is scaled by a factor of $1/9.2$. The difference between the two curves, which onset below T_{co} (arrow), is taken as the ZFN signal, e_{ZFN} .

over $T_c < T < T_d$ (Fig. 4.10). Importantly, the curve of e_{ZFN} shows a strong peak at T_{co} with a maximum value $\sim 1.33 \mu\text{V/K}$. At lower temperatures, a broad peak is observed around $T^{**} = 42 \text{ K}$, followed by another peak which is sharply centered at $T^* = 26 \text{ K}$.

Nernst signal is typically induced by a finite magnetic field. Therefore, a possible cause of ZFN effect is the presence of *spontaneous* magnetism. The formation of superconducting stripes has previously been proposed to explain such magnetism [162, 163, 165, 172, 173]. In the model, a finite magnetic field is generated by the flow of supercurrent across intrinsic Josephson junctions. In our case, the e_{ZFN} observed below T_B might be associated with such supercurrent-induced magnetism. As temperature decreases, the system develops stronger phase coherence which tends to weaken the magnetism, and causes e_{ZFN} to drop below T^{**} . Just above T_c , Gaussian fluctuations produce short-lived Cooper pairs

which can generate Nernst signal [146–148]. The sharp peak at T^* could be caused by these pairs. As temperature approaches T_c , e_{ZFN} vanishes due to the onset of global phase-coherent superconductivity.

We further note that the observed Nernst coefficient in non-zero magnetic fields for our case suggests the dominance of quasiparticle signal near T_{co} (Fig. 4.5). It is therefore reasonable that the strong e_{ZFN} peak observed at T_{co} could be also of quasiparticle origin. For instance, theories proposed that chiral ordering of charge stripes along the crystal c-axis break inversion and mirror symmetries, and lead to a non-zero e_{ZFN} [166, 174]. Evidence for such symmetry breaking does exist according to several Kerr effect experiments [167, 168].

Figure 4.10: Temperature dependence of e_{ZFN} of LBCO-0.12. The signal shows a dramatic onset below T_d which leads to a strong peak at T_{co} . A broad peak is found at T^{**} , and another sharp peak at T^* which is just above T_c .

4.4 Concluding Remarks

In summary, we performed high-resolution Nernst effect measurements on LBCO-0.12. Two peaks in v_N are resolved. The high-temperature peak onsets at the structural transition temperature T_d and is possibly affected by quasiparticle transport in the LTT structure. The low-temperature peak and the Gaussian fluctuations onset at the same temperature T_{gf} . This indicates that the former is generated by short-lived Cooper pairs in the fluctuation regime.

Several unique features are observed in the stripe phase. A non-Gaussian fluctuation regime is identified which indicates an unusual state of superconductivity. A possible scenario is the formation of superconducting stripes which are phase-incoherent across one another. Theory predicts spontaneous magnetism in the striped superconducting state, which is supported by our detection of a finite ZFN signal over a temperature range where stripes are prominent. Furthermore, we observed a strong ZFN signal that peaks at the charge stripe ordering temperature T_{co} . Chiral ordering of stripes along the c-axis, which break inversion and mirror symmetries is discussed as a possible origin for the peculiar feature.

We showed that Nernst effect measurement is a valuable tool to characterize the superconducting fluctuations and quasiparticle transport associated with stripes. The results presented here provide new insight into the effects of stripes on the electronic properties of high- T_c copper oxides. In the future, it will be useful to measure LBCO of other compositions for a systematic study of the effects across the stripe regime of the phase diagram.

5 Tunnel-Diode-Oscillator Technique

This chapter introduces the measurements of magnetic penetration depth using the tunnel-diode-oscillator (TDO) technique. The experimental technique is described in detail. We discuss the achievements made for the TDO setup in our laboratory and propose future works towards its completion.

5.1 Superfluid Density

5.1.1 Superconducting Gap Function

The superconducting ground state is a condensate of Cooper pairs. At $T = 0$, all the carrier electrons are paired and go into a single quantum-mechanical state with long-range macroscopic phase coherence. The condensate is separated from the continuum of excited states by a superconducting energy gap Δ_k developed on the Fermi surface. At low temperatures, thermal excitations break Cooper pairs into quasiparticles. For a quasiparticle of wave vector k , its energy is given by

$$E_k = \left(\varepsilon_k^2 + \Delta_k^2 \right)^{1/2} \quad (5.1)$$

where ε_k is the energy level of normal-state electron, and Δ_k the gap function determined by the microscopic pairing mechanism. In BCS theory, the strength of electron-phonon interaction does not depend on k , which leads to an isotropic system with $\Delta_k = \Delta$. Systems with such spherical symmetry are called isotropic *s*-wave superconductors. In reality, Δ_k is often modified by the crystal structure of the system. For example, in a tetragonal system where $a = b \neq c$, one expects different gap magnitude for k along *c*-axis than for k along *a*- or *b*-axis. Systems that lack spherical symmetry but have the full symmetry of the underlying crystal symmetry are called *anisotropic s*-wave superconductors.

The k -dependence of Δ_k , known as the *pairing symmetry* [175–177], classifies superconductors. In conventional superconductors, pairing of electrons occurs through the electron-phonon interaction. These systems often have *s*-wave symmetry. Unconventional superconductivity refers to the cases where the pairing symmetry is *lower* than that of the underlying crystal. In particular, there exists point or line *nodes* where $\Delta_k = 0$ for certain k on the Fermi surface. The pairing mechanisms of these materials are often not phonon-mediated.

While determination of the pairing symmetry does not necessarily specify the mechanism, it does impose general constraints on the possible models. For example, the establishment of *d*-wave pairing symmetry in high- T_c copper-oxides [178–180] is consistent with the model of antiferromagnetic spin fluctuations [181]. Specifically, it is a $d_{x^2-y^2}$ state with the gap function

$$\Delta_k = \Delta_0(\cos k_x a - \cos k_y a)/2 \quad (5.2)$$

where Δ_0 is the gap amplitude and a is the in-plane lattice constant of the system. A polar plot of $\Delta_k = \Delta_0 \cos 2\phi$ versus the azimuthal angle $\phi = \arctan(k_y/k_x)$ is shown in Fig. 5.1.

Figure 5.1: Schematic of the $d_{x^2-y^2}$ superconducting gap function, Δ_k (dashed line), as a function of the azimuthal angle $\phi = \arctan(k_y/k_x)$ on a circular Fermi surface (solid line). The gap is strongly anisotropic with nodes along the (110) directions. Green arrow indicates the location of a node where quasiparticle excitations predominately occur at low temperatures. The sign of Δ_k changes across the lobes as indicated.

5.1.2 Quasiparticle Density of States (QDOS)

For a given gap function Δ_k , the quasiparticle density of states (QDOS) is required to calculate the thermal excitations. By definition [176]

$$\begin{aligned}
 N(E) &= \sum_k \delta(E - E_k) \\
 &= \int \frac{d^3k}{(2\pi)^3} \delta(E - E_k) \\
 &= N_0 \int \frac{d\Omega}{4\pi} \int d\varepsilon \delta(E - E_k) \\
 &= N_0 \int \frac{d\Omega}{4\pi} \int dE' \frac{E'}{\sqrt{E'^2 - \Delta_k^2}} \delta(E - E') \\
 &= N_0 \int \frac{d\Omega}{4\pi} \frac{E}{\sqrt{E^2 - \Delta_k^2}}
 \end{aligned}$$

where N_0 is the normal-state density of states at the Fermi level for one spin configuration, and the relation $d\varepsilon/dE' = E'/\sqrt{E'^2 - \Delta_k^2}$ is derived from Eq. 5.1.

