Measurement of the Heat Capacity of Cuprate Superconductors in High Magnetic Fields

Jonathon B. Kemper
MEASUREMENT OF THE HEAT CAPACITY OF CUPRATE SUPERCONDUCTORS IN HIGH MAGNETIC FIELDS

By

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To my Parents, without whom this certainly would never have happened.
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\[ \Delta C(H)/T \text{ versus } T \] before (black) and after subtraction (purple stars). \[ C_{Sch}/T \] is much larger than the resulting \[ \Delta C_{elec}(H)/T \] but a \[ T \rightarrow \text{extrapolation} \] of the latter nonetheless establishes \[ \Delta \gamma \] to an uncertainty of \( \approx 5 - 10\% \). The error estimate gives rise to the error bars in fig. 5.22. The initial hint of \( C_{nuc} \) is visible below about 1.5 K. Sample mass is 5.98 mg.

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5.28 \( \Delta C_{elec}/(TH^{1/2}) \) versus \( H^{1/2} \) from field-stepped run pattern. The color scheme is the same is the same as fig. 5.27. The plot shows in stark terms the horizontal line consistent with Volovik scaling and the sloped line again follows \( \Delta C_{elec}/T \propto H \). Sample mass for all data is 3.92 mg.
5.29 $\Delta C_{\text{elec}}(H, T)/T$ versus $H$ comparison of redundant $(H, T)$ points from field-stepped and fixed field run patterns. The green line and $0.6\sqrt{H}$ curves are again guides to the eye. Sample mass for all data is 3.92 mg.

5.30 $\Delta C/T$ versus $T$ at 6 T with the field-in-plane ($\vec{H} \perp c$-axis). The red curve is a free fit to $C_{\text{Sch}}/T$ and the green curve is a guide to the eye using $g=2.0$ and $n_S=0.0032$ as determined by the $\vec{H}|_{||c}$ axis data set. Sample mass for all data is 3.92 mg.

5.31 $v_\Delta(H)$ as determined by eq. 5.1. The units are nominally $10^4$ m/s.

5.32 Comparison of $\gamma(H) - \gamma(0)$ for YBCO6.56 (purple dots) with guide to the eye following $0.47\sqrt{H}$ (purple curve) and $\Delta C_{\text{elec}}(H)/T$ for YBCO6.47 (present study, red points) versus $H$. The green line and curve are the same guides to eye as fig. 5.27 and represent $0.6\sqrt{H}$ and $0.17H$. The two $y$-axes are essentially equivalent given the temperature independence of $\Delta C_{\text{elec}}(H)/T$ for YBCO6.47.
LIST OF SYMBOLS

Below is a list of the symbols used most often within the document.

\( e \)  
Euler's number \( \approx 2.71828 \ldots \)
\( e \)  
Fundamental electric charge
\( \delta \)  
Oxygen non-stoichometry value, as in \( \text{YBa}_2\text{Cu}_3\text{O}_{6+\delta} \) and \( \text{HgBa}_2\text{CuO}_{4+\delta} \)
\( H \)  
Applied (scalar) magnetic field (teslas)
\( \dot{H} \)  
Time rate of change of magnetic field, especially in pulsed magnet systems
\( H_R \)  
Magnetic Field induced resistive transition
\( l \)  
Magnetic length
\( \Phi \)  
Magnetic flux
\( T \)  
Temperature
\( T_c \)  
Superconducting transition temperature
\( C \)  
Specific heat
\( E \)  
Total internal energy (thermodynamic)
\( Q \)  
Heat
\( P \)  
Power, heat per time
\( k_B \)  
Boltzmann constant
\( \hbar \)  
Dirac constant, i.e. reduced Planck constant
\( m \)  
Mass
\( m_e \)  
Electron mass
\( m^* \)  
Normalized electron effective mass
\( k \)  
Momentum wave vector
\( k_F \)  
Fermi momentum
\( \epsilon \)  
Quasiparticle energy level
\( \epsilon_F \)  
Fermi energy
\( \xi_k \)  
Electron-like energy level for momentum \( k \)
\( v_F \)  
Fermi velocity
\( p \)  
Hole doping
\( p \)  
Pressure
\( \gamma \)  
Sommerfeld coefficient of electronic specific heat
\( \beta \)  
Debye phonon coefficient of specific heat
\( \beta_6 \)  
Coefficient of the fifth order term (\( \sim T^5 \)) of specific heat
\( \alpha \)  
Coefficient of the quadratic term (\( \sim T^2 \)) of the specific heat
\( C_{Sch} \)  
Schottky anomaly
\( C_{nuc} \)  
Hyperfine Schottky-like specific heat contribution
\( g \)  
Landég-factor and \( C_{Sch} \) fit parameter
\( n \)  
Molar density
\( n_s \)  
Fit parameter representing molar concentration of magnetic impurities
\( \mu \)  
Magnetic moment
\( \mu_B \)  
Bohr magneton
\( \mu_N \)  
Nuclear magneton
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tr>
<td>$\Delta$</td>
<td>Energy gap, or as a prefix used to indicate a “change” or difference</td>
</tr>
<tr>
<td>$\Delta_s$</td>
<td>S-wave superconducting energy gap</td>
</tr>
<tr>
<td>$\Delta_{Sch}$</td>
<td>Schottky energy level splitting</td>
</tr>
<tr>
<td>$\Delta_0$</td>
<td>d-wave superconducting energy gap maximum</td>
</tr>
<tr>
<td>$v_\Delta$</td>
<td>d-wave gap slope</td>
</tr>
<tr>
<td>$I$</td>
<td>Electrical current</td>
</tr>
<tr>
<td>$V$</td>
<td>Electromotive force or voltage</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\omega_{ex}$</td>
<td>Excitation frequency</td>
</tr>
<tr>
<td>$f_{data}$</td>
<td>Data rate</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of particles</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>$K$</td>
<td>Thermal Conductance</td>
</tr>
<tr>
<td>$K$</td>
<td>Generic Constant</td>
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</tbody>
</table>
## LIST OF ABBREVIATIONS

Below is a list of the abbreviations more frequently used within the document.

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>YBCO</td>
<td>YBa$_2$Cu$<em>3$O$</em>{6+\delta}$</td>
</tr>
<tr>
<td>Hg1201</td>
<td>HgBa$<em>2$CuO$</em>{4+\delta}$</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>HTS</td>
<td>High Temperature Superconductivity/Superconductor</td>
</tr>
<tr>
<td>LK</td>
<td>Lifshitz-Kosevich form of quantum oscillations</td>
</tr>
<tr>
<td>qps</td>
<td>quasiparticles</td>
</tr>
<tr>
<td>SdH</td>
<td>Shubnikov-de Haas oscillations</td>
</tr>
<tr>
<td>SL</td>
<td>Simon and Lee (scaling)</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle resolved photo-emission spectroscopy</td>
</tr>
<tr>
<td>SP</td>
<td>Short pulse magnet system</td>
</tr>
<tr>
<td>MP</td>
<td>Mid pulse magnet system</td>
</tr>
<tr>
<td>LP</td>
<td>Long pulse, controlled wavefrom magnet system</td>
</tr>
<tr>
<td>SCM</td>
<td>Superconducting magnet system</td>
</tr>
<tr>
<td>res mag</td>
<td>Resistive DC magnet system</td>
</tr>
<tr>
<td>EMF</td>
<td>Electromotive Force</td>
</tr>
<tr>
<td>Nuclear Magnetic Resonance</td>
<td>NMR</td>
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</table>
ABSTRACT

The following presents the details of the study of a class of materials known as cuprate superconductors, primarily by measurement of their specific heat capacities, across two materials at very low temperatures and in very high values of applied magnetic field. The materials are YBa$_2$Cu$_3$O$_{6+\delta}$ and HgBa$_2$CuO$_{4+\delta}$ where $\delta < 1$ indicates a chemical doping by shifting the molecular oxygen content away from stoichiometric values.

The particular temperatures for this study range from 0.5 to 12 kelvin. The magnetic field range is 0 to 35 teslas. The data were produced by a unique system for heat capacity measurement primarily designed and built at Florida State University and the National High Magnetic Field Laboratory. All measurements utilizing magnetic fields above 15 teslas were carried out through the user program of the National High Magnetic Field Laboratory. Such measurements include the actual heat capacity measurements, as well as the separate instrumentation efforts which produced the thermometer calibrations enabling the accurate measurement of temperature up to 35 teslas.

The final results of the experimental effort are high-field heat capacity data of unprecedented accuracy for cuprates.

The results of the study are both consistent with previous work on cuprate specific heat capacity in magnetic fields, but also show new results. For one particular doping of YBa$_2$Cu$_3$O$_{6+\delta}$, one new result is evidence of a phase transition brought about by the application of sufficiently high magnetic field. Below 10 teslas, the portion of the heat capacity attributed to the electronic excitations of the system follow a predicted functional form which is square-root-of-field and gives way abruptly to a linear dependence on magnetic field above 10 teslas. The change from square-root to linear-in-field heat capacity is a new discovery for cuprates, and, in fact, no similar linear-in-field heat capacity has ever been observed in these materials.

For a particular composition of HgBa$_2$CuO$_{4+\delta}$ with superconducting transition temperature 72 kelvin, the electronic heat capacity increases with magnetic field in a generic way, but saturates to a constant value above 30 teslas. This saturation is expected for cuprates at sufficiently high
magnetic fields, strong enough to induce a transition from a superconductor to a normal conductor. This study implies that 30 teslas is sufficient field to bring about such a transition for the particular composition.

The presentation of detailed descriptions of experimental methodology, results, and conclusions follows.
CHAPTER 1

INTRODUCTION

The cuprate superconductors are a class of materials characterized by a perovskite lattice composed of a layered structure with ubiquitous CuO$_2$ planes [16, 11, 63], which is commonly considered to originate from electrically insulating parent compounds with superconductivity emerging upon non-stoichiometric chemical doping [10]. These compounds are also known as high temperature superconductors (HTS) and high $T_c$ materials because of the relatively high temperatures at which the superconductivity exists, more than twice that for any other known material [67].

The high superconducting critical temperature, called $T_c$ ("c" because the zero magnetic field (0-field) transition into superconductivity occurs at a critical point) is the origin of the vast interest in these materials. Upon the discovery of YBa$_2$Cu$_3$O$_{6+\delta}$ (YBCO), $T_c=92$ K [80], the highest temperature at which superconductivity was known to exist in non-cuprates was 19 K in NbSn3. This nearly five fold increase in energy scale was known to be impossible under the prevailing theory of superconductivity involving electrons forming pairs via interactions mediated by phonons [8]. While other theoretical framework exists based on other pairing mechanisms, none to date can provide a full theoretical description of the superconductivity.

This lack of theoretical understanding of HTS provides motivation for this dissertation in the broadest sense. HTS represents a potentially vast wealth of technological applications, especially if these compounds may be engineered to exist in higher temperatures and in higher magnetic fields. In a more direct sense, the motivation for this study lies in the richness and complexity of the cuprates as a physical system, even apart from the large energy scale underlying such high $T_c$, which can reach 150 K in HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ [44].

This study focuses on the superconducting compounds in the family of cuprates. In fact, the superconducting regime is a broad one in terms of composition, and so emphasis is placed on a
narrow range indicated in fig. 1.1 [20], the generic phase diagram for hole-doped cuprates.

These compounds are said to be hole-doped in the sense that $T_c$ and other properties are tuned through the density of dopant elements, which, for example, may have an oxidation state one higher than the elements they replace. The phase diagram shows the most well-known features and is derived by consolidating experimental results across many different compounds, but the exact details vary from material to material and are relatively poorly understood.

The most straightforward example of hole-doping in cuprates may be La$_{2-x}$Sr$_x$CuO$_4$. In this continuum of compounds, addition of a single Sr ion into the substance removes 1 La ion, as well as one free charge carrier, creating a “hole”. Therefore, an $x=0.1$ would be synonymous with $p=0.1$ in fig. 1.1. Cuprates may also be electron doped, adding negatively charged carriers, but this study and document focus exclusively on hole doped compounds. For simplicity, doping will be used solely to mean the addition of holes.

In this sense, La$_2$CuO$_4$ is said to be the parent compound of La$_{2-x}$Sr$_x$CuO$_4$. The parent compounds are universally antiferromagnetic (AF) Mott insulators [36] which are true electrical
Figure 1.2: Ortho-I, left, and Ortho-II, right, phases of YBCO. The Ortho-II phase has two different environments for the chain layer Copper, designated 1e and 1f, due to the absence of nearest-neighbor oxygen for 1e. The two different copper-oxide layers are known as chain and plane due to the four-fold rotational symmetry broken by the former [30] (right panel is copyrighted (2011) by the American Physical Society).

insulators due to electron-electron interactions. Doping reduces the energy scale of the antiferromagnetism while softening the insulating behavior. Very near the onset of superconductivity, that is, the lowest doping value with $T_c \neq 0$, the antiferromagnetism disappears.

The present study focuses on superconducting compounds of YBa$_2$Cu$_3$O$_{6+\delta}$ and HgBa$_2$CuO$_{4+\delta}$, or Hg1201, which are both “doped” by the addition of oxygen into layers outside the CuO$_2$ planes. In the former, the oxygen is inserted into a “chain” layer as seen in fig. 1.2 [38]. The addition of oxygen in these compounds does not yield a linearly related addition of free charge. Rather, the variations in oxygen have a complicated relationship to doping. Instead, $T_c$ is the most reliable identifier of a doping [38]. One can consider identical two samples of YBa$_2$Cu$_3$O$_{6+\delta}$ prepared with slightly different oxygen $\delta$ but with precisely the same $T_c$. This defines the $T_c$ as the identifying parameter of a single sample, rather than the nominal chemistry. The superconductivity of these compounds is very similar to that of La$_{2-x}$Sr$_x$CuO$_4$, but with $T_c$ values an approximate factor of 3 higher at comparable parts of the phase diagram. The analogy between the doping by strontium and the hole doping of all cuprates allows, thus, for an approximate understanding of the effect
of charge carrier density, or more simply, carrier density, on the different phases of interest. So while $T_c$ remains the defining feature, the chemical doping provides important information and the discussion will include both as points of reference on the phase diagram.

One of the hallmarks of superconductivity is the suppression of the density of states at the Fermi energy. This is known conventionally as the superconducting energy gap, because, in an idealized case, the density of states vanishes at the Fermi level. For isotropic superconductors, there is a gap to any electronic excitations [8]. In the cuprates, however, there are directions in momentum space along which the gap vanishes linearly [32], such that there are states vanishingly close to the Fermi level; disorder likely leads to a finite occupation of these low-lying states [34]. In addition to the cuprate’s anisotropic gap, for a broad range of doping there is a second suppression of the density of states near the Fermi energy known as the pseudogap [47]. The transition temperature associated with this pseudogap is known as $T^*$ and is shown in the phase diagram as a dashed line. Beyond optimal doping, defined as the doping corresponding to a maximum in $T_c$, there is no pseudogap and the behavior is similar to that of an ordinary metal or Fermi Liquid [50, 45]. For many years the nature of the pseudogap was very murky, but resonant ultrasound measurements eventually revealed evidence of a subtle thermodynamic phase transition at $T^*$ [61]. This type of steady unearthing of the phenomenological details continues today, indicating both the subtlety of cuprate physics, and the promise for future understanding.

Much of the literature on YBCO focuses on the nearly stoichiometric crystal with $\delta = 1$ (YBCO7), for which $T^* \approx T_c$. YBCO7 has an orthorhombic structure known as the Ortho-I phase. The high level of attention on this particular composition was due in part to the ease with which a stoichiometric solid minimizes disorder. That is, for compounds studied in the solid state, the most useful chemical formula is the one which references the composition of the crystalline unit cell, as in the case of all the formulas above; i.e. YBa$_2$Cu$_3$O$_{6.5}$ has 2 barium in a unit cell and an average across the solid of 6.5 oxygen per unit cell.

All chemical formulas with non-integers represent a near certainty of intrinsic disorder because the unit cells are not identical, and the dopants then represent scattering centers. The nearer $\delta$ or $x$ is to an integer, the more uniform the unit cells can be. A unique counter example to this
is, in fact, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, which is known as the Ortho-II phase. This phase has an orthorhombic unit cell which can be ordered as a nominal superlattice consisting of a unit cell of $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$. Fig.1.2 shows a structural comparison of the two “Ortho” structural phases. Perhaps the most fortuitous property of YBCO is that through these two phases, there exists intrinsically ordered “over-doped” and “under-doped” YBCO compositions, where the over/under modifier indicates $p$ relative to optimal doping, approximately $p=0.16$ [38]. The possibility of highly ordered structural phases maintains the hope for a true comparison of the doping effect on the electronic phases.

This work pursues such a comparison through several means. First, a review of the literature is an essential step in any scientific process; in this case, a partially chronological review is useful. This review begins with Ortho-I YBCO, and rounds out with the large volume of very recent work centering around the Ortho-II and what is known as Ortho-VIII phases, as well as Hg1201. Following this, a chapter discusses the experimental heat capacity technique, along with complementary techniques, to further enrich the current understanding of the under-doped compounds near Ortho-II YBCO, and the analogous Hg1201 compounds. A final chapter details the results at the center of the present study.

The central experimental technique of the study, heat capacity, is an essential tool in the understanding of any low energy physical system with a bulk quantity of particles, such that statistical mechanics is valid. Heat capacity is an extensive quantity defined as the change in internal energy per unit of temperature change. Specific heat capacity is the intensive cousin to heat capacity, often abbreviated as specific heat ($C$), and often normalized by mole or gram-atom. In the present study, all data is normalized by mole, including data from the references which originally published in gram-atom units.

Heat capacity measures all excitations in a system, including but not limited to: the electronic quasiparticles; those of lattice vibrations in a solid, the quantized form of which are known as phonons; and localized spin excitations, including nuclear spins. This represents a thermodynamic relationship which is a readily calculable and relatively straightforward quantity, as the second derivative of the free energy. It shows latent heats of transformation in phase transitions, and integrates to determine the change in entropy with temperature. In the zero temperature limit,
heat capacity measures the lowest energy excitations. Because of the power of statistical mechanics in this limit, the dependence on certain tuning parameters such as temperature and magnetic field can reveal much about the physics of the system. The remainder of the discussion treats these concepts in detail and uses the temperature dependence to draw as much insight from the experimental data as possible.

The motivation of the work is both speculative and well-grounded. With regard to the former, it is well known that all superconductors show interesting behavior in magnetic field, such as the famous Meissner effect, so that possibilities for unexpected observations abound. On the other hand, several measurements of heat capacity in lower fields on other cuprates have revealed a wealth of information and indicate higher fields and other dopings surely have more to offer. Further motivation for the work comes simply from the cuprate superconductors’ complicated phase diagram (see “Literature Survey”).

The unique addition of the work is in the measurement, in very high magnetic fields, of absolute, real units of heat capacity. The resulting data ranges over temperatures between 1 and 10 kelvin and magnetic field values from 0 to 35 teslas. The specific compounds studied are YBCO6.51 ($T_c=57$ K), YBCO6.47 ($T_c=49$ K), and Hg1201 ($T_c=72$ K, $p≈0.1$ with precise value of $\delta$ unknown).
CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

Any discussion of the cuprates must begin with the discovery in 1986 of compounds of “Ba-La-Cu-O” (also called LBCO) by Bednorz and Müller [10] and YBCO by Wu et al [80]. The dramatic and completely unexpected increase in $T_c$ represented by the discovery of YBCO led to what is known as the Woodstock of physics, the 1987 APS March Meeting [18, 37]. This massive enthusiasm is critical to understanding the volume of work and publications that have come forth since, and to understand that the following discussion is not an exhaustive presentation of the literature, but rather one that formed the basis of knowledge for the current study. The unprecedented energy scale represented by the $T_c = 92$ K reported by Wu et al and the vast technological utility represented by the prospect of a superconducting phase near room temperature motivates the continuation of that enthusiasm today. Beyond that, there are claims of several other interesting phases exhibited by this class of materials which may or may not relate to the behavior of the superconductivity. Electron spin behaviors include spin-ordered and spin glass [4, 29]. There is also confirmed charge order in certain cuprates as well as mounting evidence for such phases in YBCO and possibly in Hg1201 [69, 68, 22]. In order to cover as much of the complexity as possible, and because the cuprate story is more than twenty five years old, a partially chronological examination of the literature has the advantage of a natural organization that somewhat parallels improvements in sample quality and experimental technology. Since this study represents a significant refinement of an experimental technique and arguably the most accurate heat capacity measurements in magnetic field to date, a focus is placed on works most relevant to the interpretation of the specific heat results.
2.2 Early Foundations

In 1987, almost immediately after the discoveries mentioned above, Phillip Anderson proposed that the cuprates were a manifestation of his resonating valence bond (R VB) theory [5]. He asserted that the R VB state, an insulator, gives rise under doping to a pairing and charge mobility that would seem much like that of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. This marked one of the first serious attempts to explain the superconductivity, despite the lack of experimental evidence beyond simple material characterization. In fact, the following year, 1988, Siegrist et al [63] published a solution to the structure of YBCO, the first such proof. The R VB theory since then does not stand out for either success or failure, as the relative abundance of experimental evidence since 1987 has not led to any clear conclusions. This point underlines a theme of this chapter: the difficulty of both theoretical predictions and clear empirical conclusions in these materials. Nonetheless, the canonical copper-oxygen plaquette and copper-oxygen chains featured in Siegrist et al is central to most discussion of YBCO, and thus, much of the cuprate discussion at the time of the present study.

The straightforward empirical conclusions came fast at the beginning. In 1987, neutron diffraction showed the predicted antiferromagnetic order in La$_2$CuO$_{4-\delta}$, within the CuO$_2$ planes [72]. This work by D. Vaknin et al was done on polycrystalline samples, and showed little more than a small peak along the [100] direction. Fig. 2.1 is an interpretation of this result, one of the icons of early understanding of the cuprates, showing the arrangement of the spin moments in the antiferromagnetic, Mott-insulating state. D. Vaknin et al claimed a vanishing Néel temperature, $T_N$, for the stoichiometric solid and finite $T_N$ only for oxygen deficient compounds. Subsequent muon spin rotation and neutron diffraction studies found clear order for $T > 0$ in stoichiometric ($\delta = 0$) La$_2$CuO$_{4-\delta}$ [15, 23] and while others confirmed this for YBCO6 [55]. From the outset, the complex chemistry of the materials clearly created uncertainty in the details of the sample composition for these measurements. Before the sample quality reached an era of decent control, many advances came almost from brute force repetition of experiments by different groups, such with $T_N$ in La$_2$CuO$_{4-\delta}$.
One hypothesis about the superconducting state that has been long settled is whether the state of zero resistance is even superconductivity at all in the same sense of Onnes’s original discovery in 1911. That is, more precisely, whether or not Cooper pairing is responsible [70]. By using a superconducting quantum interference device (SQUID) to monitor the flux introduced into a ceramic sample of YBa$_2$Cu$_3$O$_{6+\delta}$, Gough et al [28] showed that indeed the charge quantization is by $2e$, or twice the electronic charge. This confirmed that the cuprates are strongly “type II” superconductors, meaning flux penetrates at very low applied fields. Further experiments tested the spin parity to show that, like “conventional” superconductors, the pairing is singlet [70]. These two facts prove extremely important to predictions regarding cuprate specific heat in a magnetic field. Perhaps the simplest spin-singlet symmetry other than the isotropic s-wave is d-wave. d-wave symmetry, in two dimensions, enforces 4 lines of vanishing amplitude. In 1993, Volovik [76] proposed that the density of states for a 2D superconducting gap with $d_{x^2-y^2}$ symmetry (four-fold rotational symmetry in momentum space, vanishing linearly with momentum-space angle) in a magnetic field ($H$) follows a $\sqrt{H}$. “Theoretical Background” in part loosely follows Volovik to show how this square-root-of-$H$ comes about.

The year after the Volovik paper, two landmark papers on the specific heat of cuprates focused on using the technique to probe the electronic density of states. The first, by Loram et al [40] utilized large ceramic samples and a differential calorimetry [39] to measure the electronic specific heat ($C_{elec}$) from 1.5 K to 300 K in zero magnetic field. The claims of Loram et al included the measurement of the normal state electronic specific heat via measurement above $T_c$ to give
\( C_{\text{elec}}/T \approx 18 \text{ mJ mol}^{-1} \text{ K}^{-2}. \) The implications of this result for the lowest temperatures is not clear, but taken at face value it implies a very large density of states. Given the issues in the early literature with respect to sample quality makes it relatively easy to dismiss on some level. Loram et al also showed measurements of the superconducting transition. Given that the differential method determined the ratio of heat capacities between a subject sample and a “dummy” sample which was not superconducting, their characterizations of the transition are likely to have been much more robust than those for normal state.

The second heat capacity measurement came from Moler et al [43]. Their study determined the \( H \) dependence of \( C \) for single crystal sample with \( H \) both parallel and perpendicular to the crystalline c-axis. This work was a test of Volovik’s prediction and yielded a striking indication that the cuprates do indeed house a “nodal superconductor” that much resembles one with d-wave pairing symmetry. The experiment strongly indicated \( C(H, T) \sim T \sqrt{H} \), just as predicted by Volovik. Beyond this, Moler et al provided a precise accounting of the field-dependent and zero field specific heat of YBCO6.95 at low temperatures, between 2 and 10 K. The end products of the measurements included an estimate of the specific heat of the superconducting quasiparticles in zero field, which is related to the superconducting gap strength, but these determinations require the precise characterizations of polynomial coefficients to at least third order. Any such sorting of polynomial coefficients is subject to the classic pitfalls of regression analysis. In finite field, the measurements revealed the presence of a non-monotonic feature known as a Schottky anomaly, which approximately followed the form of a Zeeman split electron. This Schottky contribution was taken to be basically extraneous and thus no more than a barrier to the analysis of the superconducting state. Thus, Moler et al revealed much of the data analysis issues associated with specific heat of clean YBCO in magnetic field, but it also showed the possible power of such measurements. The Schottky anomaly stands as a particular curiosity, because it contributes even for \( H = 0 \) where there is no true Zeeman splitting. Instead, a small effective internal field must exist. The anomaly was shown much earlier to be precisely controlled by the amount of magnetic impurity. Kim et al [31] used Cr substitution into the Cu sites to show that the anomaly, at least in polycrystalline samples, grows in magnitude linearly with the concentration of Cr dopant.
energy scale, which is given by the Zeeman splitting scale, did not vary with Cr content.

Despite the obvious role of impurities, even the most pure samples to date feature a Schottky anomaly, with one exception. Revaz et al. [52] successfully confirmed the $\sqrt{H}$ specific heat claim of Moler et al., but also showed data with effectively vanishing Schottky anomaly magnitude. The difference between the samples, besides the 4 years between the measurements, was in the very nearly stoichiometric YBCO7 measured by Revaz et al.

At this point, the d-wave nature of the superconducting state was by no means certain. Further confirmations of the specific heat result came from other groups on YBCO [79, 26] and other materials [25]. On the theoretical side, Simon and Lee [64] added more precision to the specific heat discussion by showing that the density of states in a d-wave superconductor scales (SL scaling) under variations of $T$ and $H$. In fact, Revaz et al. [52] demonstrated this relation successfully the following year. This scaling comes from the formation of the vortex lattice and the resultant length scale defined by the intervortex spacing $l$. This allowed Revaz et al. to collapse data onto a single curve by plotting $C/(T\sqrt{H})$ versus $T/\sqrt{H}$. Kopnin and Volovik also produced papers describing a scaling with a qualitatively similar result emphasizing the limits of the linearization of the DOS near the nodes [77, 33, 75]. The scaling discussion in part illuminated that theoretical picture was not straightforward and may depend on the particulars of the cuprate system [65]. The experimental results, however, were consistent with the existence of regime for which both the semiclassical method of Volovik and the treatment of the qp spectrum as a “Dirac cone” centered where the line nodes cross the Fermi level are at least qualitatively valid.

During the time of the early specific heat scaling discussion, angle resolved photo-emission (ARPES) experiments also showed strong indications of nodes in the superconducting gap in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSSCO) [62]. Unfortunately, such measurements of YBCO were hindered by sample quality issues relating to a surface state [57]. This problem is intrinsic to the chemistry and material properties of YBCO and make it a poor candidate for surface measurements relative to BSSCO. The present study does seek to make some comparisons to the BSSCO ARPES results, and so studies showing the vast similarities between BSSCO and YBCO are valuable for the discussion. ARPES showed that the pseudogap, marked by various phenomena at a temperature
typically called $T^*$, is a suppression of the density of states at the Fermi level that resembles a gap [21]. $T^*$ vanishes near optimal doping in all hole-doped HTS cuprates, at least in zero field, as determined by a broad survey of the various phenomena, including NMR and neutron scattering anomalies [24, 78]. The nature of the pseudogap and its connection to superconductivity is still unknown at this time.

Fortunately, there is no such mystery regarding the symmetry of the superconducting gap, thanks in large part to work done by Kirtley and his colleagues culminating with a detailed determination of the particular momentum space shape of the gap amplitude in YBCO. The shape of the gap is very important to specific heat measurements, because the manner in which the low-lying excitations fill in gives rise to the temperature and other determiners of $C$. The paper by Kirtley et al [32] showed SQuID measurements of the spontaneous supercurrents created in a superconducting ring. The rings were composed of varying portions of YBCO and an s-wave superconductor (Nb). The SQuID captured the spontaneous generation of supercurrents from $\pi$ phase shift between the junctions in the ring when the angle between the two superconducting junctions was right. Fig. 2.2 shows the striking result of the measurements. Despite the deviation from pure $d_{x^2-y^2}$, the form still maintains the qualitative features which give rise to d-wave specific heat scaling in magnetic field.

### 2.3 Recent Developments

The landscape changed greatly in 2007 with the discovery of quantum oscillations in YBCO6.51 [46]. The Shubinikov-de Haas (SdH) oscillations in the Hall coefficient were an emphatic proof that a Fermi liquid exists within HTS samples that also exhibit $T^* > 0$. This was followed by confirmation in the form of de Haas-van Alphen oscillations in the magnetization [59] and a doping dependence of the oscillations. The oscillations frequency was doping independent with a value near 500 T, implying a small, fixed pocket size in momentum space and evidence of a diverging cyclotron effective mass $m^*$ based on Lifshitz-Kosevich analysis of the temperature dependence of the amplitude [58].
Figure 2.2: Figure 2 from Kirtley et al., shows definitively the symmetry of the superconducting order-parameter of YBCO. The method imaged magnetic field from the spontaneous currents created by $\pi$ phase shift at a junction with the s-wave superconductor niobium. Reprinted by permission from Macmillan Publishers Ltd: Nature Physics [32], copyright (2006).

Riggs et al. [54] measured the quantum oscillations in specific heat and confirmed the frequency and found that previous reports of $m^* \approx 1.4$ for YBCO6.56 were quite consistent with the oscillations of $C$. The specific heat provided a bulk thermodynamic confirmation of the presence of a high-field Fermi liquid state, and put an upper bound on the density of states. With an LK mass $m^* = 1.4$, eq. 4.6 requires that each Fermi pocket requires $\gamma = 2 \text{ mJ mol}^{-1} \text{ K}^2$. Riggs et al. found a maximum $\gamma(H) = 5 \text{ mJ mol}^{-1} \text{ K}^2$, suggesting no more than 2 pockets. Because the structure of YBCO has two non-degenerate CuO$_2$ layers per unit cell, this suggests no more than 1 “split” pocket in momentum space.

Also in 2011, Leboeuf et al. [35] claimed evidence a Lifshitz transition from an insulating to metal phase with increasing doping. They measured resistivity versus temperature at high fields ($H > 55$ T) at several dopings. Lebouef et al. showed $dR/dT < 0$ (“insulator”) for a doping near $p=0.08$ (O6.45) and $dR/dT > 0$ (“metal”) for $p=0.09$ and higher. YBCO6.47 falls in between the two regions, corroborating the location of the transition as claimed in ref. [58]. On the insulator side of things a p approaches 0, the system becomes a Mott insulator [36]. The Mott insulator is also an antiferromagnet, and these behaviors may simply be dying off slowly. In fact, the Mott physics may reach all the way to this metal-to-insulator transition if the spin density wave reported
by Haug et al [29] is related to the antiferromagnetic order.

One of the reasons that quantum oscillations measurements were possible and abundant is the relatively low values of $H$ above which the resistivity is finite ($H_R$). Ramshaw et al [51] showed that $H_R(T \to 0)$ has a local minimum for the structural ordering known as Ortho-VIII. They use their data to provide an estimate of $H_{c2}$, the superconducting upper critical field defined by the magnetic length $l = H^{-1/2}$ approaching the coherence length $\xi$. For the present study, the $H_R(T)$ curve may be considered an absolute bound on the “normal state”. That is, for fields well below $H_R(T)$, superconductivity must be robust in the since that the superconducting gap is a constant in $H$. Across the phase diagram, this $H_R(T \to 0)$ has a minimum for $p \approx 1/8$, or just below that.

In 2012, NMR studies [81] showed an onset of charge-order near ortho-II YBCO, initially discovered as a shift in the $^{63}$Cu quadrupolar lines associated with the 2F site but not the 2E sites (see fig. 1.2) of the CuO$_2$ planes, with the e/f designation defined by the presence of nearest-neighbor Oxygen in the CuO chain layer. This splitting indicated a commensurate, field induced version of charge-order within the CuO$_2$ plane layer. The observation was, to some degree, confirmed by high-resolution x-ray scattering in 2012 [27], excepting the commensurability. Next, Wu et al [82] found that over several dopings near $p = 1/8$, various NMR phenomena have features or onsets for a field $H_{\text{charge}} = 10$-15 T. In a striking similarity, at about $p \approx 0.12$, both $H_{\text{charge}}$ and $H_R(T \to 0)$
seem to have a minimum. Ghiringhelli et al [27] confirm the importance of this p with x-ray measurements, but Chang et al [17] observed only a field enhancement of the charge-order signature, not a field-induced transition. The arguments for this discrepancy lie in the difference in timescales for the measurements. The x-ray measurements may probe very short times by using very broadband x-rays able to see fluctuations; NMR may also simply not have the resolution to pick out the particular order [12].

The YBCO mystery has seemed, thus, to unravel slowly under the progression of more and more sensitive experimental techniques. A great example of this is the work by Shekhter et al [61] to unearth the thermodynamic nature of the pseudogap transition. Using extremely sensitive resonant ultrasound measurements to probe the lattice for the slightest changes, Shekhter et al observed both the superconducting transition and $T^*$ as thermodynamic phase transitions for both underdoped (YBCO6.6) and overdoped (YBCO7) samples. The pseudogap is then likely a separate phase rather than merely a phenomenon with a characteristic temperature scale.

Finally, in December 2013, a paper by Barišić et al [9] showed SdH oscillations in Hg1201 on the underoped side for p very near that of charge-order in YBCO. The $m^* = 2.5$ and oscillations frequency, 840 T, are consistent with features of YBCO oscillations. This work indicates that it is highly unlikely for the YBCO oscillations to originate from some part of the system other than the CuO$_2$ planes, implying that there is a phase transition from superconductor to Fermi liquid. However, given no confirmation of these oscillations in Hg1201 by other experimental methods or other research groups, some questions remain.
CHAPTER 3

EXPERIMENTAL SUMMARY

3.1 Introduction

Heat capacity is an extensive quantity defined as the change in energy of a thermodynamic system per change in the temperature with some other parameter held constant, usually the volume. The most straightforward way to measure heat capacity is in a quasi-adiabatic idealization where some precise amount of heat is added directly to the system and no heat is allowed to flow in or out otherwise. The temperature subsequently varies a small amount, and system volume or pressure is kept constant. By the first law of thermodynamics, the constant volume case requires the change in internal energy to equal the added heat. Dividing the heat input (in units of energy) by the measured temperature change gives the total heat capacity. Dividing by the amount of substance gives the specific heat capacity, or specific heat. Usually this amount of substance is measured in moles, and specific heat is reported as mJ mol$^{-1}$ K$^{-1}$.

During a heat capacity measurement involving solids, especially crystalline solids, maintaining a constant volume is essentially impossible. Instead, we apply a constant pressure, and measure the heat capacity $N \times C_p$. For several reasons, the pressure is kept as close to zero as possible in all original measurements reported in this document. This means any volume change in the measured system does no work, so that relations $N \times C_p = \frac{d(E+pV)}{dT} = dE/dT$, $dQ = dE$ are assumed to be true, with $E$ the internal energy and $Q$ the heat introduced. In reality, a solid maintains its own equilibrium with “internal” pressure and the applied pressure acts only as a perturbation over vast range, from ultra-high vacuum to standard pressure and beyond. Thus, the sample thermal expansion is the crucial consideration, as it determines the degree to which the volume is constant. For the cuprates and most solids, thermal expansion is negligible over the temperature range of interest, $<10$ K. If there is any doubt, a cursory look at the specific heat data may validate that
the measurement occurs in the regime of negligible expansion, where $C_p = C_V$ may also be valid. The telltale signs of such a regime enter the discussion in later chapters, including indications of crystalline vibrations that are exclusively harmonic. This harmonicity preserves the mean positions of the lattice ions and thus the sample volume. In this limit, constant applied pressure gives way to effectively constant volume. Nonetheless, because the technique is somewhat at the mercy of the sample to hold its own volume constant, we from here on refer to the measurable quantity as $N \times C_p$, which is also abbreviated as $N \times C$. The determination of the actual values of plain $C_p$ and subsequently $C_v$ remains after the fact, and relies upon, among other things, an accurate assessment of sample mass. An accurate mass determines the amount of material to very high accuracy by assumption that the sample is essentially pure, composed of only the material expressed by the chemical formula that identifies the material.

In practice, it is impossible to prevent heat flow out of the system. This means it is critical to develop a quasi-instantaneous definition of $C$. For this, we assume that heat is introduced through some constant power $P = dQ/dt \neq dE/dt$, where $t$ is time. If the total $Q$ introduced by a source is no longer equal to the change in $E$, it complicates the relationship. We can still extract $C$ from temperature versus time curves nearby time $t_0$ in a $P = P_0 \Theta(t_0 - t) \Theta(t - t_1)$ scenario where $\Theta(t)$ is the Heaviside function. The square pulse allows for the characterization of both a heating and cooling process. The cooling process independently reveals how heat leaves the system at each temperature. In principle, the same information can be extracted by assuming a pure exponential relaxation curve and fitting under such assumption, as long as the temperature change $\Delta T$ is sufficiently small to allow linearization of $C$ and $K$, the thermal conductance. The additional assumption, however, reduces the robustness of the protocol.

The framework for these assumptions all relies on a reasonable set of classical principles in the form of Fourier heat flow analysis as well as proper experimental engineering to ensure that the use of idealizations, such as 1-D modeling, are acceptable approximations of the system. With the instantaneous method in hand, the measurement remains robust to deviations of the system from many of the assumptions. The remainder of the chapter is devoted to a demonstration of that robustness in terms of both accuracy and precision in real units of $C$. 
What follows is a discussion of the unique experimental methods employed in the research. The advancements and original contributions associated with the present study consist of significant refinements to methods developed for ref. [54], including a comprehensive rebuilding and re-imagining of the methods. Though everything that follows is underpinned by concepts we developed prior to the present study, the final product represents a novel synthesis and a unique capability.

3.2 Measuring Temperature

The measurement of the lowest temperatures attainable via liquid helium is best performed with resistive thermometers with negative temperature coefficient of resistance. These are insulators, in the sense that resistance $R \to \infty$ as $T \to 0$, yet may be configured as (thin or thick) films of reasonable resistances in the desired measurement range, usually several thousand ohms per square. While a variety of materials and techniques can measure temperature accurately at liquid $^4$He temperatures, most of these vary wildly in response to a magnetic field. A resistive thermometer (RTD) composed of zinc oxynitride is somewhat of an exception. However, it still shows unacceptably large magnetic field induced errors that must be calibrated out above about 4 T. Capacitance gauges, on the other hand, have very little magnetic field dependence, but are both lacking in sensitivity and hysteretic in temperature. They are also physically quite large. Thus we employ RTDs solely as the primary thermometers.

Calibration of thermometry in zero magnetic field is quite simple, in principle. This requires a strong thermal link between the thermometer undergoing calibration and some temperature standard, as well as a cryogenic system. Certified calibrated thermometers are widely available commercially, as are cryostats/cryogenic systems. This study and this particular calibration method uses Lakeshore Cryotronics Cernox RTDs and an Oxford Scientific HelioxTL $^3$He cryostat.

A particular complication immediately arises because of the necessarily mechanically delicate components. As can be seen in figs. 3.1 and 3.2, the thermometers are deposited onto sapphire substrates which are then suspended by 25 $\mu$m thick wires and silver epoxy. The fully wired construction comprises a single “sample platform,” or “platform” for brevity. A sample platform
includes the thermometer, substrate, a second metal film resistor for a heater, wires, and a phenolic connector with gold pins that provides structural support and mates electrically and mechanically with experimental probes. It is critical to wire the thermometers in the correct configuration before calibrating, due to the fragility of the thermometer. That is, the calibration might change during re-attachment of wires or other operations so calibration must succeed platform construction. To ensure close thermal contact between the thermometer which is the subject of calibration, and a second providing the standard, a large copper mount and radiation shield encloses both thermometers. The standard thermometer attaches to the surface of the copper mount with silver epoxy. The copper mount links to the platform via a weak copper spring that is soldered to a copper sheet that, in turn, presses on the substrate. The copper spring method guarantees that the maximum force on the platform is far less than the breaking strain for the platform wires or epoxy joints. The leads to both thermometers pass through the mount, packed in cryogenic grease and wound around the exterior of the mount. A second calibrated thermometer glued to the copper mount in a third position monitors for thermal gradients.