The integration over angles is performed within the limits $\Delta_k^2 < E^2$.

For an isotropic s -wave superconductor, $\Delta_k = \Delta$,

$$N(E) = N_0 \begin{cases} 0 & (E < \Delta) \\ \frac{E}{\sqrt{E^2 - \Delta_0^2}} & (E > \Delta) \end{cases} \quad (5.3)$$

For a d -wave superconductor, $\Delta_k = \Delta_0 \cos 2\phi$,

$$N(E) = N_0 \int_0^{2\pi} \frac{d\phi}{2\pi} \frac{E}{\sqrt{E^2 - \Delta_0^2 \cos^2 2\phi}} \quad (5.4)$$

The last integral is a complete elliptic integral of the first kind, that is,

$$N(E) = \begin{cases} \frac{2}{\pi} \frac{E}{\Delta_0} \kappa\left(\frac{E}{\Delta_0}\right) & (E < \Delta_0) \\ \frac{2}{\pi} \kappa\left(\frac{\Delta_0}{E}\right) & (E > \Delta_0) \end{cases} \quad (5.5)$$

At low temperatures, the thermal excitations are predominately the low-lying levels around the nodes. For $E \ll \Delta_0$, $\kappa(E/\Delta_0) \approx \pi/2$, and $N(E)$ can be simplified to

$$\frac{N(E)}{N_0} \approx \frac{E}{\Delta_0} \quad (5.6)$$

which has a linear dependence on E .

5.1.3 Calculation of Superfluid Density

The superfluid density n_s refers to the number of superconducting electrons in a system. The conservation of particles requires that $n_s = n - n_n$, where n is the number of carrier electrons in the normal state, and n_n is the number of

quasiparticles in the superconducting state, which can be calculated as [103]

$$n_n = n \int_{-\infty}^{\infty} d\varepsilon \left(-\frac{\partial f}{\partial E_k} \right) \quad (5.7)$$

where $E_k = (\varepsilon_k^2 + \Delta_k^2)^{1/2}$ is the quasiparticle energy, and f is the Fermi function.

The *normalized* superfluid $\rho_s = n_s/n = 1 - n_n/n$ is then

$$\rho_s = 1 + 2 \left\langle \int_0^{\infty} \frac{\partial f}{\partial E} d\varepsilon \right\rangle_{FS} \quad (5.8)$$

or in terms of E ,

$$\begin{aligned} \rho_s &= 1 + 2 \left\langle \int_0^{\infty} \frac{\partial f}{\partial E_k} \frac{N(E)}{N_0} dE \right\rangle_{FS} \\ &= 1 + 2 \left\langle \int_0^{\infty} \frac{\partial f}{\partial E_k} \frac{E}{\sqrt{E^2 - \Delta_k^2}} dE \right\rangle_{FS} \end{aligned}$$

where $\langle \dots \rangle_{FS}$ denotes the average over the FS, which entails another integral over the solid angle $d\Omega/4\pi$.

For a *s*-wave superconductor at $T \ll T_c$, the normal fluid density, after integrating Eqn. 5.7 by parts, we get

$$n_n(T) = n \sqrt{\frac{2\pi\Delta(0)}{k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \quad (T \ll T_c) \quad (5.9)$$

where $\Delta(0)$ is the zero-temperature gap value, and

$$\rho_s(T) = 1 - \sqrt{\frac{2\pi\Delta(0)}{k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \quad (T \ll T_c) \quad (5.10)$$

which shows an activated behavior due to the exponential T -dependence.

For a *d*-wave superconductor, the normal fluid density is

$$n_n \approx 2n \ln(2) \frac{T}{\Delta_0} \quad (T \ll T_c) \quad (5.11)$$

and thus

$$\rho_s(T) = 1 - 2 \ln(2) \frac{T}{\Delta_0} \quad (T \ll T_c) \quad (5.12)$$

which has a T -linear dependence. Eqns. 5.10 and 5.12 demonstrate the point that $\rho_s(T)$, or more specifically its T -dependence far below T_c , reflects the underlying pairing symmetry. This is indeed one of the main motivations to measure ρ_s of a superconductor down to the lowest temperatures.

5.2 Penetration Depth

5.2.1 London Equations

The perfect diamagnetism in the Meissner state is described by the phenomenological London equations. The superconducting electrons can be freely accelerated without any dissipation by an electric field E . The drift velocity v_s is given by

$$m \frac{dv_s}{dt} = -eE \quad (5.13)$$

where m and e are the effective mass and charge of the electron, respectively. With the current density $J = -en_s v_s$, Eqn. 5.13 can be written as

$$\frac{dJ}{dt} = -\frac{n_s e^2}{m} E \quad (5.14)$$

Applying Faraday's law of induction

$$-\frac{1}{c} \frac{\partial B}{\partial t} = \nabla \times E \quad (5.15)$$

on Eqn. 5.14, we get the following relation between J and B

$$\frac{\partial}{\partial t} \left[\nabla \times J + \frac{n_s e^2}{mc} B \right] = 0 \quad (5.16)$$

The London brothers point out that the argument of Eqn. 5.16 must vanish, that is,

$$\nabla \times J + \frac{n_s e^2}{mc} B = 0 \quad (5.17)$$

which is now known as the London equation. Applying the Maxwell equation

$$\nabla \times B = \frac{4\pi}{c} J \quad (5.18)$$

on Eqn. 5.17, we arrive at the result

$$\nabla^2 B = \frac{1}{\lambda^2} B \quad (5.19)$$

where

$$\lambda = \left(\frac{mc^2}{4\pi n_s e^2} \right)^{1/2} \quad (5.20)$$

is the so-called London penetration depth which is the characteristic length scale over which the magnetic field penetrates into the sample. Eqn. 5.20 can be rearranged as

$$n_s = \frac{mc^2}{4\pi e^2} \frac{1}{\lambda^2} \quad (5.21)$$

which shows that the superfluid density is directly proportional to $1/\lambda^2$. Thus, the measurement of penetration depth enables one to determine the corresponding superfluid density.