In this configuration, the copper mount is ready for attachment to the base of the probe. Speaking in rudimentary terms, “probe” refers to what are essentially long tubes with electrical feedthroughs that allow the passage of wires from the experimental instrumentation down into the cryogenic environment at the center of the magnet system. Once the probe is in place, minimal
Figure 3.2: Sample platform based around custom-made zinc-oxynitride thermometer (Cernox), current version, with sample. This version utilizes more of a true 4-contact measurement (contacts labeled by numbers) by removing the silver epoxy contacts from the calibrated resistance. Only the evaporated gold contacts and zinc-oxynitride film contribute to the measured resistance, improving the durability.

Exchange gas is used to provide thermal conductivity but minimize thermal gradients. Two AC resistance bridges measure the platform thermometer resistance ($R_{plat}$) and the standard thermometer resistance ($R_{st}$) as the temperature is varied slowly. A steady warming ramp averaging 0.03 K/minute precedes a step and hold cooling pattern with similar average rate of change of temperature. The data is converted into a temperature versus resistance plot via the calibration data provided by the manufacturer of the standard thermometer. Then, a second method where the platform thermometer is measured with the exact setup used during $C_p$ experiments allows a check against the first (AC bridge based) method to ensure accuracy is not marred by slight variations in the resistance measurement. The details of the $C_p$ experimental setup are described in more detail below.

The inclusion of applied magnetic field $H$ as a variable orthogonal to temperature is not straightforward, because $H$ affects most measurables at problematic levels. Finite field calibration employs two overlapping methods. Exclusively at low field, this work includes calibrations predicated on the field-independence of a capacitance gauge. This gauge provides a feedback for fixed-temperature control during slow field sweeps. The capacitance gauge and platform reside again on the copper sample mount for thermal contact. The capacitance is measured to femtofarad precision, while a home-made software (i.e. written by the author) “proportional integral differential” (PID) feedback
controller modulates a current source. The current from the source generates a Joule heating to stabilize the temperature, based on the calculation of the PID controller. Through this method, temperature errors up to 15 T can be reduced by an order of magnitude. This method is useful in any DC field setup down to 2 K, however, it is extremely expensive to carry out in a resistive magnet, whereas in a superconducting magnet system (SCM), minimal energy is consumed to maintain field. Further, for measurements in an SCM, software can automate the process with relatively little human supervision. Eddy current heating complicates matters, because the temperature controller must be set to correct slowly to prevent over correction of the temperature due to noise. One solution to the eddy current problem is to complete a sweep from -15 T to 15 T so that $dH/dt$, or $\dot{H}$, is constant for a long time and already compensated by the PID controller. For temperatures below 2 K, starting at about 1.8 K, a $^3$He vapor pressure method can be used to hold temperature constant. This involves the use of a charcoal sorb far away from field center (the vertical center of the magnet solenoid) so that its temperature can be monitored during a field sweep. By keeping the sorb temperature constant, $^3$He liquid can be maintained at a relatively constant temperature. By using multiple consecutive sweeps between -15 T and 15 T and examining $R_{\text{plat}}$ at each sign change of $H$, a linear characterization of the temperature drift can be determined. A simple subtraction removes much of this drift. It is a subtle matter to ensure the accuracy of such a method, but with sufficient effort it becomes viable with sufficiently large number of sweeps to characterize any error statistically. That is, by averaging a large number of sweeps at the same nominal temperature, we may achieve a converging accuracy. This sort of time consuming brute force method makes the application of this technique in the inefficient resistive magnets of the NHMFL DC user program economically prohibitive.

Thus, to achieve higher fields, pulsed magnets provide the best option. This seems obvious at first glance, as the protocol calls for a nominal fixing of temperature followed by a rapid cycling through the field range. This process essentially freezes out any natural temperature drift that occurs in the lead up to the pulse through the short time scale.

All pulsed field results are from the NHMFL pulsed field facility (PFF) at Los Alamos National Laboratory. The present methods of high-field calibration are based on previous efforts [53] that
utilized a magnet system called the “mid-pulse” (MP), because of the time characteristics of the pulse: a maximum field within 50 ms of pulse initialization, and subsequent decay back to 0 T within 400 ms. Unfortunately, the sudden decommissioning of the MP renders it unusable for the present work. It is noteworthy, however, as a starting point for addressing the problems that alternative magnet systems pose. The pulse profile of the MP is shown in fig. 3.3.

The calibration methods for all new data rely upon two magnet systems at the PFF: the first is a “short pulse” magnet (SP) and the other a “long pulse” or “controlled waveform” magnet system (LP). The SP profile in field versus time is quite similar to the MP, qualitatively speaking, but with a factor of 4 shorter timescale. Both the MP and SP are capacitor driven; since all electromagnets are large inductors (wire coils), the SP and MP pulse profiles must necessarily be those of textbook critically damped LCR circuits. While all the magnet systems featured in this study use a solenoid-like design, the LP is unique in its use of 3 coils to achieve various pulse profiles. For this work, the LP was run in close approximation to a triangular pulse, meaning nearly symmetric in time about the moment of peak field and linear $H(t)$ on the up-sweep and down-sweep, with a total run time near 2.5 seconds.

This dual strategy allowed for the comparison and verification of the repeatability of the data sets from each magnet system, as well as encompassing the regime of the old mid-pulse. This is necessary because of one inherent difficulty in measurement in a typical pulsed magnet system: a
rapidly changing field and qualitatively fixed profile. Such a profile leads to electrical eddy currents in any conductors and generates unacceptable levels of heating. The main countermeasures for such heating are removal of as much conductive cross section as possible and enhancement of the heat capacity of the platform and the thermal conductivity of the environment. Use of the minimum silver epoxy in attaching the leads helps to achieve the former. Attaching high heat capacity materials to the back of the platform substrates, such as vitreous selenium and paraffin, satisfies the latter point.

It is this last mitigation that stands out as the most important and most difficult to manage. Thermal conductivity in the sample environment is primarily a product of $^4$He properties. Because the platform configuration is fixed, the sapphire substrate cannot attach directly to the probe structure. The copper spring cannot be used as a thermal link because low resistivity materials like copper are prone to severe eddy current heating. This leaves only the platform’s own wires, which are poor thermal conductors, and the surrounding $^4$He as the only exit for heat. Thus, the only control over the exit thermal conductance is variation of the density of the surrounding fluid. Liquid $^4$He is an excellent thermal dissipator, such that all work between 1 and 4 K is much simplified compared to all other temperatures. If temperatures below 1 K are necessary, the best solution is simply to avoid the use of pulse-magnets and work only up to 15 T using the capacitance gauge controlled method. Above 4 K, an optimal gas density is vital. Too much gas can cause large temperature fluctuations, while too little gas can fail to sufficiently dissipate heat from eddy currents.

In contrast to the SP, the LP, with its variable field-time profile, seems to solve these problems, but it also generates several difficulties of its own. First, the magnet system is expensive to run. Second, the method by which the operators and systems control the waveform creates a secondary “ripple” effect which shows up as high frequency variation of the field, and re-introduces the problems associated with the SP. Third, the large size of the magnet requires the use of longer cabling and probe. However, by cross referencing data from the two magnet systems, the uncertainty that would come from a single calibration set up is greatly reduced.

As with any measurement, once accuracy reaches an acceptable level, precision becomes the
primary concern. The SP’s large $\dot{H}$ once again becomes an issue both as a source of noise and an intrinsic timescale. A typical route for combating poor signal-to-noise ratios involves first maximizing the signal and then reducing the noise through either filtering or physical changes to the setup.

The first step, maximization of signal, is a simple matter in a resistance measurement. In this case, a four-contact method with a fixed root-mean-square (RMS) current ($I$) and a simple high-speed voltage ($V$) measurement suffices to extract the resistance with ample resolution. By Ohm’s law, we can tune the measured voltage signal simply by increasing the applied $I$. Of course, it is vital to check that ohmic assumptions hold when beginning an experiment. Joule heating is by far the most common source of strict Ohm’s law violation during these experiments; in the interest of reducing Joule heating, which increases as the square of both voltage and current, it is worthwhile to reduce the current to about 70% of the maximum acceptable level and, therefore, reduce potential heating by about 2. As a rule, all parameter choices include some buffer within their upper bounds. This is also the case for the heat capacity experiments themselves.

The second signal to noise consideration comes in the choice of excitation signals. The choices are essentially two: a field-symmetrized DC excitation, or a high frequency AC excitation with a lock-in filter. The DC method requires twice as many pulses, in order to symmetrize the data by subtracting traces from opposite direction pulses. This process is necessary to remove the large voltages that $\dot{H}$ induces. The AC choice offers more agility in countering noise via the lock-in filter through shifts in the excitation frequency. The high-speed advantages of the AC technique also generate their own problems.

One complication comes in the AC signal generation. The maximum frequency at which these methods can succeed is about 100 kHz (a typical choice is 61.1 kHz). In this acoustic/low RF band, differential measurements reject noise much more efficiently than ground referenced measurements. While differential preamplifiers and digital data acquisition systems (DAQ) with data (sampling) rates ($f_{data}$) into the MHz (i.e. millions of digitizations per second) are readily available for subsecond record lengths, the availability of a current source capable of generating a differential signal with the right parameters is quite limited. However, a simple current transformer with huge
inductive impedance on the secondary winding can generate a differential signal with RMS voltage proportional to load resistance (constant RMS current) over a reasonable width of parameter space. In principle, this transformer (CCT) can generate a frequency and resistance independent current over a wide range of values. The drive voltage on the primary coil as well as the coil turns ratio fully determine the current in principal. In practice, it is simple to use a high-precision resistor right at the coil to accurately test the current flowing in series with the thermometer.

Because any finite frequency excitation resistance measurement is in effect an impedance measurement through finite reactance components from inductance and capacitance, a central challenge is in the somewhat pathological impedance of this circuit. Specifically, the huge impedance of the CCT and the inclusion of gain>1 preamplifiers tends to bring the measured impedance away from any attempts to calculate or fit it with a simple model. The impedance problem is exacerbated by the capacitance of the twisted pair wires running down the probe as well as cables throughout the thermometer circuit. The CCT and wires also can pick up large voltage noise from extraneous electromagnetic (EM) radiation such as 60 Hz noise from the power grid. Magnetic steel enclosures with very small EM penetration depths shield out interference, and short wire lengths avoid such problems somewhat. These solutions are not always simple to implement. Effectively, in pursuit of precision, more challenges to both precision and accuracy have been introduced, but not without good reason. The resolution of these challenges is one of the critical accomplishments of this work, and so a brief list of components from the unique instrumentation and setup follows.

The overview naturally must begin with improvements to the sample platform, highlighting the differences between Figs. 3.1 and 3.2. The addition of 2 extra gold traces results in a true twisted pair, 4-contact measurement of the thermometer. In the 2006 version, the nearest-neighbor wires are not paired such that both carry either $I$ or $V$ signals. The large separation between the members of a wire “pair” (two wires completing either the $V$ or $I$ loop) leads to large noise pickup. Under the current platform design, we attach the leads as pairs, and this minimizes the open loop area in the noisy environment of the magnet center. Further, because the wires in the 2006 version are attached with a single continuous silver epoxy joint, the contact resistance of this joint is included in the measurement. Such contact resistance is usually a few percent of the measurement, but the
Figure 3.4: Business end of the pulse field probe (bottom), shown next to a length scale and supported by a metal bench stand. A G10 garolite, or fiberglass epoxy encapsulate, tube houses the wires and an outer sleeve covers the termination with the platform. A wrapping of PTFE (aka Teflon®) just to the right of the sleeve fits snugly within the sample space to damp vibration during pulses. The second tube (top) is identical to that of the sample space bore inside the SP. Almost no metal is used to minimize inductive heating.

epoxy shows an inconsistent aging or degradation that can occasionally lead to large resistance increases. Because the purpose of an RTD is to use resistance to determine temperature, these changes are unacceptable sources of uncertainty and inaccuracy. For example, a shift of only a few percent or so in the resistance can render these thermometers useless for $C_p$ experiments until recalibrated. The 2006 version is naturally quite unreliable, but the changes leading to the current platforms have eliminated these problems almost completely.

On the precision side, by all accounts, we have exhausted the noise rejection for this platform design. This assertion remains impossible to truly test, but the logic is as follows. The thermometer film itself has an orientation-sensitive magnetoresistance,[14] rendering problematic any rotational or twisting modes of vibration in the presence of a magnetic field. Though the malleability of the wires supporting the platform reduces vibration, deformation of the SP and LP during pulses makes vibration inevitable. Noise levels during a pulse are then bounded from below by the anisotropic magnetoresistance of the thermometer. Further, the platform is oriented with the normal vector
of the contacted face of the substrate parallel to the field, counter-intuitively resulting in reduced field induced noise in the open loop of the gold contacts. To see this, one may note that induced voltages are linearly related to the rate of change of total flux within a circuit loop area. The noise directly from the pulse $\dot{H}$ is on a much slower timescale than the AC measurement signal and so this noise filters easily. The primary source of unwanted flux variations on broadband timescales is changes to the component of the (loop) area vector parallel to $\mathbf{H}$, i.e. vibrations. One can break these problematic vibrational modes into two components: transverse and rotational. The wires are not a factor in this discussion because they are tightly twisted with net open area nearly zero.

For the gold film traces (see fig. 3.2), the transverse modes are quite clearly frozen out by the stiffness of the substrate. We are left only with the variations in angle $\phi$ between the area vector of the substrate face ($\mathbf{a}$) and the magnetic field; fortunately, since flux ($\Phi$) is determined by $\mathbf{a} \cdot \mathbf{H}$, which is at a maximum for our chosen configuration, $\frac{d\Phi}{d\phi}$ is ideally vanishingly small. The net effect is that the Cernox strip itself is far more prone to random variations in magnetoresistance than the circuitry is to induced voltage noise.

As stated before, the placement of the platform at field center, as well as the transmission of current and voltage signals between the platform and the cabling, is the role of the probe (fig. 3.4). The pulsed-field probe is custom-made for this experiment, and we refer to it as the “high impedance probe” as its minimal capacitance design means that the probe itself has an extremely high characteristic impedance. We achieve the low capacitance in balance with superior noise rejection through hand-twisted wire pairs of the shortest possible length, housed in non-magnetic stainless steel capillaries. The loose twisting includes the open-area-compensating aspects of an axially symmetric (i.e. roughly helical) configuration but excludes the extra wire length and small wire separation that drives up capacitance in commercially-made tight twisted pair. The wires are firmly glued to a sapphire bit between the probe shaft and terminating connector. Mechanical anchoring such as this ensures minimal wire motion, the enemy of precise measurements. Wire anchoring is double important in field, because of the increased potential for inductive noise pickup. In contrast, freely moving wires raise noise levels and also tend to randomize noise spectra pulse to pulse. As a final touch, a wrapping of PTFE placed around the probe shaft about 20 cm from the
platform further constrains the probe within the magnet system. This wrapping may potentially prevent cooling by excluding the $^4$He gas or liquid from the bottom of the sample space, so its design includes a PTFE tube to bypass such problems.

With a decent probe, we have a strong starting point to reach the goal of high quality measurement. The remainder of the setup must maintain the paradigm set by the probe design. To prevent further addition of capacitance, we use short cables and position the CCT very near the probe head. Unfortunately, the CCT is as sensitive to vibration as the probe and sample platform, and so we clamp it down to a handrail surrounding the magnet system. Clamping the CCT offsets much of the potentially significant vibration from the proximity of the magnet and the tugging of cables. Next to the CCT, we place battery-powered high input impedance preamplifiers (preamps), which effectively decouple the 4-wire measurement circuit from the DAQ and any capacitance on the output side. These preamps have other additional benefits: a high common mode rejection ratio, a feature that screens the EMF fluctuations of the differential circuit relative to the ground that are universally problematic for differential to single-ended measurements; a gain multiple of 100 that pushes the sub-millivolt signal well into the millivolt range, making better use of the DAQ digital resolution; and low intrinsic input noise that combines with the gain to ensure that the total intrinsic circuit noise for all components is well below the minimum measurement noise, i.e. from EM radiation, vibration, and the pulsed field.

With all of the methods above in place, the precision improves vastly in comparison to a DC method while maintaining its accuracy. It all hinges, however, on the lock-in filter which is at the heart of both the heat capacity measurements as well as the thermometer calibrations. This filter is entirely software based, and while analog band pass filters pair to drive the noise down even further, the digital aspects allow a variation of the filter parameters for a single set of data with a single click. The lock-in system is not unique to these measurements, but is rather a product of the PFF and is utilized widely at that facility. However, the heat capacity measurements make special use of this technique, and the pulsed-field calibrations rely heavily on the most sophisticated possible application of the lock-in.

For an initial example of the lock-in’s advantages, we analyze the raw data with a fast Fourier
transform (FFT) over different parts of the pulse, a noise spectrum provides a digital map for
frequencies of the best signal-to-noise that the lock-in can exploit when the excitation frequency is
properly tuned. The FFT provides a good complement to the lock-in technique because of a mutual
reliance on a Fourier basis. As eq. 3.1 shows, the lock-in filter relies on the infinite dimensionality
of Fourier space and the orthogonality of all unique Fourier components.

\[ \int_0^{\infty} \sin(\omega_1 t) \sin(\omega_2 t) dt \]  

(3.1)

Where the integral is over time, \( t \), for two frequencies, \( \omega \). This inner product can be represented by
the delta function \( \delta(\omega_1 - \omega_2) \), but is hardly instructive, because the lock-in filter is both a discrete
and finite-time realization of this principle. The discrete method includes a sum which is easily
normalized by a simple division by the width of the necessarily finite time window to recover the
correct amplitude at \( \omega_{ex} \), the measurement frequency. For \( f_{data} \) much greater than \( \omega_{ex} \), the lock-in
is a superb low pass filter. If the sum is taken over an integral number of periods \( 2\pi/\omega_{ex} \), this
represents a very long time for high frequency noise and the sum acts similarly to the inner product
in this regime. Analog low pass filters can readily solve the complication of aliasing[60] from above
the Nyquist frequency \( (f_{data}/2) \) without diminishing the signal. At sufficiently high data rates, this
additional low pass filtering is mooted by the minimum response time of the circuits, which act
as effective filters on frequencies exceeding their response. For example, the 4 wire circuit can act
as an LRC filter simply through the thermometer resistance, parallel wire capacitance and series
inductance. As a high pass filter, the lock-in is equally effective, so long as there is no mixing
between the timescales of the actual resistance and the noise. One can partially see how the high
pass comes about by adding a constant to one of the sine functions in equation 3.1. The result is
two integrals: one identical to that of equation 3.1 and the other simply a constant multiplying a
periodic function: \( \int_0^{\infty} K \cdot \sin(\omega_{ex} t) dt \), where \( K \) is the constant. The result depends on the limit of
infinite time. In real experiments, it is simple to control the integrals limits, and choosing an integer
number of measurement periods forces the sum \( \sum t_i K \cdot \sin(\omega_{ex} t_i) \) to vanish. The same result is
found for a line in place of the constant as well. Thus, noise frequencies which are sufficiently slow
are removed in the same way as lines or constants. For longer sums, one might imagine that these low frequencies begin to show curvature, but this is not important because we can easily break the long sum into a sum of short sums. $\omega_{ex}$ then sets the only relevant timescale for all noise frequencies such that $\omega_i < \omega_{ex}$.

Now we ask the question: under what conditions does the lock-in fail as a filter? This is simple to understand by considering how $\delta(\omega_1 - \omega_2)$ looks for finite time. If we break (3.1) into pieces and replace $\omega_1$ with $\omega_{ex}$ and let $\omega_2 = \omega$ be arbitrary, the result is the sum:

$$\sum_{i=0}^{\infty} \int_{t_{i-1}}^{t_i} \sin(\omega_1 t)\sin(\omega_2 t)dt = \frac{1}{2} \sum_{i=0}^{\infty} \frac{\sin[t_i(-\omega_{ex} + \omega)]}{-\omega_{ex} + \omega} - \frac{\sin[t_i(\omega_{ex} + \omega)]}{\omega_{ex} + \omega}$$

(3.2)

Figure 3.5: Plot of normalized relative amplitude for finite maximum $i$ on the right hand side of eq. 3.2(red) versus $\omega$ and a Lorentzian (blue) for comparison. The plot only displays the effect for a single phase at each frequency, such that this result is for the “in-phase” part. Essentially, the amplitude acts as a multiplier to the total signal at each frequency, leaving the signal unattenuated at the measurement frequency. Here, $\omega_{ex} = 2\pi \times 1000 \text{ rad/s}$ and the averaging time window is $4/\omega_{ex}$, giving a full width at half maximum of about 155 rad/sec. The main positive feature for noise rejection is the rapid drop from the central maximum due to the periodic function. The most disadvantageous feature is the very long-tailed nature of the distribution, but this can be easily overcome with additional analog bandpass filtering.

The sum is of an infinite number of intervals of identical width $t_i - t_{i-1}$, with $t_i \omega_{ex} = 2\pi \times z$, where $z$ is an integer and the $i$th interval containing a function of $\omega$ composed of a product between a periodic function and what is approximately a Lorentzian. A Lorentzian vanishes uniformly at infinity and, the periodic function vanishes when the arguments of the sine functions become
multiples of \( \pi \). For a finite sum, \( 1/i_{\text{max}} \) determines the peak width, where \( i_{\text{max}} \) is the sum upper bound. The closest vanishing point, in this case, occurs at \( \omega_{\text{ex}}(1 \pm \frac{i_{\omega}}{2}) \). This means that for any digital lock-in technique, the noise is well-attenuated for frequencies further than \( \omega_{\text{ex}}/2 \) away from \( \omega_{\text{ex}} \). If the averaging number \( t_i\omega_{\text{ex}} \) is much more than unity, the pass band becomes very narrow.

For typical measurements in the SP, we choose an averaging number of between 2 and 5. For typical heat capacity experiments, this can range from 2 or 3 up to 50, because the measurement time scale can vary from 150 ms to 10 s. The fully discrete version of the lock-in can recreate the continuous finite (analog) version well within any data resolution (16 bit or better) over a broad band with only a data rate of \( f_{\text{data}} = 10\frac{\omega_{\text{ex}}}{2\pi} \).

Beyond the simplest principles of the digital lock-in, there exist some subtleties. During pulsed field calibrations, errors of a 1% in the AC measurement of resistance might be acceptable but are corrected by comparison to a DC measurement. For heat capacity, this kind of \textit{ex post facto} correction is also possible, but the correction is far more complicated, and corrected errors must be less than 0.25% at some temperatures. The subtleties of the digital lock-in enter at this level through changes in parameters such as \( f_{\text{data}} \). Even with analog RC filtering with cutoffs well below the Nyquist frequency, changes to the \( f_{\text{data}} \) can have a dramatic effect on the FFT spectrum. The source of this is not clear, but we are aware of this kind of sensitivity, and can manage it by studying the FFT for various data rates and checking the digital lock-in accuracy against other instruments. The issue likely has something to do with a mixing between the \( f_{\text{data}} \) and the nodes of the expressions in eq. 3.2.

The application of this technique is essentially the same for pulsed field or DC measurements. Compared to pulsed fields, for \( H = 0 \) calibrations and heat capacity experiments the primary difference is the markedly lower \( \omega_{\text{ex}} \) and the more continuous nature of the data acquisition. During a pulsed magnet experiment, the pulse duration acts as a natural timescale for data acquisition. For DC magnets or any long time scale measurement, the data must be bundled into chunks and processed in parallel or in series to data acquisition, and the frequencies and data rates do not have to achieve some minimum \textit{a priori}. These features usually have optimal settings which depend on nearly every component of an experiment. This makes the achievement of repeatable data a critical
motif of this project, above and beyond what is typical in condensed matter experimental research.

Figure 3.6: Resistance ($R_{\text{plat}}$) versus $H$ for various temperatures as produced in the SP using a high frequency AC lock-in technique to measure thermometer resistance. Moving upward within the plot at fixed $H$, the temperature decreases monotonically.

Some final pulsed calibration results are shown in fig. 3.6. These are resistance versus $H$ curves at various nominally constant temperatures, all down-sweeps. Though considered constant, the true variation in temperature can never reach 0. The lack of dependability nonetheless can be characterized by comparison between pulses of various maximum fields that all begin at the same temperature, as well as looking for hysteresis between up and down-sweeps. A few of the traces shown have a very close neighbor in temperature (and resistance) to compare points of the same nominal ($H, T$) but different $\dot{H}$ by pulsing to different maximum $H$, such as 36 T or 47 T. In this way, the data reveals any implicit dependence on $\dot{H}$. For the data set shown, temperature varies intra-pulse within a very small and quite tolerable window for all temperatures and fields, such that $R$ and ($\dot{H}$) show no correlation. This means the assumption of constant temperature during a pulse is a robust one. Indeed, pulses to 10, 20 T, 36 T, and 47 T at many of the temperatures overlay on
R versus $H$ plots within fractions of an ohm, confirming the repeatability, and therefore constancy, of temperature is well within 10 mK. The $H = 0$ values from fig. 3.6 give the temperatures of each pulse by cross-referencing to an interpolation of the 0-field calibration.

From here, all of the data from the calibrations is merged into two files. One represents the 0-field data of resistance and temperature, and the other contains data just like that of fig. 3.6. The data combines to produce a set of coefficients, paralleling methods of Lakeshore. The coefficients characterize a polynomial of $\log(T)$ as a function of $\log(R)$. The coefficients allow conversion of any resistance within the calibrated range to produce a temperature value. Although this method was developed without referring to any resources from Lakeshore[83], the information and data it supplied provides a means of confirming the bounds on the expected interpolation errors.

A calibrated platform thermometer requires much work to produce and so long term variations pose a threat to experimental efforts. A record of the room temperature resistance updated before each cool down prevent the loss of repeatability in measurements that occur far apart in time. A recalibration of the zero-field $R$ versus $T$ and subsequent adjustment of the magnetoresistance values in a careful way can alleviate such concerns. Fortunately, this was not necessary for the present work, likely owing to the new platform design.

### 3.3 Measuring Heat Capacity

In fig. 3.7, the temperature versus time plot during a square wave heat pulse is shown. While the warming curve includes both the instantaneous heat flow out as well as a heat source yielding constant power $P$, the cooling curve involves just the heat flow out. Here, we may use the previous assumptions to claim that the heat flow out is then just equal to $k_b \frac{dT}{dt}$, but this is not necessary. Instead, we may safely assume that the heat flow out of the system is an analytic function of temperature, and therefore that the $\frac{dT}{dt}$ of a truly adiabatically isolated system may be replaced by $(\frac{dT}{dt})_{warming} - (\frac{dT}{dt})_{cooling}$ in the non-adiabatic case. Then we can use the related rate
Figure 3.7: Temperature versus time showing cooling and warming curves

\[
\frac{dQ}{dt}/(\frac{dT}{dt})_{\text{total}} = \frac{dQ}{dT} \quad \text{and the previous relation gives}
\]

\[
N \times C_p = \left( \frac{dE}{dT} \right)_p = \frac{dQ}{dT}/(\frac{dT}{dt})_{\text{total}} \quad (3.3)
\]

This relation is valid as long as the sample is in thermal equilibrium with the sample platform, and as long as there is no hysteresis in the system. This is left as the proof in principle of the validity of the technique. Much has to come before any heat capacity data emerges; what follows is a back to front account of that emergence.

### 3.3.1 Hardware

As discussed above, the sample should be adiabatically isolated from the environment on any internal timescales, such that it is in complete equilibrium with the thermometer on the timescale of the measurement (a relaxation time). This isolation separates the internal and external timescales
such that the experimental $\frac{dT}{dt}$ is governed entirely by $\frac{dQ}{dt} N \times C_{total}/K$, where $K$ is the thermal conductance of the platform wires and $N \times C_{total}$ is the heat capacity of the sample and platform. For a single warming and cooling pair (fig. 3.7) $C_{total}$ and $K$ should ideally be constant or perfectly linearizable functions of $T$ within the noise. The simplest method to guarantee sample and platform equilibrium is to reduce the thermal conductance between platform and the ambient temperature of the cryogenics. Whence, the sample and platform are surrounded by vacuum which is guaranteed by the gas adsorption vapor pressure between $^4$He and brass. This pressure, below saturation of the adsorption, is very difficult to estimate, but it is well below a level significant to the heat capacity relaxation time. This leaves the dominant mode of thermal conductance in the form of the Ni-Cr wires which both suspend the platform and carry the signals and heater power. These tiny wires are chosen as a compromise between poor thermal link and sufficient mechanical durability. Further, Ni-Cr is a highly disordered material, causing the wire’s properties $(K, R)$ to be weak functions of temperature.

Though the wires meet some minimum standard of durability, they are still extremely fragile, making sample attachment one of the most challenging activities within this experimental programme. Further, the sample must not simply be stuck to the platform in a hazardous manner. With a minimally conducting thermal link beyond the platform, a strong link between sample and platform successfully ensures the necessary assumptions are valid. A poor thermal link or over use of adhesive can push the repeatability and accuracy of the measurements into an ambiguous regime. The best option for use with cuprate samples of a few milligrams seems to be a silver-paint mixture composed of Ag flake ($\approx 1\mu m$) acrylic resin and organic solvent. Other choices, including Apiezon® N grease may have a large volumetric specific heat which can overwhelm the sample signal and so we use great care to minimize the amount of adhesive. N grease is best used to maximize the surface area of contact between sample and substrate by filling in the rough surface. Thus, a thickness of adhesive more than the scale of surface roughness, roughly 1 micron or less, is not ideal. All of the present results include silver paint as the adhesive.

The platform with sample is inserted and coupled via gold-plated BeCu2 pins to an 8-pin socket mounted to the interior of a custom vacuum cell. The connectors are custom commercial units from
Ironwood electronics. The design for the remainder of the cell, save for the wires, is a product solely of the author, based on visual inspection of other vacuum cells. The parts are all in-house products of the NHMFL machine shop. The final assembly is otherwise all the work of the author. The design has three key points:

1. Silica filled epoxy with a thermal coefficient of expansion closely matched to brass and copper to prevent sheer strain decoupling for leak-proof wire feedthroughs

2. A thin-walled stainless steel tube connecting the thermometer mount, or block, to the top of the can and thermally decouples the block from the surrounding environment for temperature stability

3. A pumping capillary connects to a larger tube and seals via solder to pump out the cell while on the probe, including in situ.

Item (1) is perhaps the most critical of the above. Essentially, the difference in thermal expansion between a brittle material, such as epoxy, and a bonded surface (brass) may lead to decoupling. This does not occur in the direction normal to the interface, but along the interface via a sheer mode. In the case of epoxy wire feedthroughs that must prevent the passage of helium atoms into a vacuum space, any mismatch leading to a large sheer strain is catastrophic. Visual inspection is also not sufficient to detect a sheer strain compromising of epoxy vacuum seals because there is
often sufficient friction to hold the feedthrough firmly in place despite the decoupling. This cannot be overcome by simply increasing the surface contact through roughness. Thus, a sufficient thermal coefficient matching between the feed-through filler and the metal structure is critical.

The cell is shown circa 2011 in fig. 3.8. This cell is compatible with both $^3$He and $^4$He cryogenic systems, and achieves sub-millikelvin stability in either case. Item (2) above is a critical factor in the attainment of good stability, while item (3) enables the compatibility with the cryogenic systems. Such temperature stability is critical to achieving high final precision during experiments because there are very few filtering options that can screen temperature stability. Filtering typically relies on the signal occupying some exclusive part of parameter space, but this is unlikely for temperature fluctuations, as the thermal time scales of the system control both the measurement time scales (the relaxation time $\tau$) and the noise time scales. Fig. 3.9 shows a plot of typical temperature stability with the new vacuum cell.

Figure 3.9: Temperature of the brass “block” within the vacuum cell during measurement. Several sequential platform heating and cooling processes, similar to those in fig. 3.7, give rise to the $\sim$10 microKelvin quasi periodic variations. The background is stable to within 20 $\mu$K over 10 minutes.
At the top of the probe, another critical but often overlooked piece of equipment plays its role. The cabling that runs to the DAQ must be very long for DC field experiments. The magnets are large in both size and fringe field, creating hazards and forcing the placement of the DAQ far from the probe. This further removes the option to bring the CCT and preamplifiers closer to the probe. Thus the cable becomes more important and more potentially detrimental. The added length increases capacitance, potential noise pickup from EM radiation, and potential triboelectric noise from ambient vibrations. The choice of cable can balance these issues.

As mentioned above, vacuum environment is critical and so vacuum degradation can be potentially fatal for an experiment. Luckily, the effect of vacuum degradation is very dramatic thus easy to detect. Slight degradations do not harm the measurement in any insidious manner, and the measurement itself can be a clear indication of the vacuum. If the thermal conductance from the platform to the vacuum cell is higher than optimal, the heat requirements to affect temperature rise rapidly. Further, the relaxation time necessarily drops dramatically as well. These two facts give simple diagnostic criteria for vacuum degradation, as they are very unlikely to coincide if the vacuum does not falter.

An unexpectedly short relaxation time can also indicate another fatal incident: that of sample detachment. The loss of heat capacity on the platform associated with sample detachment must necessarily drop the relaxation time but without changing the thermal conductance, and thus the change of temperature from the start of heating \( t = 0 \) to \( t \gg \tau \) for a given Joule heating power is sample independent. This makes for an easy distinction between sample detachment and vacuum degradation. Our response to a sample detachment is the immediate removal of the probe, followed by re-attachment, and reinsertion of the probe. In the case of vacuum degradation, probe removal is far more complicated because of the risk associated with thermal expansion of trapped gases. We take great care in ensuring a minimal pressure inside the cell during removal to prevent explosion. Liquid helium accumulation is especially dangerous as the volume expansion to room temperature is approximately a factor of 750, which for fixed volume translates to 750 times greater pressure. Pressures of greater than 10 atm are capable of creating serious projectile safety hazards. The heat capacity measurement itself is extremely sensitive to small amounts of gas and acts as the
proverbial “canary” in the cryogenic vacuum can to warn of even tiny leaks. If there is any indication of a small leak, all cryogens that surround the cell are removed by pumping. A slow process of probe extraction ensures that the accumulated gases may escape through the leak. If the leak appears sufficiently large as determined by the brevity of the interval over which the measurement is compromised, we may connect a helium leak detector to the sample space via a flange at the probe for more precise characterization of the leak. Further, in the most extreme cases, we can attach a turbomolecular pump and constantly evacuate the vacuum cell during removal.

With such hazards averted, all that remains is data concerns. This includes, for example, signal to noise issues associated with proper grounding and the choice of frequency. Although managing these problems is generally similar for heat capacity measurements and pulsed field resistivity measurement, the details are key. The timescale of measurements associated with pulsed magnets is fixed by the capacitance and inductance of the magnet system. The timescale of heat capacity measurements is set by the heat capacity of the sample and the thermal conductance $K$ between the platform and the immediate environment. All heat capacity and thermal conductance must by definition vanish at $T=0$. Thus, low temperature heat capacity measurements can include huge changes in principle in $\tau = N \times C/K$. In practice, the sample phonons dominate $C$, and the platform wires dominate $K$. The result for a typical cuprate sample is shown in fig. 3.10. This factor of five variation in the measurement timescale places particular demands on the DAQ. $f_{\text{data}}$ must be fast enough to keep up with changes on millisecond timescales while accruing data over very long time windows.

### 3.3.2 Software

In general, given a fixed background of noise, there are only two methods to manage signal to noise: change the measurement frequency to optimize the use of filtering, or increase the time window to allow for more averaging. Since the measurement timescale is controlled by the sample characteristics themselves, optimizing the platform temperature versus time pattern is critical and nontrivial. That is, choosing the length of time for a warming and cooling cycle as well as the number of cycles at a given temperature setpoint is an act of balancing. Increasing the efficiency
of the process through a number of advancements and technological implementation has made this balancing act far more straightforward.

Figure 3.10: Typical relaxation time versus temperature.

The primary advancement in improving averaging methods is the powerful coupling of the precise fitting shown in fig. 3.7 with the lock-in technique. Because the lock-in is a digital, discrete method, it is no more than an averaging technique with a floating frequency center. That is, whereas an infinitely long simple average results in an infinitely sharp peak centered around $\omega=0$, the infinitely long average within a discrete lock-in produces an infinitely sharp peak at $\omega = \omega_{\text{exc}}$. Fitting locked-in data points acts as an average over the entire fit window with no additional signal degradation. The only signal degradation at all comes from the finite product $\tau \omega_{\text{exc}}$. For $\tau \omega_{\text{exc}} \approx 1$, the signal degradation is severe. Typical values are $n \omega_{\text{exc}} \tau \approx 200 - 2000$ (where $n$ is the number of averaged sine periods), which translates to $\frac{dT}{dt}$ within 0.3% of the true value in the worst case. This translates identically into a final error to the heat capacity of accuracy. In practice, these errors
are rarely visible, and there is a simple post-experiment method to determine the extent of such errors on any data set.

\[
V_{\text{RMS}} = \sum_{l=1}^{N} \sin \left( \frac{2\pi l}{\omega_{\text{exc}} \Delta t_{\text{data}}} \right) V(t_l)
\] (3.4)

Equation 3.4 is the lock-in sum equation for a signal voltage \( V(t_i) \) and for a data period \( \Delta t_{\text{data}}^{-1} \) that generates a single data point \( V_{\text{RMS}} \). During an experiment, the dimensionless quantity \( \frac{2\pi N}{\omega_{\text{exc}} \Delta t_{\text{data}}} \) need be at least one. Increasing the lock-in time constant is then by definition taking an arithmetic mean of more \( V_{\text{RMS}} \) points. By varying the number \( n \) of \( V_{\text{RMS}} \) included in a rolling mean and then plotting the measured heat capacity \( N \times C_{\text{measured}} \) versus \( n \), a cutoff maximum \( n \) emerges. If the max \( n \approx 1 \), \( \omega_{\text{exc}} \) is too low for the experiment, and \( N \times C_{\text{measured}} \) systematically overestimates the true \( N \times C \).

The overall result is a tunable system that can admit the narrowest possible signal band while also inhabiting the cleanest possible signal band. Of course, this is restricted by circuit reactance as discussed above, but the useful range of frequencies is still large enough to ensure an extremely agile system. The combination of lock-in filtering and fitting is not particularly novel, but the specific form of the curve to fit works in concert well with the lock-in from the perspective of managing voltage noise. However, when examining the problem of local temperature noise, which acts as a (near-unity) multiplier of the raw signal, the lock-in plus fitting method shows its true power. External temperature fluctuations are damped for timescales \( \ll \tau \), and local fluctuations (for example, the minute fluctuations in the thermal radiation) in the opposite regime \( \gg \tau \). For intermediate timescales \( \sim \tau \), the brute force strategy works best: maximizing the final signal, i.e. \( \frac{dT}{dt} \) to overwhelm the noise. Rather than push up the heater power and drive the system far from equilibrium, simply the focusing data acquisition over a 2 \( \tau \) period and repeating many times achieves a high \( \frac{dT}{dt} \) and still respects the assumptions of the measurement. The lock-in plus fitting is crucial to achieve a reasonable noise rejection over a short time window while not attenuating the signal significantly.

In practice, the application of a square wave heating pattern results in a particularly advantageous \( T \) versus \( t \) pattern resembling an exponential “sawtooth.” The sawtooth forces the system
into a special quasi-equilibrium such that the average warming rate during a single finite P half-period in the heater square pulse equals the average cooling rate during a corresponding P=0 half-period (See fig. 3.11). The advantage comes from the simplicity of assessing the symmetry of a single warming/cooling “tooth,” which manifests as $\frac{\tau_{\text{warming}}}{\tau_{\text{cooling}}} = 1$ in the ideal case. If non-ideality is apparent, the $\tau$ ratio does not yield a direct estimate of the distortion of the measured heat capacity, but a non-unity value does act as a cue to vary the parameters such as the maximum heater power and the period of the square pulse to check for a convergence. If the ratio is quite far from unity, re-attaching the sample to the platform usually improves equilibrium. In the majority of measurements for this study $1 < \frac{\tau_{\text{warming}}}{\tau_{\text{cooling}}} < 1.02$.

![Figure 3.11](image)

Figure 3.11: (left) Temperature ‘sawtooth” waveform (blue, left axis) and heater square waveform (red, right axis). The precise timing of the data is critical as the heater waveform is used as a data trigger to chop the sawtooth into individual “teeth” and then pare each tooth into a pair of one warming and one cooling curve for fitting by exponential. (right) Overlayed teeth from a single sawtooth waveform near 6.8 K. The numbered legend corresponds to the chronological ordering of the teeth. Though the teeth are nearly identical, the noise results in a relative standard deviation of about 0.25% in $\frac{dT}{dt}$.

The particular data acquisition pattern involving the square heating waveform and sawtooth temperature waveform is original to the present study. Its purpose is to allow a uniform time width (i.e. length of the sawtooth) at all temperatures and fields without wasted time. The sawtooth greatly out performs the method of fig. 3.7, which uses a single square heating pulse.
The sample temperature must saturate back to the block temperature upon cooling because data processing follows each “tooth”. In order to achieve sufficient symmetry between warming and cooling, the warming curve must also nearly saturate to some upper temperature. When $\tau$ is large, this process can take up much time, with much waste. For small $\tau$, data processing in between each warming/cooling pair wastes time even further, meaning less time for actual data acquisition. For example, if $\tau=.5$ s, for the square pulse method a single temperature tooth might be 4 s wide, but data processing might take 1 s. 20% of the time is wasted. Typical relaxation times are as low as 0.15 s, resulting in the potential time waste at more than 50%.

Presently, the software processes all the data while the system moves towards a new temperature or field setpoint. To recount, the sawtooth saves time in temperature stabilization and data acquisition from two directions.
3.4 Miscellaneous and Troubleshooting

3.4.1 Cuprate Specific Issues

While cuprates are particularly interesting materials to study in high magnetic fields, the layered nature of the material turns the superconductivity towards a violent, anisotropic interaction with $H$. The superconducting state is highly diamagnetic, with the Meissner state excluding all $H$ from the sample. In cuprates, this diamagnetism has particularly weak minimum for $H$ parallel to the CuO$_2$ planes, and thus the sample torque at most other orientations is large. The experiments in the present study focus primarily on a perpendicular orientation, or $H||$ the c-axis, which maximizes the effect of field on the superconductivity. Positioning the sample in such an orientation is relatively simple, as the samples’ largest faces are typically parallel to the planes, and these faces adhere easily to the platform. Simply placing the platform such that the axis of highest symmetry is very nearly identical to that of the solenoid of the magnet system accomplishes the goal, and because the sample is not highly sensitive to small angle misalignments, no great struggle must take place. However, upon increasing $H$ from 0, such an alignment represents a highly unstable mechanical equilibrium, and the sample is likely to jump off the platform, or take the chip with it, so strong is the torque in the superconducting state. This torque seems reasonably independent of field ramp rate, as expected for an anisotropic superconductor. Thus, the only solution is to remove superconductivity temporarily by heating and holding the sample above $T_c$ before and during field ramps.