5.2.2 Magnetic Susceptibility

Consider a superconducting slab of finite thickness $2d$. A magnetic field H_0 is applied along the z direction, i.e. parallel to its surface. Assume that the plane $x = 0$ is in the center of the slab and that its surfaces coincide with the planes $x = \pm d$. Enforcing the boundary conditions $B(\pm d) = H_0$, the solution to Eqn. 5.19 is given by [182]

$$B_z(x) = H_0 \frac{\cosh(x/\lambda)}{\cosh(d/\lambda)} \quad (5.22)$$

The average field within the slab is

$$\langle B_z \rangle = \int_{-d}^d dx B(x) = H_0 \frac{\lambda}{d} \tanh\left(\frac{d}{\lambda}\right) \quad (5.23)$$

Since $\langle B_z \rangle = H_0 + 4\pi M$, where M is the magnetization in the slab,

$$\begin{aligned} M &= \frac{1}{4\pi} (\langle B_z \rangle - H_0) \\ &= \frac{H_0}{4\pi} \left(\frac{\lambda}{d} \tanh\left(\frac{d}{\lambda}\right) - 1 \right) \end{aligned}$$

The susceptibility $\chi = M/H_0$ is thus

$$4\pi\chi = 1 - \frac{\lambda}{d} \tanh\left(\frac{d}{\lambda}\right) \quad (5.24)$$

For $\lambda \ll d$, $\tanh(d/\lambda) = 1$, hence

$$-4\pi\chi = 1 - \frac{\lambda}{d} \quad (5.25)$$

The above result can be modified to take into account of the finite size of real sample. For a slab of dimension $2w \times 2w \times 2d$, where $2d$ is the thickness along

which the magnetic field H_0 is applied, Eqn. 5.25 is modified to [183]

$$-4\pi\chi = 1 - \frac{\lambda}{R_{3D}} \quad (5.26)$$

where

$$R_{3D} = \frac{w}{2} \times \frac{1}{F(2d/w)} \quad (5.27)$$

and

$$F(2d/w) = \left[1 + \left(1 + \frac{2d}{w} \right)^2 \right] \arctan \left(\frac{w}{2d} \right) - \frac{2d}{w} \quad (5.28)$$

Thus, we see that the for a superconducting sample, its magnetic susceptibility is a function of penetration depth.

5.3 Tunnel-Diode-Oscillator Technique

The tunnel diode oscillator (TDO) technique was first implemented by Craig Van der Griff [184,185] to measure the dielectric constant of liquid helium. It was later modified to measure the London penetration depth of superconductor [186,187]. The technique can achieve ~ 1 ppb stability in resonant frequency, which is essential to resolve the T -dependence of penetration depth. The latter information is crucial to distinguish the pairing symmetry which provides experimental clue for the mechanism. For example, the observation of a linear dependence $\Delta\lambda \propto T$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ provides the earliest evidence of nodes in the superconducting gap function, and rules out the conventional s -wave pairing commonly associated with electron-phonon interactions [188]. Another example which is relevant to our work presented in the next chapter is the observation of $\lambda \sim T^2$ for $T < 0.3T_c$ in the skutterudite superconductor $\text{PrOs}_4\text{Sb}_{12}$ [189]. The

result reveals a gap function with two point nodes on the Fermi surface which suggests unconventional pairing possibly mediated by quadrupolar fluctuations. In this section we discuss the essential elements that enables the self-resonant oscillation, and the calibration procedure that translates the measured values of frequency to λ . Descriptions for the implementation of TDO technique follows closely that of Ref. [190].

5.3.1 Low-Temperature Circuit

The schematics of the low-temperature circuit is shown in Fig. 5.2. Dc current is supplied to the circuit through the same coaxial cable used to carry the rf signal out to the room-temperature electronics (Fig. 5.4). Resistors R_1 and R_2 form a voltage divider which dc biases the tunnel diode to the state of negative differential resistance. Resistor R_p prevents parasitic oscillation that arises due to the stray capacitance of the tunnel diode, which can seriously degrades the oscillator performance. Bypass capacitor C_B forms a short circuit to the signal at resonant frequency. The coupling capacitor C_c passes only a small fraction of the signal to the room temperature electronics. The weak coupling ensures that the oscillator circuit is isolated from the latter while being measured, which is important to maintain the oscillation against the outside world. At resonance, the tunnel diode acts as the rf power source that cancels the dissipative losses of the LC tank circuit. A resonant frequency ~ 21 MHz is typically achieved with $R_1 = 1400\Omega$, $R_2 = 300\Omega$, $R_p = 200\Omega$, $C_c = 20\text{pF}$, and $C_B = 10\text{nF}$.

The tunnel diode is a heavily doped p-n junction with negative differential resistance in the I-V characteristics (Fig. 5.3), which is caused by quantum-mechanical tunneling of electrons across the depletion layer [191, 192]. The diode must be biased in this region to cancel the dissipate losses of the tuned circuit and sustain the resonant oscillation.

Figure 5.2: Schematic of the TDO low-temperature circuit.

Figure 5.3: I-V curves of a tunnel diode BD3, at room temperature, 77 K, and 4 K. The values of R_n are calculated from the inverse slopes of the solid lines shown. Taken from [190].

5.3.2 Room-Temperature Circuit

The dc current to the oscillator circuit is generated by a high-stability reference voltage source that provides a 10 V output. A low-noise op-amp is used as a buffer to maintain the voltage stability. A potentiometer is used to tune the dc bias for the tunnel diode. The current is determined by monitoring the voltage drop across a high-precision resistor (typically 4.7 k Ω), and filtered before passing out to the low-temperature electronics that is held in the cryostat,

through a semi-rigid coaxial cable.

Figure 5.4: Schematic of the TDO room-temperature circuit.

The same semi-rigid coaxial cable is used to carry the very small TDO signal (~ 20 MHz) back up to the room-temperature electronics. At the front end of the receiver is a rf amplifier. A low-noise rf amplifier of typical gain factor of ~ 100 is used. The output of the rf amplifier is monitored by a spectrum analyzer, and then heterodyned by a double-balanced mixer that shifts the signal to an audio frequency of ~ 20 kHz. The mixer output is bandpass filtered and amplified before it is read by a high-resolution frequency counter. The frequency counter is equipped with a 10 MHz time base which enables a stability of 1ppb. The time base is also used to synchronize the local oscillator.

5.3.3 Measurements of $\Delta\lambda(T)$ and $\rho_s(T)$

When a current I is applied to an inductor coil, it creates an energy

$$U = \frac{1}{2}LI_0^2 \quad (5.29)$$

where L_0 is the self-inductance of the coil. The energy is stored in magnetic field generated by the current. In the presence of a superconducting sample, the field distribution is changed due to the diamagnetic response of the sample. This leads to the following expression for the energy change

$$\Delta U = \frac{1}{2} (L_s - L_0) I^2 = \frac{1}{2} \int_V dr^3 \mathbf{M} \cdot \mathbf{B}_0 \quad (5.30)$$

where L_s is the self-inductance of the coil with the sample, $\mathbf{M}$ the magnetization of the sample, and $\mathbf{B}_0$ the initial magnetic field without the sample. For a small ellipsoid sample placed in the uniform part of the coil field, the magnetization is uniform and equal to

$$\mathbf{M} = \frac{4\pi\chi}{1 + N\chi} \mathbf{B}_0 \quad (5.31)$$

where N is the demagnetization factor, and χ is the volume magnetic susceptibility. Substituting 5.31 into 5.30, and recall that $L_0 I^2 / 2 = B_0^2 V_c / 8\pi$ for an uniform coil field, one arrives at

$$\frac{L_s - L_0}{L_0} = \frac{4\pi\chi}{1 + N\chi} \frac{V_s}{V_c} \quad (5.32)$$

where V_s is the sample volume, V_c is the coil volume. For a non-uniform coil field, the ratio V_s/V_c is replaced by the geometrical filling factor

$$F = \frac{\int_{V_s} dr^3 B_0^2(r) d^3r}{\int_{V_c} dr^3 B_0^2(r) d^3r} \quad (5.33)$$

In the superconducting phase, $\chi \approx -1$ due to the Meissner effect. Thus, Eqn. 5.32 is simplified to

$$\frac{L_s - L_0}{L_0} = \frac{4\pi\chi}{1 - N} \frac{V_s}{V_c} \quad (5.34)$$

The resonant frequency of the TDO oscillator circuit is $f = 1/2\pi\sqrt{LC}$, where $L = L_p + L_T$ is the sum of primary and tapping coil inductance, and C the capacitance. For an infinitesimal change $\Delta L \ll L$, the corresponding change in the frequency is

$$\frac{\delta f}{f} = -\frac{1}{2} \frac{\delta L}{L} \quad (5.35)$$

Substituting $\delta L = L_s - L_0$ and $\delta f = f_s - f_0$ into Eqn. 5.35, where the subscripts denote respectively the presence and absence of the sample in the primary coil, one obtains

$$\begin{aligned} \frac{f_s - f_0}{f_0} &= -\frac{1}{2} \frac{L_s - L_0}{L_0} \\ &= -\frac{4\pi\chi}{2(1-N)} \frac{V_s}{V_c} \end{aligned}$$

where Eqn. 5.34 has been used. In the experiment, the quantity $\Delta f(T) = \delta f(T) - \delta f(T_0)$ is measured, where T_0 is the base temperature of the cryostat. Thus

$$\frac{\Delta f(T)}{f_0} = -\frac{4\pi}{2(1-N)} \frac{V_s}{V_c} \Delta\chi(T) \quad (5.36)$$

where $\Delta\chi(T) = \chi(T) - \chi(T_0)$. For a superconducting slab, its magnetic susceptibility is related to the magnetic penetration depth (Eqn. 5.26)

$$4\pi\Delta\chi(T) = \frac{\Delta\lambda(T)}{R_{3D}} \quad (5.37)$$

where $\Delta\lambda(T) = \lambda(T) - \lambda(T_0)$. Combining Eqns. 5.36 and 5.37, one arrives at

$$\frac{\Delta f(T)}{f_0} = -\frac{4\pi}{2(1-N)} \frac{V_s}{V_c} \frac{1}{R_{3D}} \Delta\lambda(T) \quad (5.38)$$

or

$$\Delta\lambda(T) = G\Delta f(T) \quad (5.39)$$

where $G = -(2R_{3D}(1 - N)V_c) / (V_s f_0)$ is the proportional factor. This the central result which shows that $\Delta\lambda(T)$ can be determined from the measured values of $\Delta f(T)$.

At low temperatures ($T \ll T_c$), an exponential or power-law fit to $\Delta\lambda(T)$ allows one to determine the pairing symmetry of the material. Although TDO technique does not provide the absolute value of $\lambda(0)$, the quantity can be obtained from other measurements such as muon spin resonance or low field ac magnetic susceptibility. Knowing $\lambda(0)$ allows one to determine the normalized superfluid density

$$\begin{aligned} \rho_s(T) &= \frac{n_s}{n} \\ &= \frac{\lambda^2(0)}{\lambda^2(T)} \\ &= \frac{\lambda^2(0)}{\lambda^2(0) + \Delta\lambda^2(T)} \\ &= \frac{1}{1 + (\Delta\lambda(T)/\lambda(0))^2} \end{aligned}$$

The profile of $\rho_s(T)$ often provides useful information that complements the determination of pairing symmetry. For example, model fits of the quantity allows one to determine the presence of multiple superconducting gaps [193].

5.4 TDO Setup at NTU

The usefulness of TDO technique in addressing several fundamental problems of superconductivity, notably the determination of pairing symmetry, motivates us to set up a TDO apparatus at NTU. The technique will add to the versatile

combination of experimental tools in our laboratory which are specially designed and employed to investigate the fundamentals of unconventional superconductor. In particular, the compatibility of this technique with dilution refrigerator allows studies of many low T_c superconductors down to the mK temperature regime, which is a highly non-trivial task awaiting to be addressed.

It is worth noting that the technique can also be employed to investigate the surface-enhanced superconductivity presented in chapter 3. When the coil field is applied perpendicular to the c-axis, screening current flows primarily in the ab-plane surface and through the side edges of the sample [194–196]. The presence of a superconducting surface enhances the screening current and hence the diamagnetic susceptibility of the sample, which can be measured with high precision in the experiment.

The experimental setup is technically demanding, and takes a longer time to deliver on the side of other accomplished projects described in the preceeding chapters. This section presents the important steps that we have achieved so far. Based on this groundwork, the setup is expected to be completed by the next PhD student. Future work such as the testing of apparatus in our custom-made dilution refrigerator is discussed.

5.4.1 Electronics

The electronic instruments that we use are listed in Tab.5.1. Note that the tracking bandpass filter, instead of the usual lock-in output, of Stanford Research System SR530 is used to process the mixer output. The “signal monitor” on the back of the instrument provides access to the preamplified and filter signal. We use another local oscillator DS345 (also synchronized with the frequency counter time base) to set the lock-in reference frequency $f_{\text{ref}} = 20$ kHz. The bandwidth is given by $f_{\text{ref}}/5 = 4$ kHz.

Instruments	Model
Tunnel diode	Aeroflex/Metelics MBD1057-H20
Reference voltage	Texas Instruments REF10
Buffer Op-Amp	Texas Instruments OPA 177
Rf amplifier	Mini-circuits ZFL500LN (2 units cascaded)
Frequency mixer	Mini-circuits ZLW-2
Local oscillator	SRS DS345
Bandpass filter	SRS SR510
Frequency counter	Agilent 53132A
Spectrum analyzer	Agilent N9320B

Table 5.1: A list of instruments used in the TDO setup.

Inductance coils are homemade with high-purity copper wires of diameter 0.05 mm. Typically, the primary coil has a diameter ~ 3 mm and ~ 30 turns that are evenly spaced by a distance of 0.05 mm. The spacing results in a lower stray capacitance than a tightly-wound coil of the same inductance. Stycast 1266 A/B is applied to permanently set the coil. The tapping coil is made in the same way but with fewer turns. The exact number of turns needs to be tuned by trial-and-error to achieve and optimize the resonant oscillation.

5.4.2 TDO Cell

Cryogenic temperature is required for the optimal performance of TDO technique. For example, R_n of tunnel diode is enhanced at low temperatures. Furthermore, the electronic components need to have a temperature stability bet-

ter than 1 mK to minimize thermal fluctuations which affects the signal-to-noise level. Therefore, in the experiment the low-temperature electronics are mounted on a copper stage that is thermally anchored at 4 K. The stage is further enclosed by a radiation can to enhance temperature stability.

Figure 5.5: Schematic of the TDO cell. The low-temperature electronics are mounted on the electronic stage and enclosed by a radiation shield. The primary coil is placed inside a holder that is attached to the electronic stage through G10 rods. A sapphire rod (O.D. 1 mm) is attached to the sample stage. In the measurement, the sample is glued on the other end of the sapphire rod. The temperature of the sample stage is taken as the sample temperature. A Vespel tube attaches the electronic stage to the cold finger. All parts are made of high-purity copper unless specified otherwise.