This heating provides the added benefit of removing the history dependence of the sample: at sufficiently high fields, typically $>1$ T, there is essentially no Meissner effect and thus $H=B$, the magnetic field within the sample, as long as the sample is cooled in static field (FC). Under these conditions a uniform vortex lattice may form. Zero field cooling (ZFC) and subsequent changes in $H$ make inhomogeneous $B$ likely because the particulars of the demagnetization and pinning by magnetic centers prevent the magnetic flux from entering the sample smoothly and thus flux builds up near sharp edges where the demagnetization is strongest. Repeatability when utilizing ZFC is elusive, in contrast with the FC mode.
An exception to the FC rule occurs for $H$ sufficiently high to de-pin all vortices. This resistive state allows flux in and out of the sample reversibly. Under such conditions, data acquisition can occur while the field is sweeping sufficiently slowly. Over all, this effect essentially rules out cuprate heat capacity measurements in pulsed magnetic fields: the sample can not be heated while the low $H$ regime is traversed and cooled subsequently to any desirable temperature set point within the pulse timeframe or with any practical accuracy.

These vortex issues may also lead to noise during experiments. When the magnet system undergoes current fluctuations, it is readily apparent in the temperature data. The apparent temperature fluctuation is larger at low temperatures to a degree much more severe than expected for Cernox magnetoresistance errors. Thus, the likely source is a magnetocaloric effect owing to tiny variations in flux. This issues become much more severe at the maximum field of the magnet system because anomalous large fluctuations are more common, and the background field noise scales as the square of the field setpoint.

### 3.4.2 Helium Liquid Levitation

An interesting peripheral problem is that of helium liquid levitation. It provides a motivation for the use of more sophisticated cryostats and some of the design of the vacuum cell. The levitation occurs because of the diamagnetic nature of $^3$He and $^4$He arising from their closed atomic shells. The nucleus of $^4$He is also a closed shell and has 0 nuclear magnetic moment, to close approximation, while the nucleus of $^3$He is paramagnetic, the small $\mathbf{J} \cdot \mathbf{H}$ Zeeman coupling is dwarfed by the electronic diamagnetism, with the latter about a factor of 10 larger. The insignificance of the nuclear effects comes simply from the large nuclear mass, rendering nuclear magnetic moments about three orders of magnitude weaker than electronic ones.

When a strong magnetic field is applied to a fluid, the macroscopic effect depends on the density. Thus, for a diamagnetic fluid in the presence of a dipolar force, there exists a threshold such that the diamagnetic coupling becomes larger than the gravitational coupling. In a uniform magnetic field, this produces no force. However, for a solenoid, there is a region of significant inhomogeneity of field. $F = \nabla H \int \mathbf{x} H dV - mg$ gives the local force on the fluid, where the magnitude of gravitational
acceleration is $g$ and $\chi$ is the volume susceptibility, meaning that regions of higher density will experience more force for a fluid of fixed atomic dipole moment. For a solenoid, the geometry determines the field inhomogeneity, and thus the gradient scales linearly with field. If the solenoid is oriented with $g$ along the highest symmetry axis as most high field magnets are, as the field is increased, the fluid above solenoid center will eventually experience an inversion of the buoyant force, driving any bubbles to field center and lifting the liquid.

At the NHMFL, the magnet systems are such that $\nabla H \int \chi H dV > |mg|$ does occur. As with any macroscopic mechanical effect, the consequences manifest suddenly. The effect is akin to moving two ferromagnets together in an attempt to levitate one with the other. The interval of distance between the two magnets supporting levitation is extremely narrow and the levitation itself represents an unstable equilibrium. For the diamagnetic fluid, it is not levitation that is the unstable equilibrium (liquid/gas phase separation and the buoyant force serve to stabilize the liquid levitation), but rather the homogeneous state where gravitational and diamagnetic couplings are similar such that there is no buoyant force. This fact meshes perfectly with the experience of a dramatic effect of sudden cooling in $^3$He systems upon lowering the field below a repeatable threshold. This sudden cooling is the effect of the liquid crashing back toward field center as the field strength is reduced below the inversion threshold. The question then arises as to why this does not occur for $^4$He cryostats. The inversion of the buoyant force does occur at lower fields for $^4$He, but the key missing ingredient is nucleation of bubbles. $^4$He has substantially more agile thermal properties, as well as a readily attainable superfluid phase. Further, the historically abundant supply of $^4$He allows for large volumes of liquid, and thus mass, that provide significant weight above the inversion zone and may squeeze the gas back into liquid form. A final check through quantitative comparison yields agreement between experiments and the hypothesis. For the Hybrid magnet system, the $^3$He levitation collapses at about 27 T with a calculated $H$ between 27 and 28 T. For the 35 T resistive magnets, the calculated value is just above 17 T. The rumored[2] value of these magnets’ “bubble collapse” is 18 T.

The consequences of these facts are the difficulty of performing experiments below 1.4 K at high fields in simple dewar cryostats and lost experiment time from bubble nucleation due to insufficient
vacuum cell design. The present experiments have circumvented the issues by designing a vacuum cell which requires little heat to reach temperature setpoints as well using $^4$He cryostats that can reach temperatures as low as 1.2 K, alleviating the need for $^3$He somewhat.
CHAPTER 4

THEORETICAL BACKGROUND

This chapter will give a brief overview of the basic theoretical concepts informing the results of the study. The full theoretical details are beyond the scope of the work, but the literature survey discusses the central results of the more complicated calculations. The point of what follows is more in the spirit of motivation than in achieving a highly accurate quantitative picture to explain the experimental results.

4.1 Various Contributions to Specific Heat

The principle phase of interest in the cuprates is superconductivity. To study such a phase with specific heat, one must return to statistical mechanics to imagine what the signature of such a phase might be. From a single particle point of view, the specific heat of elemental solids in the low temperature limit is \[ C = \gamma T + \beta T^3. \] \( \gamma \), as shown below, is due to the electronic excitations while \( \beta \) is from the quantized lattice vibrations known as phonons. Each component has a unique signature in the temperature dependence. Band insulators, for example, have \( \gamma = 0 \) because there are no electronic excitations, and thus no electronic density of states (DOS) at the Fermi level \( g(\epsilon_F) \). Superconductivity, as a unique phase, has a unique signature. In reality, no material is free from interactions, and thus the single particle treatment is incomplete. However, in the case of real metals, Fermi liquid theory shows there is a simple renormalization of the electronic structure, characterizable through the replacement of the electron mass by an effective mass parameter for the electronic-like quasiparticles (qps) which describe the low energy excitations of the system [7]. Therefore, it is still quite helpful and informative to approach many systems with a simple non-interacting statistical mechanics treatment.
In real and ideal systems, the particulars of the temperature dependence and coefficients come from the energy dispersion $\epsilon(k)$ (where $k$ is the momentum wave vector) and the bosonic or fermionic nature of the quasiparticles (qps). The Sommerfeld treatment of the electron gas includes just these properties and assumes $\epsilon(k) \sim k^2$ such that $\epsilon(k = 0) = 0$. For fermions:

$$E/V = \int \frac{\epsilon(k)g(\epsilon)}{e^{(\epsilon-\epsilon_F)/k_BT} + 1} d\epsilon$$

(4.1)

where $E$ is the total internal energy. The particulars of $g(\epsilon)$ are not important because the Fermi energy sets a large energy scale compared to the thermal energy and via the Sommerfeld expansion only a constant $g(\epsilon_F)$ matters at low temperature. Of course, if, in a real material, $g(\epsilon)$ is non-analytic very near $\epsilon_F$, then there are complications. The point here is to keep all functions well-behaved for now by assuming a nearly free collection of electrons, and a smooth dispersion gives a $g(\epsilon)$ such that with $C = C_v = N^{-1}dE/d\epsilon$ equation 4.1 becomes, to lowest order:

$$C = \frac{\pi^2 k_B^2 g(\epsilon_F) T}{3n}$$

(4.2)

in which, for three dimensions

$$g(\epsilon_F) = \frac{mk_F}{\pi^2 \hbar^2}$$

(4.3)

Where $k_B$ is the Boltzmann constant; $n$ is the molar density; $k_F$ is the Fermi vector, which depends on carrier density and dimensionality; and $m \equiv m^* \times m_e$ is the dimensionful effective electron mass for dimensionless effective mass

$$m^* = \frac{\hbar^2}{m_e} \left( \frac{d^2\epsilon(k)}{dk^2} \right)^{-1}$$

(4.4)

The effective mass encompasses all electron interactions for a Fermi liquid and is the only free parameter in two dimensions (2D) where $g(\epsilon)$ is a constant. If the Fermi liquid is in an anisotropic crystal, $m^*$ is a function of $k$ which enters into the specific heat simply as the geometric average over all directions. These statements may not hold true for systems other than Fermi liquids, but an effective mass parameter may serve a similar purpose in other situations. Since the cuprates are 2D systems, it is worthwhile to specifically note the 2D result. In terms of specific heat by area
(the 2D version of volume), the 2D result is:

\[
(N/A) \times C = \frac{\pi k_B^2 m}{3h^2} T \tag{4.5}
\]

To convert to molar specific heat, one must multiply by the CuO$_2$ plane area per mole is about 0.15 nm$^2$ for YBCO [30] this gives

\[
C = 1.48 \times (\text{mJ/mol K}^2)m^*T \tag{4.6}
\]

When $T$ is in units of K. This simply means that if the highly anisotropic cuprates contain any Fermi liquid behavior, one should expect that for each closed Fermi surface, or pocket, $\gamma=1.48\times m^*$ mJ mol$^{-1}$ K$^{-2}$, with the measured $\gamma$ equal to a sum over the contributions from each pocket. Where $m^*$ is once again the geometric average around the pocket. As a corollary, one can answer the question of $C_p/C_v$. In the 3D (free electron) case, for $T \to 0$,

\[
\frac{C_p}{C_v} = 1 + \frac{\pi^2}{3} \left( \frac{k_B T}{\epsilon_F} \right)^2 \tag{4.7}
\]

which demonstrates that Fermi liquid specific heat converges to a single value in the low temperature limit, and there is no concern of conflating $C_p$ and $C_v$. This point is somewhat mooted in the limit where the following treatment is valid: that of harmonic acoustic phonons.

In the case of phonons, any macroscopic single crystal solid is three dimensional. Though the phonon contribution carries less interesting information for specific heat measurements because they couple so weakly to electrons. However, they are also the largest contributor to specific heat in many materials, except at lowest temperatures, and therefore their contribution cannot simply be ignored. Phonons are bosons with a linearly vanishing long-wavelength dispersion along all three Cartesian directions and thus

\[
E/V = \int \frac{\epsilon(k)g(\epsilon)}{\epsilon(\epsilon)/k_B T - 1} d\epsilon \tag{4.8}
\]

with $\epsilon(k) = \hbar c_{s,\mathbf{k}}$, and $c_{s,\mathbf{k}}$ is the velocity of propagation which depends only on the direction of the unit vector $\mathbf{\hat{k}}$ and the mode (transverse or sheer) $s$. That is, since the phonon is a propagating lattice
vibration, the vibrational displacement may be decomposed into a three component Cartesian basis, and the direction of propagation may also occur in any of three directions for each vibrational mode. The low temperature approximation for the specific heat employs an averaged velocity $c_s$ for all phonon modes and directions, again in the long wavelength limit [7]. This is an apt approximation given both low temperatures and long wavelengths correspond to low energy. Thus with $c_s$ and the linearity of the dispersion completely determining the density of states, the resulting integral follows:

$$g(\epsilon)d\epsilon = \frac{3\epsilon^2}{2\pi^2 (\hbar c_s)^3}d\epsilon \quad (4.9)$$

$$E/V = \frac{3}{2\pi^2 (\hbar c_s)^3} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/k_BT} - 1}d\epsilon \quad (4.10)$$

Substitution by $x = \epsilon/k_BT$ and differentiation by $T$ gives:

$$N \times C/V = k_B \frac{3(k_BT)^3}{2\pi^2 (\hbar c_s)^3} \int_0^\infty \frac{x^3}{e^x - 1}dx = k_B \frac{2\pi^2 (k_BT)^3}{5 (\hbar c_s)^3}$$

$$C = k_B \frac{2\pi^2 (k_BT)^3}{5 (\hbar c_s)^3} n^{-1} \quad (4.11)$$

Where $n$ is again the molar density. This format converts into the Debye form with the introduction of the conventional Debye temperature defined through a cut off of the $E$ integral at energies for which the wavevector $k$ equals the inverse average lattice spacing: $2\pi r_a^{-1} = 2\pi \sqrt{3N/4\pi V}$. Using this scale to define a temperature gives $\Theta_D = \frac{\hbar c_s r_a}{2\pi k_B} = \frac{\hbar c_s V}{k_B 6N\pi^2}$. Whence,

$$C = N_A k_B \frac{12\pi^4}{5} \left( \frac{T}{\Theta_D} \right)^3 \quad (4.12)$$

The Debye result is an approximation but still succeeds in accurately describing the phonon specific heat well, especially in simpler, isotropic crystals (i.e. monatomic) [49].

The next contribution relevant to study of the cuprates is that of the Schottky anomaly. The canonical Schottky anomaly arises from a population of localized Zeeman split moments. The
density of states in this case is incredibly simple: \( N/V \Delta Z \), the spins per volume over the splitting in energy, where \( \Delta Z = g \mu_B H \), \( \mu_B \) is the Bohr magneton and \( g \) is the Landé g-factor. Because this is a two level system, integration is replaced by a “sum” over a single term and the specific heat just:

\[
C_{Sch} = n_s \left( \frac{g \mu_B H}{k_B T^2} \right)^2 \frac{N_A}{2} \frac{e^{g \mu_B H/k_B T}}{(e^{g \mu_B H/k_B T} + 1)^2}
\]  

(4.14)

Here, \( n_s \) is the dimensionless molar fraction for the concentration of spins (or impurities) rather than the molar density, and \( N/N_A \) is the amount of sample in moles. Figure 4.1 shows a map in the \( H-T \) plane of this function for typical fields and temperatures as well as a \( g \) of 2. Since specific heat is often plotted in the form \( C/T \) versus \( T \), a second map of the anomaly in this form is instructive for later discussion. This function has two limiting behaviors: exponential in \( H/T \) in the low temperature/high-field limit, and \( H^2/T^2 \) for the opposite limit. The latter is especially important for the nuclear Schottky anomaly, which has a characteristic energy defined by the nuclear Zeeman splitting at least 1000-2000 times smaller than the electronic Zeeman. This factor
is simply a consequence of the much larger nuclear mass, because the nuclear magneton $\mu_N \propto m_N^{-1}$, the inverse nuclear mass. The smaller magneton means the peak of a Zeeman split nuclear Schottky sits much lower, on the order of 0.001 T K$^{-1}$, or 10 mK at 10 Tesla. This is completely dependent on the nuclear moment $J_N$, however; nuclei such as oxygen have vanishing $J$ and thus are totally degenerate at virtually all temperatures and fields.

$$F_{Sch} \equiv \frac{e^{\Delta_{Sch} H/T}}{(e^{\Delta_{Sch} H/T} + 1)^2} = \frac{1}{2(Cosh(x) + 1)}$$

Eq. 4.15, where $\Delta_{Sch} \equiv \mu/k_B$, determines the limiting scale. When $x = \Delta_{Sch} H/T$ is small, $F_{Sch}$ approaches 0.25. It reaches 99% of this value by $x=0.2$. For large $x$, the function increases exponentially but for $T > 1$ K and nuclear Zeeman energy scales, $\Delta_{Sch} \approx 0.001$, $x \ll 0.2$ for any experimentally achievable value of $H$. This puts the $C$ due to nuclear Schottky ($C_{nuc}$) firmly in the $H^2/T^2$ regime. In the case of real systems, the nuclei need not follow a simple Zeeman splitting, modifying the $H^2$ form slightly, but still following $1/T^2$.

### 4.2 Superconductivity

The theory of Bardeen, Cooper, and Schrieffer (BCS) provides an elegant foundation for an understanding of superconductivity, though not directly applicable to cuprates [8]. The theory demonstrated how a very weak coupling, through what is known as the Cooper instability [19] can gap excitations in a Fermi liquid system such that the gap is pinned to the chemical potential. Because the ground state of the system consists of free pairs of charged particles protected against scattering, a “superfluid” velocity may exist, giving rise to a resistance free current (supercurrent) that defines a “superconductor”.

This supercurrent is of great interest to present study because of the way in which changes occur to the DOS. But first, one must ask what the low temperature specific heat of a static superconductor looks like. For this, BCS and Bogoliubov [13] provide the first step in the form of
the quasiparticle spectrum for a system with a superconducting gap:

\[ \epsilon(k) = \left( \xi_k^2 + \Delta_s(k)^2 \right)^{1/2} \]  \ (4.16)

Here, \( \xi_k = \hbar k^2/2m - \epsilon_F \) are the electron-like states, and \( \Delta_s \) is the superconducting gap. If the gap is constant, the specific heat versus temperature shows an exponential behavior much like the low temperature limit of a Schottky anomaly. This is because the gap to excitations at the Fermi level excludes the linear \( T \) part of the Fermi distribution and leaves available only the states in the vanishing exponential tail of the distribution. The specific heat is thus necessarily greatly suppressed compared to the normal state of a metal, analogous to a weak band insulator with \( \epsilon_F \) pinned to the center of gap.

Unlike the superconductors originally treated by BCS, many cuprates are best described by \( d_{x^2-y^2} \) (d-wave) symmetry [32]. This means the superconducting gap is a nontrivial function of \( k \):

\[ \Delta_s(k) = \Delta_0 \sin(2\theta_k) \]

where \( \Delta_0 \) is the gap maximum and \( \theta_k \) is the k-space angle about the center of the 2D reciprocal lattice unit cell, or more specifically, the Brillouin zone (see fig. 2.2. The gap has (approximately) four-fold rotational symmetry and necessarily vanishes linearly at what are called line nodes, or, more simply, the nodes. Because excitations near the location of the gap maximum are greatly suppressed, all low lying excitations live near the nodes. Rotation of the coordinate system such that the Cartesian component \( k_x \) corresponds to \( \theta_k = 0 \) and substitution by \( \sin(2\theta) = 2\sin(\theta)\cos(\theta) = 2xy/x^2+y^2 \) leads to the expression

\[ \epsilon(k) = \left( \xi_k^2 + 4\Delta_0^2 (k_x k_y)^2 \left( \frac{k_x^2}{k^2} \right) \right)^{1/2} \approx \left( \xi_k^2 + 4\Delta_0^2 \frac{k_y^2}{k^2} \right)^{1/2} \]  \ (4.17)

Where \( \epsilon(k) \) vanishes linearly for \( k \to k_x = k_F \). A notable aspect of this qp spectrum is that it represents an anisotropic Dirac cone, i.e. a dispersion linear in \( |k - k_{node}| \) with a vanishing density of states at the chemical potential. The linearly vanishing DOS forces the \( T \) linear term of Fermi liquids to zero uniformly along with \( g(\epsilon_F) \) and thus a term of higher order must take its place.

The \( \frac{d\epsilon}{dk} \) in the cone can be characterized as a geometric mean of the components along \( k_x \) and \( k_y \), \( v_F \) and \( v_{\Delta} \) respectively, and thus the DOS is \( g(\epsilon)d\epsilon \sim \frac{\epsilon}{v_F v_{\Delta}} \). Finally the total energy of excitations
\[ E \sim \frac{1}{v_F \Delta} \int_0^\infty \frac{\epsilon^2}{e^{\epsilon/k_BT} + 1} d\epsilon \] (4.18)

Figure 4.2: Example of Dirac-like dispersion from a \( d_{x^2-y^2} \) gapped electronic system with an anisotropy ratio of \( m_{\text{Fermi}}/m_{\Delta} = 5 \)

With the usual substitution for Fermi systems \( x = \frac{e}{k_BT} \) the specific heat is:

\[ C \sim \frac{k_B^3 T^2}{v_F \Delta} \int_0^\infty \frac{x^2}{e^x + 1} dx \] (4.19)

Kopnin and Volovik give, more precisely, in \( C \) per area \([33]\):

\[ (N/A) \times C = 18\zeta(3) \frac{k_B^3 T^2}{\pi \hbar^2 v_F \Delta} \] (4.20)

From which, the specific heat is simply

\[ C = 18\zeta(3) \frac{k_B^3 T^2}{n \pi \hbar^2 v_F \Delta} \equiv \alpha T^2 \] (4.21)

Where the above equations come from a semiclassical approach, with \( n \) representing the molar density (per area) of the CuO\(_2\) unit cells. For YBCO, for each CuO\(_2\) layer in a unit cell, this gives

\[ C \approx \left\{ 1.48 \times 10^8 \text{ mJ mol}^{-1} \text{K}^{-3} (\text{m/s})^2 \right\} \left( \frac{T^2}{v_F \Delta} \right) \] (4.22)

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Assuming a particular $v_\Delta$ and $v_F$, such that the anisotropy ratio $v_F/v_\Delta = 10$ and $\hbar v_F = 1$ eV Å, gives $\alpha \approx 0.05$ mJ mol$^{-1}$ K$^{-3}$. At 1 K, this represents a contribution less than 10% of $\gamma$ for pure copper. This is important because of the difficult in sorting out small contributions in a real system with large phonon and Schottky contributions.