The primary coil is located above the copper stage and its temperature is stabilized at 1 K. The sample is suspended by a single-crystalline sapphire rod (O.D.=1.0 mm) and loaded into the middle of the primary coil without mechanical contact with the latter. The magnetic susceptibility of sapphire is essentially independent of temperature or magnetic field [197]. This property ensures that the changes in frequency measured by the system purely correspond to changes

in magnetic susceptibility of the sample. The other end of the sapphire rod is secured on a copper block, also known as the sample stage. The temperature of the copper block is monitored and controlled with a set of RuO_2 sensor and heater, and measured as the sample temperature T . The copper block is attached to the cryostat cold finger through a G10 spacer. An alignment tube made of Vespel attaches the electronic stage to the cold finger.

In the experiment, the frequency counter measures $f = f_{\text{LO}} - f_{\text{RF}}$, where f_{LO} is the frequency of the local oscillator, and f_{RF} is the resonant frequency of the oscillator circuit. The change in frequency $\Delta f(T) = f(T) - f(T_0)$ is recorded as raw data. The corresponding change in penetration depth $\Delta \lambda(T) = \lambda(T) - \lambda(T_0)$ can be determined from the relation $\Delta \lambda = G \Delta f$ (Eqn. 5.39).

Figure 5.6: Photograph of the TDO cell. The parts are disassembled for clarity. (a) Radiation shield, (b) primary coil holder, (c) electronic stage, (d) Nylon tube (to be replaced by Vespel), (e) sample stage. A sapphire rod of O.D. 1 mm (not shown) is glued to the sample stage with high thermal conductivity silver epoxy, as indicated by the green arrow.

Oscillation at 77.4 K

The TDO oscillation self-resonates when the impedance of the oscillator circuit is matched to R_n of the tunnel diode. In reality, it requires trial-and-error efforts to tune the number of turns of the tapping coil before optimal matching is attained. Each time, the oscillator circuit is tested at liquid nitrogen temperature (77.4 K) using an exchange-gas probe. An oscillation that occurs at 77.4 K (test temperature) will also appear at 4 K which is the working temperature for the circuit. This is because the electronic characteristics, including the IV profile of the tunnel diode, do not change significantly between the two temperatures. Fig. 5.7 shows the oscillation ~ 21 MHz which we attain at 77.4 K. The detection indicates successful impedance matching, that is, an operational oscillator circuit.

Figure 5.7: The detection of TDO resonant oscillation ~ 21 MHz at 77.4 K. The figure plots the intensity vs. frequency over a span of 0-40 MHz, taken from the spectrum analyzer. Courtesy of Sourav Mitra.

5.4.3 Future Works

The next phase is to setup the TDO in our custom-made dilution refrigerator DR500 (Fig. 5.8, Janis system), which offers a base temperature of ~ 10 mK. It is a dry system, which means that external supply of liquid Helium is not

required for the experiment. The cooling source is a pulse-tube cryo-refrigerator which brings the mixing chamber to ~ 1 K. Subsequent pumping on the He3/He4 mixture cools the mixing chamber to the cryostat base temperature. DR500 can be operated in two modes. In the first mode, known as the “cold-finger mode”, the experimental setup is directly mounted on the cold finger of the system and thus directly heat sunk at the mixing chamber. In the second mode, known as the “top-loader mode”, the experimental setup is mounted on the stage of a “top-loading probe” and subsequently loaded into the cryostat. The probe is essentially a long mechanical structure that conveniently sends the experimental setup from room temperature to the cryostat cold finger. Thermal links are made between the probe and the mixing chamber, which cool the probe stage to the system base temperature (Fig. 5.9).

Figure 5.8: Photograph of the the cryogen-free dilution fridge DR500. The vacuum jacket has been removed. The 1st and 2nd stages of the pulse-tube regrigertor, still, intermediate cold plate, and the mixing chamber of the cryostat are specified.

Figure 5.9: Schematic of the top-loading probe for the DR500 system. Left panel shows the bottom part of the top-loading probe. The probe stage and thermal link are made of OFHC copper with gold plating. The thermal link is thermally anchored to the mixing chamber of DR500. Hence, the probe stage can be regarded as the cold finger for TDO experiment. Right panel shows the magnified view of the probe stage. Also shown is the TDO cell attached to the probe stage. This is the working configuration of TDO experiment in the “top-loader mode”.

The DR500 is a powerful system that allows access to mK temperature regime. This allows us to measure the penetration depth down to the lowest temperatures, which is important for the criteria $T < 0.3T_c$ to be met so that the exponential or power-law fits to $\Delta\lambda(T)$ can be applied. Thus, the TDO built on DR500 will be a powerful probe that enables studies of unconventional superconductors with low T_c such as the heavy-fermion systems.

6 Penetration Depth Study of

LaOs₄Sb₁₂

The filled skutterudites have the chemical formula RM_4X_{12} (R = rare earth or alkaline earth; M = Fe, Ru, Os, Co, Rh, Ir; X = P, As, Sb). These materials exhibit a broad range of strongly-correlated phenomena. A notable case is the heavy-fermion superconductivity of $\text{PrOs}_4\text{Sb}_{12}$, whose origin is still a subject of active research despite intensive efforts in the past decade. In this chapter, we discuss the problems faced in clarifying the pairing symmetry of this system, and how a detailed study of the reference material LaOs_4Sb_4 can provide valuable information.

While setting up the TDO technique, I analyzed the penetration depth data of LaOs_4Sb_4 in order to gain experience and develop analytical tools for the related topics. The data were originally taken by D. Vandervelde and E. E. M. Chia in Urbana. This chapter summarizes our results which had been published in Ref. [193].

6.1 Skutterudite $\text{PrOs}_4\text{Sb}_{12}$

The skutterudite $\text{PrOs}_4\text{Sb}_{12}$ has been receiving much attention due to the discovery of its unconventional heavy-fermion superconductivity. Unlike other heavy-fermion systems, its f electrons do not have a magnetic ground state. It has also

been suggested that the interaction between the conduction electrons and the electric quadrupolar moments of Pr atoms might be responsible for the pairing of electrons. Therefore, this system provides a platform for the study of quadrupolar fluctuations and their possible roles for superconductivity [198–201].

An important step in clarifying its superconductivity is to determine the symmetry of the superconducting gap. Conflicting results had been reported. On one hand, scanning tunneling microscopy (STM), muon spin rotation (μSR), and nuclear quadrupolar relaxation (NQR) experiments point to an isotropic superconducting energy gap [202–204]. On the other hand, magnetic penetration depth, angle-dependent thermal conductivity, and neutron scattering measurements revealed point nodes on the superconducting gap [205–207]. Angle-dependent thermal conductivity data revealed two distinct superconducting phases of twofold and fourfold symmetries, both with point nodes on the superconducting gap [206].