Again, this chapter is primarily an exercise, especially given the questionable applicability of Fermi liquid framework, but some useful points still emerge. In eq. 4.21, the result depends on the velocity parameters and thus there is hope that specific heat can give detailed quantitative information about the electronic structure, the central goal of this work. However, this chapter focuses solely on the clean limit, such that the gap is a function only of $k$ and not of $r$, the spatial coordinate, and that the eigenstates are states of definite $k$. For $s$-wave superconductors, the quasiparticle spectrum seems to be essentially unchanged in the high-impurity or dirty limit [6], but this may not be the case for systems that already possess gapless excitations even in the clean limit. In fact, the effects of impurities pose serious questions in the discussion of the Hg1201 results in the next chapter. Further, in the quantum case, magnetic field immediately changes the landscape such that the gap is function of $r$ and thus there are no eigenstates of $k$. Semiclassical treatments approximate the finite field case by assuming states of definite $k$ despite the presence of the vortex lattice.

In order to evaluate a superconductor in magnetic field, it is natural to consider just how the field enters the system. For such a problem, quantum mechanics instructs that any flux must enter the sample in quantities that are integer multiples of the flux quantum $\frac{\pi \hbar}{e}$ for Cooper pairs. A simple model then for a superconductor in a magnetic field involves a superconducting annulus with an inner diameter equal to the superconducting coherence length $\xi$ with a single flux quantum through the center. In the annulus there exists a superfluid flow depending on the distance from the center.

If a thin wire of inner radius much much larger than the coherence length replaces the annulus, an arbitrary flux may pass through the center, and a uniform superflow exists in the wire. In this case, Bogliubov suggests a Doppler shift in the density of states [13]. The low-energy quasiparticle
spectrum is then
\[ \epsilon(k) = \left( \xi_k^2 + 4\Delta_0^2 \frac{k_y^2}{k^2} \right)^{1/2} + \hbar k \cdot v_s \quad (4.23) \]

where \( v_s \) is the superfluid velocity. The Doppler shift has the effect of pulling states back toward the chemical potential, leading to a finite \( g(\epsilon_F) \) from the nodes. The specific heat then must exhibit a linear-in-\( T \) term that is analogous to that of a Fermi liquid, but not due to Fermi liquid excitations. The qps are instead Bogoliubov-de Gennes (BdG) named for the theorists most credited with the understanding of superconducting single particles excitations. The coefficient of the linear term, \( \gamma_s \), is proportional to the superfluid velocity. Because the Dirac point sits at \( k_F \), the Doppler shift averages effectively to \( \sim k_F v_s \) [76].

In a real superconductor in a homogeneous magnetic field, the flux quanta sit at the centers of superconducting vortices, which are structures of rotational superfluid flow arranged into a 2D lattice [3]. One can imagine a supercurrent as constrained to move in a cyclotron-style orbit such that the (semiclassical) superfluid velocity is then \( v_s = \frac{\hbar}{2mr} \) where \( r \) is the distance from the vortex center. From Volovik [76], the details of the vortex lattice matter very little such that the effective \( v_s \) is just the average, which is then determined by the average vortex separation, or \( l \sim 1/\sqrt{H} \), the inverse of the square root of the number of vortices per area (this vortex density is almost by definition proportional to \( H \)). By integrating over the unit cell, the effective change to \( g(0) \) is determined by \( \frac{\hbar v_F}{2l} \) with \( v_F = k_F/m \). The specific heat need only be modified by replacing \( g(\epsilon) \sim \epsilon \) with the Doppler shifted DOS, \( g(\hbar v_F/l) \sim \hbar v_F/l \). The result then only depends on \( l \) and \( v_\Delta \):

\[ C = \eta \frac{1}{k_B v_\Delta} \int_0^\infty \frac{x}{e^x + 1} dx, \quad \int_0^\infty \frac{x}{e^x + 1} dx = \frac{\pi^2}{12} \quad (4.24) \]

The prefactor is a coefficient which depends on the particulars of evaluating the integration, but which will not modify the results in such a way as to replace the factor \( \frac{T}{v_\Delta} \). This dependence is expected to hold so long as the superconducting gap is not significantly altered by the field, and so long as \( v_F >> v_\Delta \), which empirically seems to be satisfied by \( v_F/v_\Delta > 5 \) [54, 66]. An important fact here is that \( H \) must be perpendicular to the CuO\(_2\) planes for any of above results to be meaningful in cuprates.

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Figure 4.3: Constant $\epsilon(k)$ contours (eq. 4.23), one centered at each of the nodes in k-space (see fig. 4.4), showing the Doppler shifted Dirac cones (anistropy $v_F/v_\Delta \approx 5$) for $v_s$ along $k_x = k_y$ direction. (a)-(d) represent nodes along the directions $(k_x, k_y) = (-1, 1), (1, 1), (1, -1),$ and $(-1, -1)$ respectively, all centered at $|k| = k_f$. Only (b) has a finite DOS represented by the circumference of the white ellipse, with white representing the $\epsilon < 0$ or “pair-broken” states. The Doppler shift “tips” each cone by a completely negligible amount.

There is, however, another effect which may be isotropic and produces a finite DOS in d-wave superconductors in magnetic field is Zeeman effect [84]. In principle, the magnetic field spin polarizes the qps and shifts the spectrum in a manner similar to the “orbital” Doppler shift, but linearly in field rather than $\sim \sqrt{H}$. The spin polarization also must “break pairs” in some sense even at 0-temperature so that the lowest energy states of the cone are filled in by Zeeman. Further, there is no constraint on the shape of the Dirac cone [84] and since the energy shift is only a function of $g\mu_B H$, both $v_F$ and $v_\Delta$ now appear in the DOS equally. The result is

$$C = \frac{2\pi k_F^2 g\mu_B H}{3v_Fv_\Delta} T$$ (4.25)
Figure 4.4: Schematic depicting the d-wave gap and approximate positions of the nodes as shown in (a)-(d) from fig. 4.3. The small red disks sit at $k_F$ on the nodal lines for some imaginary system. The disks roughly approximate the area of each panel in fig. 4.3, with corresponding lettering. The blue polar plot shows the relative strength of $\Delta_s(k)$.

Where eq. 4.25 comes from ref [84] via a mean field method. The next logical question to ask is, if the Zeeman effect is nearly isotropic, what happens when the field is applied parallel to the c-axis and both orbital and Zeeman effects are active? If the orbital effect is well-behaved, the Doppler shift and Zeeman, under a simple picture, have mutually exclusive effects on the DOS. That is, when the Zeeman energy scale is much greater than the orbital scale, the specific heat follows the Zeeman result. The same is true when the roles are reversed. Fig. 4.5 shows a plot of the approximate DOS under the orbital effect, with increasing Zeeman. The orbital effect, as seen in fig. 4.3 Doppler shifts each node differently, such that a vortex lattice (in the right regime) results in a $g(\epsilon)$ that is essentially constant in the low energy limit. However, once the Zeeman scale sufficiently exceeds the orbital scale, all of the nodes are degenerate and the orbital effect plays no role whatsoever. More precisely, for large $H$, the DOS does not follow $g\mu_B H + A_c \sqrt{H}$, but just $g\mu_B H$.

Finally, the following discussion demonstrates the field effects on Fermi liquid specific heat.
Figure 4.5: Rough plot of $g(\epsilon)$ versus $\epsilon$ under 4 different conditions all in the clean limit for a d-wave superconductor: (black, solid) $H=0$, (red, solid) an orbital, Doppler shifted case with no Zeeman effect, (blue, dashed) orbital with small Zeeman effect, (orange, dashed) orbital and Zeeman effect of comparable energy scales. Based on a clean limit from ref [34]

for the purposes of distinguishing normal metals from d-wave superconductors. In all cases, the limit $k_B T << \epsilon_F$ must be in full effect for $\epsilon_F$ defined as the energy difference between the band bottom and the chemical potential. This is not always the case as some systems respond well to gating (field effect carrier density tuning) or doping such that the chemical potential can sit at the band bottom. However, this is rare and difficult to do, so that the desired limit predominates. Thus, with the Sommerfeld expansion valid, the leading order term depends on $g(\epsilon_F)$. The field may couple through d-wave orbital effects, the Landau quantization (which was ignored for the d-wave and beyond the scope of this work), and the Zeeman coupling. For small fields, the Landau levels are typically washed out by scattering in metals, and the Zeeman effect is negligible since $g\mu_B H << \epsilon_F$. In two dimensions, the DOS is constant in energy (for parabolic dispersion), and there is no effect on $C$ from $H$. An alternative to this is graphene, which has linear dispersion. However, graphene also experiences no net effect from Zeeman under the prevailing assumptions, as the changes in DOS of the spin up and spin down qp populations cancel (see fig 4.6). This point extends to normal metals in 1D and 3D for somewhat larger fields but still $g\mu_B H << \epsilon_F$, since $g(\epsilon) \approx g(\epsilon_F) \pm g'(\epsilon_F)g\mu_B H$. When the Landau levels become sufficiently widely spaced, quantum oscillations become visible. These have a form $\sim A(H)\cos(\kappa/H)$ where $A(H)$ is a field dependent amplitude and $\kappa$ is a constant that depends on the extremal cross sections of the Fermi surface
normal to the magnetic field. These oscillations are very particular in form and typically have “frequencies” of at least 100 T, making them distinct from other field induced behaviors.

The conclusion upon combining all the considerations above is that there exists a reasonable expectation that a d-wave superconductor should show a distinct field dependence in $C$ as the experimental literature demonstrates ($\sim \sqrt{H}$). One may also expect to extract particular facts about the superconducting gap through the parameter $v_\Delta$ as well as through the deviations from the expected form at the highest achievable fields. In the next chapter, some of the results will show a match to the theory at low fields in one case, along with dramatic and varying deviations for highest fields.

![Graphene-like dispersion with Zeeman effect](image)

**Figure 4.6:** Graphene-like dispersion with Zeeman effect for $g\mu_B H = (a) 0$, (b) $0.4\epsilon_F$ and (c) $0.8\epsilon_F$ to exaggerate the effect of field. As the spin up ($S_z$ aligned with field) pocket grows, the spin down pocket shrinks by an equal amount, such that the sum of circular circumferences the define the density of states is constant.
CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

The vast majority of the focus of the following section devotes itself to YBCO because it is currently the most widely studied system, and because the results appear to be more meaningful and reliable than for Hg1201. The interest in Hg1201 is bolstered by the fact that quantum oscillations (SdH) [9] appear to be a feature of this material as in YBCO for approximately the same doping. As seen in the “Literature Survey”, this is a new discovery at the time of writing. The data on Hg1201 serve as an interesting contrast to YBCO because of the qualitative differences in the data. In a more technical sense, the Hg1201 shows very clearly the various pitfalls of specific heat data. For example, because the heat capacity measurement must necessarily sum all of the excitations of the system, any inclusions or phase separations in the samples completely distort the specific heat. In cases where sample issues appear, only qualitative conclusions are robust.

In contrast, the repeatability of measurements on YBCO samples of nominally identical composition is essential to the interpretation of the results in a broader sense. Below, YBCO6.51 precedes the culminating work on YBCO6.47. While the measurements on YBCO6.51 are of great interest and lead to definite conclusions, the data also demonstrates some of the experimental difficulties in producing reliable data. In fact, the YBCO6.51 results are based entirely on the quasi-relaxation time method of fig. 3.7 rather than the sawtooth (fig. 3.11). Further, the YBCO6.51 data set utilized a different thermometer and calibration, guaranteeing differences in addenda and small but significant (at a statistical level) disagreements in absolute values. The difficulties of achieving high quality data on YBCO6.51 in large part motivated the redesign of many components. The primary results of this study pertain to YBCO6.47. The data is both the most repeatable and most repeatable of the study, while leading to the most interesting results.
The sections below are divided into “low-field” versus “high-field” discussions, pertaining approximately to data below and above 15 T, respectively. In practical terms, the low-field regime is the range of $H$ most involved in the determination of the electronic Schottky anomaly while the prominence of the nuclear Schottky-like feature defines the high-field side. The value of 15 T refers to the maximum $H$ supplied by the Oxford superconducting magnet used in many of the measurements.

5.2 HgBa$_2$CuO$_{4+\delta}$

5.2.1 Hg1201 Samples

![Graph showing total heat capacities (N×C) over T of sample D (black squares) and sample E (red circles) and addenda (Green circles) plotted versus $T^2$. The green dashed line and black line are guides to the eye. These traces are as measured, meaning the addenda or any other contribution has been subtracted from them.]

Fig. 5.1 shows the total 0-field heat capacities of some Hg1201 samples plus the calorimeter heat capacity (addenda). Plot is of $N \times C/T$ versus $T^2$ to immediately show deviations from $C/T =$
\[ \gamma + \beta T^2 \]. The deviations are readily apparent, but the phonon contribution still dominates over a large portion of the temperature range. The low temperature “upturn” is the high temperature side of the electronic Schottky anomaly, \( C_{Sch} \), which is apparently due to weakly interacting localized spins. The details of the \( C_{Sch} \) analysis are left for later. The readily visible non-linearity at higher values of \( T^2 \) makes clear analysis quite difficult. The only clear conclusion from fig. 5.1 is that the heat capacity of one sample is larger than the other. In total, this study includes measurement of 5 crystals of masses from 1.5-7.8 mg, called alphabetically sample “A” through sample “E”. The most striking fact about the collection of samples is that despite coming from an identical annealing batch, with identical \( T_c = 72 \) K (\( \rho \approx 0.1 \)), but in fig 5.1 the crystal of larger mass (E, 2.6 mg) has less heat capacity than the smaller sample (D, 2.3 mg). This means the specific heat is markedly different from crystal to crystal. Samples A and B results include various \( H \) up to 34.5 T, while C through E include low field results only. The primary purpose of the measurements including the latter three samples is to establish the variability of \( \gamma(0) \).

Fig. 5.3 shows the specific heat of sample B (7.6 mg), plotted as \( C/T \) versus \( T^2 \), and the effect of field. A striking observation here is that the 0-field \( \gamma \) term is a full factor of ten large than the value for copper, 0.7 mJ mol\(^{-1}\) K\(^2\). This implies a giant DOS coming from only a small fraction of the Fermi surface near the nodes. This value is not intrinsic to the sample, as several other samples from this annealing batch give various \( \gamma \) ranging from about 4 to 10 mJ mol\(^{-1}\) K\(^2\) while all samples have \( T_c = 72 \) K with transitions of similar width (fig. 5.2). All of these facts are in direct contrast to the expected vanishing DOS and \( \gamma = 0 \) for a d-wave superconductor. In some sense, fig. 5.3 implies that either disorder scattering carries an energy scale of the same order as a 35 T magnetic field, or part of the sample is not Hg1201. Either one of these possibilities renders analysis quite difficult. Nonetheless, the large and somewhat straightforward apparent field dependence motivates further analysis.

### 5.2.2 Hg1201 Low-field: Determining the Contributions

Information about the field dependent contributions is far more accessible after subtraction of the addenda, \( \gamma(0) \), and \( \beta T^2 \) contributions from \( C/T \), which leaves only the field dependent
Figure 5.2: Magnetization curves showing the $T_c$ for three samples, (top) “C,” (left) “D,” and (right) “E.”. The transitions are all very sharp and within 0.5 K, implying the samples have nearly identical superconducting parts. [1]

part ($\Delta C/T$). The subtraction comes from fitting a line, $C/T = \gamma + \beta T^2$, to the total $C/T$ versus $T^2$ determined by a single measurement at 0-field. No addenda measurement is necessary to determine $\Delta C/T$. Rather, attempting to subtract both addenda and the sample 0-field $C/T$
Figure 5.3: Specific heat as $C/T$ versus $T^2$ for sample B at $H=0$, 30, 35 T. The phonon term is insensitive to field as expected, but the curves at high field appear to be shifted up, an indication of enhanced $\gamma$.

needlessly complicates matters. Slight variations between experiments, such as the amount of silver paint on the platform and thermal cycling effects on the thermometers guarantees extra inaccuracies in subtracting addenda. This method assures a much higher accuracy in the relative measurement. The purpose of the using a fit, rather than an interpolation of the $C(H=0)/T$ is that there are field dependent contributions that are non-zero when $H=0$. This includes $C_{Sch}/T$ and $\alpha T$.

Several checks ensure the correct assessment of the contributions. The $\beta T^2$ term is assumed field independent, but this is corroborated by the parallel traces $C(H = 34.5 \text{ T})/T$ and $C(0)/T$ versus $T^2$ (fig. 5.3). To prevent confusion due to the Schottky anomaly, the data is fit only over temperatures at which $C_{Sch}/T$ is insignificant. For most cuprates this temperature is 2 or 3 K. In the linear fit $\gamma(0)$ is simply the $T = 0$ intercept. Unfortunately, the large $\gamma(0)$ small dynamic range of fitting make any hope of extracting the relatively small $C/T \sim \alpha T$ contribution hopeless. Ideally,
a fit of $C(0)/T$ versus $T$ with $\gamma + \alpha T + \beta T^2 + \beta_5 T^4$ would fully characterize all contributions, where $\beta_5$ is defined as the contribution $C \sim \beta_5 T^5$ from higher order terms in the Sommerfeld, Debye approximation, etc. Due to the difficulties of deciding all of these coefficients, the focus remains on the largest expected contributions, leaving $C/T = \gamma + \beta T^2$ as the only reasonable fit choice, thus $\Delta C(H)/T \equiv C(H)/T - \gamma(0) - \beta T^2$ for Hg1201.

![Figure 5.4: Specific heat plotted as $\Delta C/T$ (see text) versus $T$ (black squares) at 4 T for sample A. The Schottky anomaly is clearly visible, and the fit (red curve) uses the Schottky function Eq. 4.11, where $g$, $n_s$ and an additional offset $\Delta \gamma \equiv \gamma(H) - \gamma(0)$ are fit parameters. In this case $g=1.98$ and $n_s \approx 0.005$ mol$^{-1}$. For this sample, $T_c=72$ K.](image)

Fig. 5.4 shows the simplifying advantage of plotting the subtracted data as $\Delta C/T$: $C$ must vanish as $T \rightarrow 0$ and so has no constant contributions; all other contributions have at least one contribution with non-vanishing power of $T$. A more sophisticated statement is that deducing a power law requires very robust levels of signal to noise and dynamic range, whereas claiming that a function is a constant within some range is much simpler. By reducing $C$ by one power of $T$, $\gamma$ gains such an ease of interpretation, and there is no contribution $C/T \propto T^{-1}$ to complicate matters.
Even with this slight improvement, coaxing out the contributions is no simple matter. Fig. 5.4 is clearly dominated by the Schottky contribution \( C_{Sch}/T \) as it is the only exponentially peaked function (hence “anomaly”). In fact, at \( T \) corresponding to the peak, \( C_{Sch}(H = 4T)/T \) is larger than the \( \beta T^2 \). Despite any other contributions, it is then simple to fit Fig. 5.4 with a Schottky function plus some offset corresponding to \( \Delta \gamma \equiv \gamma(H) - \gamma(H = 0) \), with \( g, n_s \) and \( \Delta \gamma \) as fit parameters. Unfortunately, with no knowledge of the underlying functional form of the monotonic contributions, such as higher order terms from the Sommerfeld expansion or the crossover of Simon and Lee scaling, there is no practical, fully independent method to parametrize the Schottky anomaly. Even if one could reliably set \( H \) to some very small values, and measure for \( T \) with similarly small values, in order to vanish all other contributions, the low field broadening of the anomaly means that these parameters may not be valid at higher fields.

The solution, though not perfect, is to fit \( \Delta C/T \) versus \( T \) with the simple \( g, n_s \) and \( \Delta \gamma \) scheme at various fields and attempt to establish a pattern. That is, one may then plot or tabulate \( g, n_s \) and \( \Delta \gamma \) to check their field dependence. Fitting versus \( H \) rather than \( T \) may add an extra dimension to the analysis. However, no new information is available this way, and the utter difficulty of sweeping \( H \) as established in chapter 3 renders this a secondary method at best.

Hg1201 stands as a particular test case for the method described above, mainly because of the relatively large anomaly. If the sample shows field independent parameters \( g \) and \( n_s \), not only is it the simplest case empirically, but it is also the simplest physical scenario. That is, a set of totally free, localized spins must have a field independent \( g \), and the number of the spins cannot change with field. It is only when interactions become significant with effects similar to that of a field of order 1 T that complications arise. Field dependent parameters make the inference of the pure Schottky contribution essentially impossible. Fortunately, at sufficiently high field, the contribution is frozen out by the widening of the Zeeman “gap”.

At lower field, where the \( C_{Sch} \) peak intrudes, no matter how sophisticated the model, if the samples themselves containing confounding behaviors, the data is impossible to interpret without knowledge of the details of the composition of any extraneous parts of the samples. This fact comes firmly to bear in fig. 5.5. Sample B shows a strong field dependence, but the field dependence is
Figure 5.5: $H=0$ and 9 T $C/T$ versus $T^2$ with no subtractions. Two different attempts to measure $C(0)/T$. The right panel is a zoomed version of the left panel to show the lack of field dependence at lowest temperatures, where the 9 T data approaches almost within error to the green line fit of $C(0)/T$. At higher temperature, the 9 T data is clearly increasing more slowly with $T^2$ than the 0-field. Both of these behaviors are consistent with little to no $\Delta C_{\text{elec}}(9T)$.

incompatible with a large $\Delta \gamma(H)$. Instead, a comparison of the subtraction-free 9 T with the 0 T data shows either an insignificant $\Delta C_{\text{elec}}(9T)$ or at least the impossibility of determining a reliable value. It is possible and altogether likely that the insignificance is down to a large threshold for discerning such changes, much larger than the statistical signal to noise in the total $C$, as well as a small change relative to the bare signal to noise. A simpler way to state it is that the samples contain a sort of intrinsic noise in the form of extraneous contributions to $C$, as well as relatively small changes in $C_{\text{elec}}$ relative to the data scatter. Certainly then, any chance of extracting a power law form such as $C_{\text{elec}} \sim H^{1/2}$ dissolves in the face of poor final “signal to noise.”

Without the possibility of asserting a regime of expected behavior, the high field results lose some of their power to questions about sample quality and the details of the driving physics. The uniformity of $T_c$ from sample to sample within the annealing batch establishes superconductivity as a strong player in this system. A d-wave superconductor should have some field dependence in any case, and such a dependence is strongly indicated in fig. 5.3 for sample B. To reconcile the apparently vanishing $\Delta \gamma(9 \text{T})$ with the relatively large $\Delta \gamma(30 \text{T})$, one must imagine that the temperature
dependence is sufficiently odd so as to hide smaller $\Delta \gamma$ or that converging energy scales of a complex nature produce a non-monotonic field dependence distinct from $C_{Sch}$. Unfortunately, none of this speculation brings about anything useful other than to suggest the level to which disorder obfuscates the interesting physical results. Thus, moving into the high field regime, expectations must be honed to searching for a blunt, rather than subtle, result.

5.2.3 Hg1201 High-field Results

Fig. 5.6 moves the discussion in this direction, showing a possible apparent saturation in $\Delta C/T$, in sample A with $T_c=72$ K. However, there is still clear contamination from both $C_{Sch}$ as well as the nuclear Schottky anomaly $C_{nuc}$, and further subtraction makes the picture more clear.

![Figure 5.6: High field $\Delta C/T$ versus $T$ for sample A with $T_c=72$ K. The black dashed line is the estimate of $C_{Sch}(20 \text{ T})$, with the $g = 2$ and $n_s=0.005$.](image)

In the “high field” regime, the particulars of the electronic Schottky subtraction are less important because the peak magnitude goes as $1/H$. A subtraction of all data for $H > 20$ T by the simple fit to 4 T should suffice within 10 to 20% as long as $g$ and $n_s$ do not have extreme field
dependence. The top panel of fig. 5.7 is the result after the $C_{Sch}/T$ subtraction. $C_{Sch}(20 \, \text{T})$ clearly saturates to very near zero below 2 K, making this region insensitive to this subtraction.

The remaining $C_{nuc}$ is visible in the top panel of fig. 5.7 as an initial drop in $\Delta C/T$ with increasing $T$. This is the high temperature limit of the full $C_{nuc}$. It is quite clear from the strong $H$ dependence of $C_{nuc}$ that coupling to the field is the dominant energy scale. This guarantees the system is in the $C_{nuc} \, H^2/T^2$ regime and the particulars of the energy level structure are irrelevant. In principle, there may be small corrections to this, but for a fixed field, $C_{nuc}/T \propto T^{-3}$ is a robust assumption. In order to reach the final destination of $\Delta C_{\text{elec}}/T$, a simple fit with one free parameter, $aT^{-3}$ from $\approx 1$-$2 \, \text{K}$, should suffice. The parameter $a$ is virtually unconstrained for each $\Delta C(H)/T$ versus $T$ trace. If $a$ does not follow $H^2$ at least approximately, this raises suspicions as to the true origin of the $aT^{-3}$ behavior. In this case, $a$ is well behaved enough, following $u + vH^2$ closely, where $u$ and $v$ are real number constants.

![Figure 5.7](image)

Figure 5.7: (top) High field $\Delta C/T$ versus $T$ for sample A with $T_c=72 \, \text{K}$, showing only the electronic and nuclear Schottky-like contributions, plus superfluous higher order contributions. (bottom) After subtraction of the nuclear piece, only the electronic part remains. The data collapses above $\sim 30 \, \text{T}$ onto a single curve.
For the discussion of the YBCO results, the preceding discussion serves as a loose road map that is applicable with far more rigor. For Hg1201, the conclusions are less ambitious and thus require less certainty. From fig. 5.7 (bottom), one can see that $C_{\text{elec}}$ does appear to reach a field independent region for temperatures below 4 K and fields greater than 30 T. This result is somewhat in contradiction with ref. [54], (Riggs et al), which claims an increasing $C_{\text{elec}}$ for all fields up to 45 T, once quantum oscillations are removed, despite a resistive transition of $H = 28$ T at 1.5 K. That is, when the Riggs et al crystal is not in the 0-resistance state (one definition of superconductor), the data does not look strictly “normal” conducting. The Hg1201 results show a resistive transition very near $H = 28$ T as well (see fig. 5.8), but $C_{\text{elec}}$ loses its field dependence. This conclusion is made all the more robust when comparing sample A and B. Fig. 5.9

![Figure 5.8: Contact-less conductivity measurement by Tunnel Diode Oscillator (TDO) of the Hg1201 sample B. The plot is of the change in resonant frequency (left axis, black) and its second derivative (right axis, red) versus $H$. The TDO measures the resonance frequency of an LR circuit, with L the inductance containing a contribution from a wire coil enclosing the sample. Thus, L depends on the sample AC susceptibility, which for metals is the skin depth $\sqrt{\mu R \rho}$ where $\mu_R$ is the relative permeability and $\rho$ is the resistivity. The superconducting transition is visible as a sharp drop in the resonant frequency due to rapidly decreasing diamagnetism. The orange dashed line approximates the onset of the transition, with the magenta showing the midpoint.](image)
Figure 5.9: High field $\Delta C/T$ (left) after $C_{\text{Sch}}$ subtractions, and magnetization curves (right) at 10 Oe showing the $T_c$ for samples A and B. $C_{\text{nuc}}$ is left in for scale. The absolute values of $\Delta C/T$ between A and B differ by a small amount, but the case for saturation appears robust. [1]

The saturation appears to be a robust conclusion, despite other considerations, because sample B, with identical $T_c$, shows the same behavior. The 30 T and 34.5 T traces in fig 5.9 for sample B are essentially identical below 4 K except for $C_{\text{nuc}}$, which serves to demonstrate that the sample still responds to field even though $C_{\text{elec}}$ does not. The unusual temperature dependence, i.e. the “dip” just above 4 K appears in both samples and appears most pronounced at the highest fields. Given the complications of the sample at $H = 0$, and that 34.5 is just above the midpoint of the resistive transition at 1.6 K, it is not surprising that the temperature dependence defies a simple form. For example, the sharp rise above 6 K are consistent with the $H=0$ deviations from $C/T = \gamma + \beta T^2$.

The conclusion that a saturation of $C_{\text{elec}}$ occurs above the resistive transition is not altogether unexpected. All that need happen for such a saturation is a simultaneous saturation of the vortex population. However, as the literature shows, it is not altogether clear whether the resistive transition represents the “destruction of superconductivity” or rather simply vortex motion. In at least one picture, disorder that does not reduce $T_c$ is more likely to increase the pinning potential for vortices, bringing the $H_r$ closer to $H_c2$. Whether or not this picture is accurate and whether $H_c2$ is reduced by disorder is not immediately clear either. One possible alternative to a simple
saturation is a region in which DOS rapidly increases with increasing field as the superconducting gap dies off and the magnetic length approaches the coherence length. Though fig. 5.7 may allow for this scenario, the definition of “rapid” in this case must be contextualized to consider that the $H=0$ DOS is already more than half of the total DOS at 34.5 T. If the low field data were more straightforward, it would certainly provide the proper clues.

This brings about a good point to note the major conclusions of the Hg1201. Simply in terms of experimental considerations, clean samples, those of low $\gamma(H = 0)$, have distinct advantages over those samples of larger such values, besides just the ability to call the samples clean and therefore reliable. The large Schottky anomaly and residual DOS produce both direct and indirect confounding effects on $\Delta C/T$.

5.3 $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ Introduction

As seen in the literature review, YBCO has received a lot of attention during the time of writing and the duration of the present study. Mirroring such curiosity, the hope for this study is that the presence of quantum oscillations indicates a highly ordered, pure material. Further, the discovery of the charge ordered state indicates an incredibly rich phase diagram, possibly with several different orders that coexist in different ways in different parts of the $H−T−p$ phase diagram.

The simplest place to begin the discussion of YBCO is in the $H,T \to 0$ limit. The only tuning parameter is then $\delta$, or more relevantly speaking, $p$. Recall that $p$ has, in the clean limit, a one-to-one correspondence to $\delta$, but that small disorder effects are significant enough to break down that correspondence. Following ref. [38] the following discussion uses $T_c$ as a tuning parameter to infer $p$.

A brief aside for a final note: Riggs et al is central to the following discussion, and the results from that study, though not directly part of the present study, fold in inextricably to the overall results. All results mentioned below for YBCO6.56 come directly from that work, but are treated similarly to the original results, though with proper citation. This is in part because the original results below come, in part and in some sense, from the same crystal as the YBCO6.56 results.
That is, one crystal piece has been subjected to oxygen annealing to adjust the O content followed by detwinning on two separate occasions. The first anneal changed the O content from 6.56 to 6.51, while the second anneal, more than a year later, brought the O to 6.47. Between the time of the publication of Riggs et al and the start of the present study, the YBCO6.56 fractured. In order to maintain a large enough sample mass, a second piece of sample joined the first annealing ensemble. During the detwinning process after the second anneal, the original sample piece fractured again, such that the YBCO6.47 study included 3 pieces of sample. Thus, besides small strain effects and oxygen ordering, much of the total sample material remains the same, at least in terms of composition. However, twin boundaries likely contribute more disorder (before detwinning at least) than any other source, and so the process of incidentally twinning during O annealing, and then intentionally detwinning completely resets the disorder. By this token, any assertion that the crystals are identical save O content stands as altogether unlikely. Nonetheless, O tuning a single set of crystals is by far the most controlled way to make a doping comparison.

5.4 YBCO6.51

5.4.1 Introduction

The results on YBCO6.51 are altogether incomplete. They stand as an interesting intermediate step, and there are some compelling conclusions available from the data. However, the experimental physics is ever evolving, and the following discussion comes from the “adolescent” period of the specific heat measurements. Data at the very highest fields is not useful beyond suggesting coarse constraints on the DOS. For more intermediate fields (10-15 T), calibration gaps leave large uncertainties in explaining unexpected deviations from the forms outlined in the theory chapter. The following discussion then serves mostly as an exercise in build up to the YBCO6.47, but the conclusions, few as they may be, are reliable.

The YBCO6.51 measurements were performed over the ranges $H=0$-15 T and $T=1$-10K. The goal of these measurements was to determine the $\gamma(0)$ to high accuracy and determine the specifics of $C_{\text{elec}}$, such as whether $C_{\text{elec}}/T = A_c \sqrt{H} + \gamma(0)$ where $A_c$ is a constant parameter.
Figure 5.10: SQuID magnetometry curves at 2 Oe for the samples of YBCO651. The left panel shows field cooled (FC, red) and zero-field cooled (ZFC, blue) for the 4 mg sample and the inset is the derivative \(\frac{d\mu}{dT}\) of the magnetic moment versus \(T\). The aspect ratio of the 2 mg sample is much large than the 4 mg sample, driving up the demagnetization factor and thus the SQuID response. The two derivative curves match within resolution of the SQuID temperature stability.

### 5.4.2 Samples

The two samples of YBCO6.51 have \(T_c=57.3\) K at the midpoint of the transition defined by the maximum derivative from a SQuID (Superconducting Quantum Interference Device) magnetometer shown in fig. 5.10. The \(T_c\) of each sample is identical within the resolution of the measurement, with a full-width at half maximum (FWHM) of about 0.3 K. This uniformity is even better than that for the Hg1201 samples A-E. The sample masses are 2.06 mg and 4.05 mg, but all measurements included both crystals, except in one case as described below.

From ref. [38], \(T_c\) gives \(p=0.01\). This doping is essentially the Ortho-II ordered state, and corresponds to the first for which quantum oscillations are observed.[46] The expectation is then that disorder is minimal and so \(\gamma(0)\) should be minimal too. Fig. 5.11 shows that there is a substantial \(\gamma(0)=2.3 \text{ mJ mol}^{-1} \text{ K}^{-2}\), but far smaller than those of Hg1201.
Figure 5.11: $C/T$ versus $T^2$ from the difference between the full 6 mg sample ensemble and the 2 mg piece by itself.

5.4.3 YBCO6.51 Low-field Contributions

The determination of the addenda for this pair of samples happens to follow from a fortunate mishap. In the middle of an experimental run, the magnetocaloric effects of field ramps at temperatures $>10$ K determine the approximate $H_r(T)$. However, the field ramps carry a risk of torquing the sample off of the platform. Instead of using a traditional direct measurement of addenda, the YBCO6.51 0-field result is simply the difference between the measurement of the full 6 mg of sample and a measurement of the 2 mg sample alone. The measurements do not suffer from concerns about thermal cycling because sample removal may accidentally occur in situ via a field sweep. This “method” may remove the 4 mg sample leaving only the 2 mg piece, with subsequent measurement providing the basis for an accurate addenda subtraction, including silver paint.

The beauty of the $C/T$ versus $T^2$ curve is readily apparent in fig. 5.11; the deviations from linearity enter as the usual low temperature upturn from $C_{Sch}$, and a parabolic term ($\propto (T^2)^2$) less than 10,000 times smaller than $\beta=0.39$ mJ mol$^{-1}$ K$^{-4}$. Such a term is expected in a Fermi liquid from higher order terms in the Sommerfeld expansion as well as the Debye approximation. The absence of such higher order terms is a strong sign that $C=C_v$ holds to high precision, primarily because the harmonicity of phonons that the validity of the Debye approximation requires also
implies that the system has a volume independent of temperature. There is now good reason for application of eq. 4.6, a relation with particular power to evaluate the nature of the Fermi surface that may be lurking at higher fields once superconductivity succumbs. Further, this strengthens any statements about physical parameters such as $v_\Delta$, which $C(H)$ should determine within typical the disagreement between two different experimental probes such as thermal conductivity and ARPES.\[74\]

Despite the linearity that the samples demonstrate in $C/T$ versus $T^2$ plots, and the relatively small $\gamma(0)$ there is a serious pitfall about the form. That is, if there is a reasonable expectation that both the $C \propto T^5$ term ($\beta_5$) and the $\alpha T^2$ term are significant, there is also a reasonable chance that the two could in some sense cancel each other versus $T^2$. If $\alpha/\beta_5$ is within the right range, the linear combination $\alpha(T^2)^{1/2} + \beta_5(T^2)^2$ may appear as a line plotted versus some domain of $T^2$ due to the opposite curvature of each term. Fig. 5.12 shows a situation for which the Schottky anomaly would obscure the non-linear part at lower temperature while the remainder above $T^2 = 9K^2$ easily achieves sufficient linearity within the data scatter.

If $\alpha$ were a field-independent quantity, the confounding nature of its relationship with $\beta_5$ would be of no consequence to understanding the field dependence. Unfortunately, $\alpha$ is only truly valid for vanishing field where the thermal length dominates over the magnetic length $l$. In the cartoon picture based on the simple d-wave BdG spectrum, as soon as the Doppler shift carries the Dirac
point away from the chemical potential much further than $k_B T$, the $\alpha T^2$ term becomes negligible.

Fortunately, a plot of $C/T$ versus $T$ forces all powers of $T$ into forms of positive, semi-definite curvature. Unfortunately, this method of plotting does not leave a clear route for separation of the different powers.

Figure 5.13: (left) $C/T$ versus $T$ plot of the $(H=0)$ data (blue squares) from fig. 5.11. It is possible to fit (red curve) a finite $\alpha$, but the value is very unconstrained. The table shows one set of parameter outcomes.(right) $\Delta C(H = 1 \, T)/T$ versus $T$ (black circles) as determined by the parameters from (left). A fit (red) with the form $C_{Sch} + \Delta \gamma$ shows that the data becomes a constant well within the data scatter above $\sim 4 \, K$; $\alpha$ from the fit is so small, it can be set to 0 without significant effect.

The method this study employs for separating out the major contributions is more an exercise in consistency and understanding of the robustness versus the limitations of conclusions from fits with multiple parameters than some attempt to disentangle and ascertain the true values of parameters such as the Debye temperature. After all, the absolute field dependence of $C_{elec}$ is the real goal of the technique, not the particulars of $\Delta C_{elec}$ versus $T$ at each field. Fig. 5.13 gives a starting point to bound $\alpha$, in concert with predictions from the literature, while $\Delta C(H > 0)/T$ traces serve as a testing ground for each fit of $C(H = 0)/T$. Specifically, $\Delta C/T = C(H)/T - \gamma(0) - \beta T^2 - \beta_5 T^4$, with the final choice of parameters being that which gives the result nearest to $\Delta C(1T)/T = C_{Sch}/T + \Delta \gamma$ (here, $C_{nuc}$ is negligible). Fortunately, as seen in fig. 5.13 (right panel), the most naïve fit yields the desired result form for $\Delta C(1 \, T)/T$, and $\alpha$ can in fact be set to zero.
The selection of a particular choice of parameters does not certify it as highly accurate; however, because $C_{Sch}(1T)/T \sim T^{-3}$ above 3 K, it does stand out as the most natural choice. In any case, if $\Delta C_{elec}/T \neq \Delta \gamma$, then the best fit to the form $\Delta C(H)/T = (C_{Sch} + C_{nuc})/T + \Delta \gamma$ must utilize field dependent $g$ and $n_s$ parameters. In the most rigorous approach, $g$ and $n_s$ are fixed parameters so that any additional field and temperature dependence comes out. In that case, a simple determination of $\Delta \gamma$ is not reasonable nor relevant. Again, the prevailing paradigm for the discussion is the extraction of $\Delta C_{elec}(H,T)$, which, for the YBCO discussion, is defined simply as what remains after all subtractions. The subtraction procedure should be *uniform across all fields and temperatures* with only $H$ and $T$ for varying.

Given that $g$ and $n_s$ may be field dependent in fact, and that really any component may behave outside of assumption, a useful determination of the best fixed $g$ and $n_s$ defies simple approaches. There are three routes one may take: (1) fit $\Delta C/T$ *ad hoc* at each field and devise some average of the parameters, (2) fit globally for fields where the $C_{Sch}$ peak is visible, (3) determine $n_s$ in the low end of the field range where $C_{Sch}$ is most sharply peaked, and track the temperature of the peak across the whole field range to determine $g$. In the end, the present study settled on a combination of these methods.

Route (1) gives a range of values for $g$ and $n_s$ to help constrain further fitting and explicitly makes clear the range of fields where $g$ is most field dependent. In this case, for fields $< 3T$, $g$ is far more field dependent; this is exactly as expected since $C_{Sch}(H = 0)$ would vanish uniformly if Zeeman splitting by $2g\mu H$ is the only effect, but for YBCO $C_{Sch} \neq 0$ for any field. Route (2) gives a statistical portrait of things, including the most precise mean for the parameters. Route (3) yields results which use the fewest assumptions, at least initially. Unfortunately, since the $C_{Sch}(H)/T$ versus $T$ peak shrinks as $1/H$ and broadens as well, any underlying temperature dependence shifts the maximum of $\Delta C(H)/T$ away from that of $C_{Sch}(H)/T$. Thus if Route (1) gives non-constant $g$, route (3) is likely to do the same.

The choice for the present study combines route (2) and (3), while using (1) to find where the minimum Zeeman “limit” $\Delta_{Sch} \sim H$ is essentially satisfied. Fig. 5.14 shows a collection of curves from 3 T to 8 T used to determine $g$. The fits suggest that $\Delta C(3T)/T$ best determines $n_s=0.0023$. 