Multiband Superconductivity

Multiband superconductivity has been proposed as a reconciliation for these conflicting results. According to several groups, $\text{PrOs}_4\text{Sb}_{12}$ is a two-band superconductor, with nodes on one band and an isotropic gap on the other [208–210]. Specifically, at $T < 100$ mK, the field dependence of thermal conductivity $\kappa(H)$ shows a rapid rise at $H \sim 50$ Oe which was attributed to the excitations of quasiparticles due to the penetration of vortices at $H > H_{c1}$ for a nodal superconducting gap. Another rise in $\kappa(H)$ is observed near $H \sim 0.8$ T. However, it shows a more gentle field dependence and eventually saturates at the upper critical field H_{c2} . This behavior is well consistent with a fully gapped Fermi surface.

It is known that the measurement of superfluid density $\rho(T)$ probes the super-

conducting gap amplitude. However, the data reported by Chia and co-workers cannot be fit over the entire temperature range with the assumption of one superconducting gap [205]. For $T > 0.3T_c$, their fit deviates downward from $\rho(T)$ with increasing temperature, which suggest the presence of another gap not considered in the calculation.

Another evidence for multiband superconductivity is provided by the recent measurements of point-contact Andreev reflection spectroscopy by Curnoe and co-workers [211]. The observed zero-bias peaks and spectral dips in the conductance spectra is well fit by an unconventional superconducting gap of $C_3 \times \mathcal{K}$ symmetry, and in addition, another gap of s -wave symmetry. Notably, such multiband scenario is consistent with the results of thermal conductivity measurements [208–210].

6.2 Isostructural $\text{LaOs}_4\text{Sb}_{12}$

$\text{LaOs}_4\text{Sb}_{12}$ (superconducting transition temperature $T_c = 0.74$ K) and $\text{PrOs}_4\text{Sb}_{12}$ ($T_c = 1.85$ K) are isostructural superconductors. The substitution of La by Pr introduces the 4f electrons while largely preserving the crystal structure [212–214] and Fermi surface topology [213]. The 4f energy levels of the Pr^{3+} ion are split by the crystal electric field (CEF), resulting in a nonmagnetic Γ_1 singlet ground state, a 0.7-meV Γ_5 first excited state, and an 11-meV Γ_4 second excited state (in O_h cubic symmetry) [215]. The higher T_c of $\text{PrOs}_4\text{Sb}_{12}$ compared to $\text{LaOs}_4\text{Sb}_{12}$ is attributed to the type of scattering between the conduction electrons and these low-lying CEF-split 4f levels [215–218]: the inelastic scattering of the conduction electron by the $\Gamma_1 \rightarrow \Gamma_5$ transition has a strong quadrupole matrix element that enhances pair formation and consequently T_c . This interaction, known as aspherical Coulomb scattering, overcomes the magnetic pair-breaking effect due to the $s - f$ exchange scattering of the conduction electron by the

$\Gamma_1 \rightarrow \Gamma_4$ transition, which has a strong dipole matrix element that suppresses T_c . The f -electrons thus play an important role in skutterudite/heavy-fermion superconductivity via the CEF-split f -electron energy levels.

Since it has been shown that PrOs₄Sb₁₂ is a two-band superconductor with different pairing symmetries on each band, we want to find out if LaOs₄Sb₁₂ is a multiband superconductor as well, and if so, whether the symmetries of these multiple gaps are different. Such an investigation of LaOs₄Sb₁₂ would allow us to determine whether the f -electrons are necessary for the formation of multiband superconductivity. In general, multiband superconductivity arises when there are more than one conduction bands *and* the pair couplings within each band are of different magnitudes [219]. Though filled skutterudites generically contain two holelike conduction bands, observations of multiband superconductivity were only reported for PrOs₄Sb₁₂ and PrRu₄Sb₁₂, both containing f electrons [210]. These f -electrons might exert different degrees of influence on the pair coupling within each band, hence giving rise to multiband superconductivity. In this context, it is tempting to attribute multiband superconductivity in Pr-based skutterudites to the presence of f -electrons.

There has been evidence that LaOs₄Sb₁₂ is a weak-coupling s -wave superconductor ($T_c = 0.74$ K). Specific heat measurement showed a discontinuity jump at T_c which is evaluated to be $\Delta C/\gamma T_c = 1.46$ [220], close to the BCS value of 1.43. Sb-NQR measurement showed a coherence peak at T_c and exponential temperature (T) dependence at low temperatures [204]. The data can be fitted by an isotropic gap with $\Delta(0) \approx 1.6k_B T_c$ [204, 221] or an anisotropic gap $\Delta(\theta) = \delta + (\Delta - \delta)\sin\theta$ with $\Delta = 1.73k_B T_c$ and $\delta = 1.21k_B T_c$ [222]. However, multiband superconductivity has never been reported for this material.

Magnetic penetration depth has been shown to be a valuable tool for probing multiband superconductivity, for instance, in the well-known multiband superconductor MgB₂ [223]. At low temperatures, the deviation $\Delta\lambda(T) = \lambda(T) - \lambda(0)$

is sensitive to the low-energy excitations of quasiparticles across the superconducting gap. Consequently, the symmetry of the energy gap can be determined from the temperature dependence of $\lambda(T)$. In addition, fits to the superfluid density over the entire temperature range of measurement allows one to detect the presence of multiple gaps as well as their temperature dependencies. In this chapter, we report the measurement and analysis of magnetic penetration depth $\lambda(T)$ in single crystals of $\text{LaOs}_4\text{Sb}_{12}$ down to 85 mK. We found that, at low temperatures, $\lambda(T)$ exhibits an exponential temperature dependence consistent with an *s*-wave gap symmetry. Fitting the data to a BCS *s*-wave expression gives a minimum gap value that is significantly smaller than the BCS value, suggestive of multiband superconductivity. The superfluid density data over the entire temperature range are best fit by a two-band *s*-wave model.

6.3 Data and Analysis

Details of sample growth and characterization are described in Ref. [213]. Four-probe resistivity ($\rho(T)$) data were taken on two $\text{LaOs}_4\text{Sb}_{12}$ single crystals (named sample 1 and sample 2) using Quantum Design PPMS from 2 to 300 K, shown in Fig. 6.1(a). Superposed on the same figure are data taken from another sample of the same batch, shortly after the sample was grown. We see that the three data sets lie on top of one another. The resistivity at low temperatures ($T < 10$ K) flattens out, implying that impurity scattering is dominant at this temperature range. The residual resistivity ratio (RRR), defined to be $\text{RRR} = \rho(300 \text{ K}) / \rho(2 \text{ K})$, is calculated to be 127 for sample 1 and 108 for 2, implying that sample 1 is of slightly better quality than sample 2. Fig. 6.1(b) shows the normalized resistivity of $\text{LaOs}_4\text{Sb}_{12}$ sample 1 and the $\text{PrOs}_4\text{Sb}_{12}$ sample used in the penetration depth paper of Ref. [205]; their values are consistent with that in Ref. [224].

Figure 6.1: (a) Temperature dependence of the resistivity $\rho(T)$, from 2 to 300 K, of LaOs₄Sb₁₂ samples 1 (diamonds) and 2 (squares). Solid circles denote data from another sample of the same batch, taken shortly after the sample was grown. (b) Normalized resistivity of LaOs₄Sb₁₂ sample 1 (open circles) and the PrOs₄Sb₁₂ sample of Ref. [205] (solid squares).

Penetration depth measurements were performed (in Urbana) utilizing a 21-MHz self-resonant tunnel diode oscillator (8) with a noise level of 2 parts in 10^9 and low drift. The sample was positioned in the center of an induction coil which forms part of the LC resonant tank circuit. The $\Delta\lambda(T)$ is directly proportional to the

change in resonant frequency $\Delta f(T)$ of the oscillator, with the proportionality factor G dependent on sample and coil geometries. For a square sample of side $2w$, thickness $2d$, demagnetization N , and volume V , G is known to vary as $G \propto R_{3D}(1 - N)/V$, where $R_{3D} = w/[2(1 + (1 + 2d/w)^2) \arctan(w/2d) - 2d/w]$ is the effective sample dimension [225]. For our sample $2w \approx 0.59$ mm and $2d \approx 0.13$ mm. The value of G was determined from a high-purity Al single crystal by fitting the data to the extreme nonlocal expression and then adjusting for relative sample dimensions. The magnitude of the ac field inside the induction coil was estimated to be less than 40 mOe, and the cryostat was surrounded by a bilayer Mu-metal shield that reduced the dc field to less than 1 mOe.

The single crystal sapphire rod which held the sample with GE varnish was attached to the mixing chamber of an Oxford Kelvinox 25 dilution refrigerator to provide cooling. During the experiment, the probing ac field of the inductor coil was directed along the c-axis of the sample and the in-plane penetration depth λ_{ab} was measured. Since the compound $\text{LaOs}_4\text{Sb}_{12}$ has a cubic crystal structure, we omit the distinction between axes.

As $\lambda(0) \approx 4700$ Å in $\text{LaOs}_4\text{Sb}_{12}$ [226] it probes a significant depth into the sample and is therefore less sensitive to surface quality, giving a result representative of the bulk. At low temperatures ($T \lesssim T_c/3$), it is well established that $\lambda(T)$ of an isotropic s -wave superconductor will asymptotically approach an exponential behavior given by [227]

$$\Delta\lambda(T) = \lambda(0) \sqrt{\frac{\pi\Delta(0)}{2k_B T}} \exp\left(-\frac{\Delta(0)}{k_B T}\right) \quad (6.1)$$

where $\lambda(0)$ and $\Delta(0)$ are the zero temperature values of λ and the energy gap. For a weakly anisotropic gap or multiple gaps, Eq. 6.1 will still follow but now with $\Delta(0)$ replaced by the minimum gap value in the system, and $\lambda(0)$ by an effective value which depends on the details of gap anisotropy.

An exponential temperature dependence characteristic of an *s*-wave energy gap is observed in both samples over the temperature range 85 mK to 0.26 K. Fig. 6.2 shows the low-temperature variation of $\lambda(T)$ in sample 1. The inset in Fig. 6.2 shows $\lambda(T)$ of both samples over the entire temperature range. It is clear from the inset, from the sharper superconducting transition and the larger T_c (midpoint), that sample 1 is of higher quality than sample 2, consistent with resistivity data. For sample 1, $\lambda(T)$ starts to fall at 0.76 K and reaches the transition midpoint at 0.68 K, consistent with the reported value of $T_c = 0.74$ K in other experiments [204, 226, 228].

Figure 6.2: Temperature dependence of the penetration depth $\Delta\lambda(T)$ in sample 1 at low temperatures. The solid line is a fit to Eq.(1). Inset: $\Delta\lambda(T)$ over the entire temperature range for samples 1 (open circles) and 2 (solid squares).

The low temperature data of sample 1 was fitted to Eq. 6.1 up to 0.25 K ($\sim T_c/3$), as shown by the solid line in Fig. 6.2. The zero temperature gap value $\Delta(0)$ obtained from the fitting was found to be (0.99 ± 0.05) K or $(1.34 \pm 0.07)k_B T_c$ (assuming $T_c = 0.74$ K), where the error corresponds to fitting the data up to $T = 0.23$ K and $T = 0.26$ K respectively. For sample 2, fitting the low temperature

data to Eq. (1) gives $\Delta(0) = (1.06 \pm 0.5) \text{ K}$ or $\Delta(0) = (1.43 \pm 0.07)k_B T_c$, slightly larger than the value obtained in sample 1. We also fitted the low temperature data to a power law $\Delta\lambda(T) \sim T^n$ and obtained $n=4$, excluding the possibility of line nodes in the energy gap which gives $\Delta\lambda(T) \sim T$ or $\Delta\lambda(T) \sim T^2$ in the presence of impurities [229]. As sample 1 has a sharper transition near T_c , we will focus on it for the rest of this chapter. The value $\Delta(0) = 1.34k_B T_c$ is significantly smaller than the weak-coupling BCS value of $1.76k_B T_c$. This suggests the possibility of anisotropic gap or multiple gaps (multiband superconductivity).

The scenario of multiple gaps is more likely since in addition we have also observed an unusually long suppression of the normalized superfluid density $\rho(T) = \lambda^2(0)/\lambda^2(T)$ near T_c which could not be due to gap anisotropy (Fig. 6.2). On the contrary, the presence of multiple gaps often results in suppression of $\rho(T)$ near T_c due to the smaller energy gap [230, 231]. The feature should be intrinsic to the material since it has been observed in two more samples and it could not be caused by some magnetic ordering as μSR experiment had observed no spontaneous magnetism even down to 20 mK [226].

We propose a two-band model to fit our data. In this model, the Hamiltonian is given by

$$\begin{aligned}
 H = & \sum_{i,k\sigma} \epsilon_{i,k} c_{i,k\sigma}^+ c_{i,k\sigma} + \sum_{i,kk'} V_{i,kk'} c_{i,k'\uparrow}^+ c_{i,-k'\downarrow}^+ c_{i,-k\downarrow} c_{i,k\uparrow} \\
 & + \sum_{kk'} V_{3,kk'} c_{1,k'\uparrow}^+ c_{1,-k'\downarrow}^+ c_{2,-k\downarrow} c_{2,k\uparrow} + H.c.
 \end{aligned} \tag{6.2}$$

where $i=1,2$ represents the first and second bands. $c_{1,k\sigma}$ and $c_{2,k\sigma}$ are the corresponding electron operator. $V_{1,kk'} = V_1 \gamma_{1,k} \gamma_{1,k'}$ and $V_{2,kk'} = V_2 \gamma_{2,k} \gamma_{2,k'}$ are the reduced pair coupling for the two bands. $V_{3,kk'} = V_3 \gamma_{1,k} \gamma_{2,k'}$ is the interband pair coupling. This model has been used to describe the two band superconductor

MgB₂ [232].

Taking the BCS mean-field approximation, the interaction between the two band is decoupled as

$$\begin{aligned}
 H \approx & \sum_{ik\sigma} \epsilon_{i,k} c_{i,k\sigma}^\dagger c_{i,k\sigma} + \\
 & + \left(\Delta_i \sum_k \gamma_{i,k} c_{i,k\uparrow}^\dagger c_{i,-k\downarrow}^\dagger + \Delta_i^* \sum_k \gamma_k c_{i,-k\downarrow} c_{i,k\uparrow} \right)
 \end{aligned} \tag{6.3}$$

where $\Delta_1 = \sum_k (V_1 \gamma_{1,k} \langle c_{1,-k\downarrow} c_{1,k\uparrow} \rangle + V_3 \gamma_{2,k} \langle c_{2,-k\downarrow} c_{2,k\uparrow} \rangle)$ and

$\Delta_2 = \sum_k (V_2 \gamma_{2,k} \langle c_{2,-k\downarrow} c_{2,k\uparrow} \rangle + V_3 \gamma_{1,k} \langle c_{1,-k\downarrow} c_{1,k\uparrow} \rangle)$.

We propose the tight-binding band dispersion

$$\begin{aligned}
 \epsilon_{i,k} = & -2t_i (\cos k_x + \cos k_y + \cos k_z) \\
 & + 4t'_i (\cos k_x \cos k_y + \cos k_x \cos k_z + \cos k_y \cos k_z) \\
 & - \mu_i
 \end{aligned} \tag{6.4}$$

Here $t_i (i = 1, 2)$ are the hopping constants, t'_i are the next nearest-neighbor hopping, μ_i are the chemical potentials of the two bands and we consider the three dimensional case. The same tight-binding band dispersion with a slight modification due to antiferromagnetism has been used to describe multiband superconductivity in electron-doped cuprate superconductor Pr_{2-x}Ce_xCuO₄ [231].

We next solve, self-consistently, a set of equations of $\Delta_1, \Delta_2, \mu_1, \mu_2$ obtained by $\delta F / \delta x = 0$ ($x = \Delta_1, \Delta_2, \mu_1, \mu_2$), where $F = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} \ln e^{-\beta H}$ is the free energy, for given model parameters $t_i, t'_i, V_i, V_3, n_1, n_2$. The superfluid density along a certain direction, such as x -direction, is given by

$$\rho_s^x = \sum_{i=1,2} \sum_k \left(\left\langle \frac{\partial^2 \epsilon_{i,k}}{\partial k_x^2} \right\rangle + 2 \left(\frac{\partial \epsilon_{i,k}}{\partial k_x} \right) \frac{\partial f(E_{i,k})}{\partial E_{i,k}} \right)$$

where $f(E_{i,k})$ is the Fermi function. In our fitting, we assume two bands to have s -wave gaps, namely, $\gamma_{1,k} = \gamma_{2,k} = 1$. The choice of gap symmetry is supported by the low temperature exponential behavior in $\Delta\lambda$ (this work) and Sb-NQR experiment [204]. For $\text{LaOs}_4\text{Sb}_{12}$, the model parameters used are $(n_1, t_1, t'_1, V_1, n_2, t_2, t'_2, V_2, V_3) = (0.08, t_2/4.4, -0.25t_2, 0.08t_2, 0.25, t_2, -0.3t_2, 0.103t_2, 0.0008t_2)$. Here the hopping integral $t_2 = 1$ is taken as the unit of energy in the whole fitting and is related to critical temperature as $T_c \approx 0.049t_2$.

Figure 6.3: Experimental data (open circles) and theoretical fit (solid line) for the normalized superfluid density $\rho(T)$ of sample 1. Inset: temperature dependence of the two energy gaps from the theoretical fit.

From the fitting, we obtained $\Delta_1(0) = 1.69k_B T_c$, $\Delta_2(0) = 1.30k_B T_c$, and $n_2/n_1 = 3.13$. The calculated value of $\Delta_2(0) = 1.30k_B T_c$ agrees well with the value of the zero-temperature gap value $\Delta(0) = 1.34 \pm 0.07k_B T_c$ obtained from low temperature data of $\Delta\lambda(T)$. The two values agree since at low temperatures the smaller energy gap will be the effective gap for quasiparticle excitation. The calculated value of $\Delta_1(0) = 1.69k_B T_c$ is also consistent with the weak-coupling value of $1.76k_B T_c$ [204, 220]. Fig. 6.3 shows that the experimental data of $\rho(T)$,

in particular the long suppression near T_c , can be well fitted by our two-band model. The long suppression is effectively caused by the smaller gap Δ_2 which vanishes at higher temperatures due to interband coupling with the bigger gap Δ_1 (Inset of Fig. 6.3).

6.4 Concluding Remarks

Our present finding reveals a two-band *s*-wave superconductivity in $\text{LaOs}_4\text{Sb}_{12}$. Given the close Fermi topology of $\text{PrOs}_4\text{Sb}_{12}$ and $\text{LaOs}_4\text{Sb}_{12}$, the present result shows that multiband superconductivity of $\text{PrOs}_4\text{Sb}_{12}$ persists even when the *f*-electrons are removed. This excludes *f*-electrons from being the origin of multiband superconductivity in $\text{PrOs}_4\text{Sb}_{12}$. Although *f*-electrons are not responsible for multiband superconductivity, they may however influence the behavior of each band. Our present finding of *s*-wave symmetry in both bands suggests that the two bands evolve differently in the presence of *f*-electrons, namely into a nodal band and a fully gapped band in $\text{PrOs}_4\text{Sb}_{12}$. This unconventional effect of *f*-electrons in $\text{PrOs}_4\text{Sb}_{12}$ may be related to the weakly split CEF levels [198, 199, 215], since it was found that the nodal feature disappears once $\text{PrOs}_4\text{Sb}_{12}$ is doped with Ru [233, 234]. We therefore suggest that theoretical models for $\text{PrOs}_4\text{Sb}_{12}$ should take multiband superconductivity of $\text{LaOs}_4\text{Sb}_{12}$ as a starting point, and develop the subsequent modifications in superconducting properties due to *f*-electrons.

The magnetic penetration depth of $\text{PrOs}_4\text{Sb}_{12}$ and $\text{PrRu}_4\text{Sb}_{12}$ was measured with the same experimental technique employed here [205, 233, 234]. We tried to fit the data of $\text{PrOs}_4\text{Sb}_{12}$ with a similar two-band model, but it was not successful. This is consistent with the unconventional (point-node) nature of one of its gaps. Also, we were able to fit the $\text{PrRu}_4\text{Sb}_{12}$ data using just one superconducting gap, showing that the multiband superconductivity of $\text{PrRu}_4\text{Sb}_{12}$, as shown

in thermal conductivity data [210], does not significantly affect the magnetic penetration depth data. It will be useful to resolve this discrepancy on the number of pairing gaps in $\text{PrRu}_4\text{Sb}_{12}$. This can be done, for example, through a re-measurement of TDO data down to even lower temperatures with our dilution fridge setup (section 5.4.3). Based on the result, a systematic investigation on Ru-doped $\text{LaOs}_4\text{Sb}_{12}$ will allow us to further pinpoint the origin of multigap pairing among skutterudite superconductors.

In summary, we report measurements of the magnetic penetration depth $\lambda(T)$ in single crystals of $\text{LaOs}_4\text{Sb}_{12}$ down to 85 mK. We find that $\lambda(T)$ exhibits an exponential temperature dependence at low temperatures with the zero-temperature gap value $\Delta(0)=(1.34\pm0.07)k_B T_c$. Our results show that $\text{LaOs}_4\text{Sb}_{12}$ is a two-band *s*-wave superconductor. Given the close Fermi topology of $\text{PrOs}_4\text{Sb}_{12}$ and $\text{LaOs}_4\text{Sb}_{12}$, this suggests that the *f*-electrons are not the origin of multiband superconductivity in these two materials.

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