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Figure 5.14: $\Delta C/T$ versus $T$ plot of for 3, 4, 5, and 8 T. The red curves are the results of the global Schottky function fit with only $g$ free (best fit value 2.08), with $n_s$ determined by $\Delta C(3T)/T$.

The global fit gives $g = 2.08 \pm 0.002$.

In order to remove $C_{\text{nuc}}$, which is necessary above 6 T and significant above 4 T, the data is plotted as $\Delta C(H)/T$ versus $T^{-3}$ and then fit with a line. In fact, the intercept of such a fit gives a decent determination of $\Delta \gamma$ as long as the fit is decent enough in the first place. Fig. 5.15 shows an example of such a plot for $\Delta C(18 \, \text{T})/T$. The data at high T has no $C_{\text{Sch}}$ subtraction, because at such high $H$, a significant range of $H/T$ is available such that there is little $C_{\text{Sch}}-C_{\text{nuc}}$ cross contamination. Once the nuclear Schottky is out of the way, a rudimentary plot of $\Delta \gamma$ emerges (fig. 5.16, left panel). Clearly, the plot demonstrates a sub-linear dependence, but the scatter is far too large to permit a precise inference. A direct comparison between YBCO6.51 (left fig. 5.16) and YBCO6.56 (right fig. 5.16),[54] shows a marked change in $A_c$, increasing from 0.65 to 0.47 mJ mol$^{-1}$ K$^{-2}$ T$^{-1/2}$.

There are two possible ways to interpret the discrepancy: an $\approx 50\%$ decrease in $v_\Delta$ from $p=0.1$ to 0.09, or a simple variation based on differences in data analysis. Looking simply at the statistical errors in $A_c$, there is no chance of a random difference. Thus, differences in $A_c$ must either be real or down to systematic differences not evident in the data scatter. One possible source of systematic error is in differences in the definition of $\Delta \gamma$ or the manner in which the quantity is
Figure 5.15: \( \Delta C(18 \text{T})/T \) versus \( T^{-3} \). The slope of the fit line (red) is determined by \( \approx n(\mu_N H)^2 \). The intercept is a close approximation to \( \Delta \gamma(18 \text{T}) \).

determined. Riggs et al utilizes a fitting of \( C \) versus \( T \) rather than \( C/T \) versus \( T \) to determine the \( g \) and \( n_s \) Schottky anomaly parameters. Thus, it is useful to employ multiple methods of assessing \( \Delta \gamma(H) \) to determine the effect of procedure on the stated outcome. \textit{A priori}, however, there is no reason to place preference on \( \Delta \gamma \) over a simple plot of \( \Delta C(H)/T \) versus \( H \), or even better, a scaling plot of \( C/(TH^{1/2}) \) versus \( H^{1/2}/T \). [64] The strength and weakness of both plots is in removing the “fiddling” of the human author. On one hand, this removes bias, but on the other, it removes the filtering of data by one knowledgeable of the pitfalls of the experiment. The data may possess artifacts which are \textit{prima facie} disqualifiers of sound interpretation, but with the lens of the likely systematic errors of the experimental setup, the data may have an altogether more powerful interpretation. A successful experiment includes a minimum of such confusion, with expertise going
Figure 5.16: (left) $\Delta \gamma$ versus $H$ for YBCO6.51. A fit to $A_c \sqrt{H}$ (red) serves the purpose of comparison rather than a precise determination of a power law. (right) $\Delta \gamma$ versus $H$ plot for YBCO6.56 from Riggs et al. The methods of extraction for the two plots are quite different but the results are quite similar.

to prevent such errors before data collection, rather than the interpretation and correction of the resulting artifacts after the fact.

Fortunately, a reexamination of the $\Delta \gamma$ extraction procedure, upon plotting versus $H$, yields no significant changes to the interpretation, as seen in fig. 5.17. There is still a field dependence of negative curvature, quite consistent with an approximately $H^q$ law, where $q \approx 1/2$. The simple conclusion is that the doping difference between O6.51 and O6.56 does not lead to any radical changes in the superconducting electronic structure up to 15 T. Such a fact may well meet with expectations, but the cuprates are known to defy expectation.

In summary, the differences between YBCO6.51 and YBCO6.56, where significant, are small. This includes a possible mild enhancement of both the $\gamma(H = 0)$ and $A_c$ parameters, as well as an approximately 25% increase in the Schottky peak magnitude. If this data is representative of all YBCO6.51, the conclusions are that the superconducting gap is mostly unchanged in the $H, T \rightarrow$ limit. The enhancement of the Schottky magnitude possibly come due to an extrinsic disordering that occur due to sample handling, or perhaps there are intrinsically more free local moments. As the YBCO6.47 section shows, this trend in Schottky magnitude continues to lower doping.
Figure 5.17: $\Delta \gamma$ versus $H$ for 2 different procedures, the first (blue squares) is identical to fig. 5.16 left panel, and the second (red squares) involves an extrapolation of a low temperature subset (1.2-1.6 K) of $\Delta C(H)/T$ to determine $\Delta \gamma$. The blue and red continuous curves are fits to $A_c \sqrt{H}$, but again serve more as guides to the eye.

The doping independence of $\gamma(H = 0)$ contrasts with the large enhancement of $m^*$ (up to a factor of 2) indicated by SdH measurements, implying that the $H = 0$ state is not affected noticeably by the high $H$ physics. There is no reason in principle why an enhancement of a Fermi liquid $m^*$ should be visible in the superconducting state, but also no reason a priori for the physics driving $m^*$ to be invisible there, especially given the finite $\gamma(0)$ and that $\alpha \sim v_F \sim k_F/m^*$.

## 5.5 YBCO6.47

### 5.5.1 Introduction

YBCO6.47 is still a relatively mysterious entity in the spectrum of YBCO at the time of writing. The vortex solid in this material persists up to 45 T or more at lowest temperatures.[51] Such a high melting field value makes it unattractive to study with probes seeking to contrast the resistive state with the vortex solid. This drawback is less important for specific heat, which probes the resistive and superconducting state equally well. The interest in YBCO6.47 results from its position on the phase diagram in a gray area near $p=0.085$ between spin-order and charge order, and high field “insulating” ($\frac{dR}{dT} < 0$, $T \to 0$) and “metallic” ($\frac{dR}{dT} > 0$, $T \to 0$) phases. The phase diagram
in fig. 5.18 shows the confluence of phases including, upon increasing doping, a possible crossover from a insulating high field state for $p < 0.08$ to a metallic one of visible Shubnikov-de Haas (SdH) oscillations for $p > 0.09$. The insulating nature is defined simply as sample resistance increasing as $T \to 0$. Over the same range, the spin-ordering temperature vanishes and the charge-ordering temperature ($T_{\text{charge}}$) becomes finite.\[17, \ 27, \ 29, \ 56\] In the case of NMR measurement, the charge-ordering field $H_{\text{charge}}$, defined as before as the sudden field-induced onset of certain NMR/NQR phenomena,\[82\] may also become finite where $T_{\text{charge}}$ does, but the doping dependence weakly suggests $H_{\text{charge}} > 45 \, \text{T}$ for YBCO6.47.

Given the high irreversibility field and the particular intrigue of the phase diagram, the goal of heat capacity measurement is to probe the excitations of the superconducting state and detect the particulars of evolution with field. This is interesting in its own right but also stands out in

Figure 5.18: YBCO $H - T - p$ phase diagram. The orange rectangle shows the field/doping range of the YBCO6.47 measurements. The charge order is established by NMR \[82\] and x-ray measurements\[27\]; spin order (green) is determined by $\mu$SR and neutron diffraction and muon spin rotation,\[29, \ 56\] The red rectangle encompasses Riggs et al figure 1\[54\]. The sine wave curves are a schematic representation of the SdH measurements and the insulating region indicates unbounded resistance for $T \to 0$ as well as vanishing SdH amplitude.\[58, \ 35\]
Figure 5.19: YBCO6.47 C/T versus $T^2$ for $H = 0$. Sample mass is 3.92 mg. The results are consistent with both YBCO6.51 and 6.56. The small variation in $\beta$ between dopings is within the addenda error. The usual 0-field Schottky is visible below $\approx 4$ K$^2$

contrast to Riggs et al and its depiction of the crossover from solely d-wave superconductor into a mixed, vortex liquid-like state for which some part of the system must be Fermi liquid.

5.5.2 Samples

The sample pieces for the experiments are just as described above. The $T_c$ of the samples at the midpoint is 49 K, with a similar sharpness in the transition to the YBCO6.51 curves, implying an upper bound on the doping “inhomogeneity” of $p = 0.082-0.086$. In fact, since $T_c$ changes rapidly with doping in this range, 8 K for an Oxygen shift of just 0.04, the doping homogeneity is likely much higher (i.e. narrower width of possible p) since similar transition widths are seen even near optimal doping where $T_c$ is nearly independent of O content.[38]. Some results include measurement of only 3.92 mg of sample mass, while other data below comes from the full 5.98 mg of available mass. All data includes measurement of two separate sample pieces that make up the 3.92 mg mass. The measurements on the 5.98 mg of mass simply include an additional 2.06 mg piece. This additional piece does not significantly alter the quantitative results. All results where $H > 15$ T include only the 3.92 mg of sample. The main discrepancy between the two is in the small difference in the Schottky $n_s$ parameter, with about 10% difference between $n_s$ with and without
Figure 5.20: YBCO6.47 C/T versus T² for H = 0, 34.5 T. Sample mass is 3.92 mg again. The result shows an essentially field-independent β

the additional sample piece. Finally, unless otherwise noted the error bars for any of the following C data are ± one standard deviation of a single data collection. A single collection refers to one pair of values (H, T) (such as one complete sawtooth waveform) as explained in “Experimental Summary.”

5.5.3 YBCO6.47 Low-field Contributions

Fig. 5.19 shows the 0-field data after addenda subtraction for 3.92 mg of sample mass. The values of β and γ(0) are consistent with YBCO6.56 and 6.51. This fact is significant for two reasons. The SdH measurements led to claims of divergent cyclotron mass near YBCO6.47.[58] If the high-field electronic structure giving rise to the SdH oscillations is essentially unchanged from 0-field, such a mass enhancement should show up as a large decrease in v_F, since the SdH frequency, related to k_F, is unchanged across all measurements. The unchanging nature of the 0-field C implies that v_F is not wildly suppressed, since the still invisible contribution ∼ αT² should enhance along with the mass, such that α becomes significant. This fact does not decisively rule out the possibility of enhanced mass for H = 0, but it does greatly constrain the possibility.

Moving forward, three possibilities present themselves. One, α is so small at higher doping that even a large enhancement is not visible, two, the mass enhancement exists only at high fields, or three, the mass enhancement interpretation of the SdH data is incorrect. The implications
for the specific heat results follow the three paths, respectively, as: one, the suppression of $v_F$
also suppresses $v_\Delta$ to generate a much stronger square-root-of-$H$, two, a field-induced electronic
renormalization occurs at some range of $H$, or three, $C$ is more or less identical to that at other
dopings. One may also manifest, in a purely naive assessment, as a breakdown of the SL scaling
for the case where $v_F \gg v_\Delta$ is not true.

The usual strategy of invoking $C(H)$ for highest field to establish $\beta$ independent of $H$ works well
for these samples as shown in fig.5.20. The 34.5 T data has essentially no Schottky contamination
above 3 K, and the phonon term appears to be field independent within 1%. As established
previously, the phonon field-independence is expected at the level of resolution in specific heat.
Thus, with the corroboration of the 34.5 T data, the remaining discussion takes $\beta$ as an assumption.

As outlined in the section on YBCO6.51, the procedure to extract $\Delta C_{\text{elec}}(H)/T$ includes an
initial subtraction of the nominally field independent 0-field parameters $\gamma(0)$, $\beta$, and $\beta_5$. From here,
a determination of the Schottky contributions with field independent parameters should leave the
contribution of interest behind. As with YBCO6.51, the choice of the three parameters depends

![Figure 5.21: $\Delta C(H)/T$ versus $T$ at various $H$. Sample mass is 5.98 mg. The red curve is a fit
of $C_{\text{Sch}}/T$ plus a constant to the 3 T data to establish $n_s$. A global fit determines $g=2.0$ with
insignificant error.](image-url)

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on the value \( \alpha \), and there is no independent way to choose or determine \( \alpha \). Therefore, the choice of \( \alpha \) within reasonable bounds that yields \( \Delta C(H = 1 \text{ T})/T \) is the field and temperature dependence of that contribution carries information, at the very least, about how well-suited the subtraction procedure is. To establish the Schottky parameters \( g \) and \( n_s \), the procedure is as before, with the 3 T data set establishing \( n_s \), and a global fit from 3 to 9 T establishing \( g \). Fig. 5.21 shows \( \Delta C(H)/T \) versus \( T \) for 3 to 9 T, from which \( n_s = 0.0035 \pm 0.0003 \) and \( g = 2.0 \) with statistical error (< 0.01) far below the systematic errors.

The resulting \( C_{elec} \) shows an immediate coherence seen in the SL scaling [64] (See “Literature Survey”) and \( \Delta \gamma \) versus \( H \) plots (fig. 5.22). This is somewhat surprising given the dominating nature of \( C_{Sch} \) as seen in fig. 5.23. The scaling plot establishes that, to within about 20%, the SL scaling function is a constant, consistent with Volovik’s treatment. Further, the \( \Delta \gamma \) versus \( H \) form is best fit by \( \sim H^q \) where \( q = 0.5 \) within the statistical error. The precise value of \( A_c \) depends somewhat on the subtraction procedure, which is expected given the unstable nature of

![Figure 5.22: (left) SL scaling plot. The scaling function appears to be a constant within the data scatter. The extrapolated intercept is about 0.7 ±0.05 mJ mol\(^{-1} \) K\(^{-2} \) T\(^{-1/2} \), which is analogous to the fit parameter \( A_c \), with the dashed red box indicating the uncertainty. (right) \( \Delta \gamma \) versus \( H \) for YBCO6.47 for two different subtraction and extrapolation methods; the error bars are the authors best estimate based on traces after subtraction (see fig. 5.23). Fitting with \( A_c \sqrt{H} \) yield \( A_c = 0.68 \) (0.57) mJ mol\(^{-1} \) K\(^{-2} \) T\(^{-1/2} \) for the upper (lower) trace, represented by the red (black) curve. Sample mass for all data is 5.98 mg]
To generate a somewhat more rigorous portrait of $C(H)$, the present study does not rely solely on a single run pattern, but includes orthogonal cuts through the $H-T$ plane. These cuts include fixed $H$, swept $T$, the source of all previous data, as well as fixed $T$ “stepped” $H$. The two directions through the $H-T$ plane provide a sort of quasi-independent perspective on the problem. The data, shown in fig. 5.24, requires the same subtractions as the data taken at fixed field, but this data from the “field-stepped” run pattern is a posteriori more likely to independently establish the form of $\Delta C(H)/T$ versus $H$ since the subtractions are sourced from determinations versus $T$. This is a subtle point that, in ideal experimental circumstances is untrue. To see the reasons for it one must be aware that the large subtractions make the system susceptible to small artifacts such as changes in preamplifier temperature that may affect the thermometer resistance measurement. While such an issue is a 0.1% effect on the resistance measurement, and a 1% effect on the bare heat capacity, it might be a 20% effect on $\Delta C_{\text{elec}}(H)/T$. Therefore, by moving more rapidly through the available
range of $H$ with a higher data density (0.25 T steps, for example), the possibility for unaccountable errors drops. Further, if the fixed field and field-stepped data show less than perfect conformity, the discrepancies provide an accurate depiction for what would otherwise be unknown systematic errors. This is evident in fig. 5.24 in the lack of perfect matching between the data from the two different run patterns.

An examination of the cause of such a discrepancy could never be exhaustive, but one telling and notable aspect comes out in the details of the field-stepped run pattern. As the “Experimental Summary” mentions, the cuprate samples must not superconduct while $H$ sweeps if the experiment is to survive and maintain repeatability. In order to march the sample through the field regime, one cannot simply fix the sample temperature and change the current in the magnet coil. Instead, the sample must be heated, subjected to sweeping field while resistive, and subsequently cooled to the set-point temperature. A single field-stepped run includes a single set-point temperature, i.e. 1.9 K. The achievement of high data density on the $H$ axis requires many of these warming and cooling cycles; in fact, the sample temperature must change by nearly the value of $T_c$ twice per “final” data point, meaning one averaged value of $C(H, T)$ at some specific point $(H_1, T_1)$. To manage such a feat within a reasonable period of time, the temperature ramping must take place over just a few minutes. The potential for non-equilibrium in the setup and sample is small, but in terms of the final extraction of $\Delta C_{\text{elec}}/T$, small rapidly becomes significant. This fact is manifest in fig. 5.24 (right) in the form of a data point which shows the effect after the sample had remained cold overnight. Its value relative to its neighbors shows the size of possible error. The fact that two other points measured 24 hours apart, one chronologically before and one after the deviated point, but both immediately after warming and cooling by 50 K, show quite precisely the role of thermal history of the system. A repeat of such a process confirms this fact. The further fact that the field-stepped run pattern confirms the conclusions of the fixed-field despite such behaviors is encouraging and quite important for the high-field data.

A final comment on $\alpha$: the most the data might reliably establish is an upper bound, $\alpha < 0.2$ mJ mol$^{-1}$ K$^{-3}$. This is a firm bound, but the exact value is not rigorously established; rather it is the product of an assumption based on experience. This assumption is simply that the magnetic
field should cause the least effect to the temperature dependence of a system which is already temperature independent. Since the YBCO6.47 $\Delta C_{\text{elec}}/T$ in fig. 5.26 appears to have at least the same temperature dependence at all fields, the most likely scenario, and the one precisely portrayed in fig. 5.26 is that there is no temperature dependence at all. This is achieved by a small $\alpha$, one that agrees with zero field fitting, but cannot be claimed by the zero field fit alone. Including sufficiently large values of $\alpha > 0.2$ mJ mol$^{-1}$ K$^{-3}$ forces a large temperature dependence to emerge in $\Delta C_{\text{elec}}/T$ at all finite fields.

![Figure 5.24: (left) Comparison of field-stepped (black) and fixed field (red hollow triangles) $\Delta C_{\text{elec}}/T$ at 1.9 K plotted versus $H$; the 1 T and 2 T points (red solid triangles) are estimated by extrapolation (see fig. 5.26). The agreement is mostly within error bar, but a few significant deviations are visible. The red dashed line depicts $0.6\sqrt{H}$. (right) The same field-stepped data as (left), now compared to a single final data point (marked with orange x) taken after the sample temperature and field remained constant for 24 hours. The difference between the x’ed point at 5 T and the points within the main curve is $< 1\%$ of the total heat capacity, but 10% of $\Delta C_{\text{elec}}(H)/T$. Sample mass for all data is 3.92 mg.]

**5.5.4 YBCO6.47 High-field Results**

For these higher fields, the removal of $C_{\text{nuc}}$ involves some reasonable complications, but remains constrained by the relation $C_{\text{nuc}}(H)/T \sim T^{-3}$. Each $\Delta C(H,T)/T$ versus $T$ curve above 4 T shows a visible $C_{\text{nuc}}/T$ as a line when plotted versus $T^{-3}$. Because of the complicated NMR results, there is no particular reason to expect $C_{\text{nuc}}(H)/T \sim H^2$ as in the simplest case of a collection of free
(Zeeman split) nuclei. Instead, the constraint of $\sim H^2$ is relaxed to any second order polynomial and the $H \to 0$ Knight shift from NMR is used as a justification for a finite $H = 0$ intercept (see fig. 5.25). Secondly, the negligible values of $C_{\text{nuc}}(T > 3\text{K})/T$ at all fields measured guarantees a significant portion of the data is immune to any mistreatment of the $C_{\text{nuc}}$ subtraction.

![Figure 5.25: (right) $\Delta C/T$ versus $T^{-3}$ at 33 T (black circles) to characterize $C_{\text{nuc}}/T$. The slope of the linear fit (red line) gives the coefficient $K(H)$ where $C_{\text{nuc}}/T \approx K(H)/T^{-3}$ for $k_B T \gg 2g\mu_N H$. (right) High field dependence of of $K(H)$ (black squares) with a second order polynomial fit (red curve).](image)

The SL scaling plot of fig. 5.22 demonstrates that temperature independence of $\Delta C_{\text{elec}}/T$ up to 12 T, such that any plot versus $H$ at fixed $T$ should provide essentially the same information. As $H$ approaches the resistive transition $H_R(T)$ that the $T$ dependence may evolve as the Volovik effect breaks down on approach to $H_{c2}$, where the vortices begin to “overlap.” In fact, fig. 5.26 shows this is not the case. The $\Delta C_{\text{elec}}(H, T)/T$ includes no obvious breaks or changes above $H_R(T)$, which ref. [51] determines via resistivity measurements. To reiterate, the definition of the “electronic” specific heat is $\Delta C_{\text{elec}}(H, T)/T \equiv C/T - \gamma(0) - \beta T^2 - \beta_5 T^4 - (C_{\text{Sch}} + C_{\text{nuc}})/T$. The data in fig. 5.24 is essentially the same but requires no $C_{\text{nuc}}/T$ subtraction because it is negligible for the $H/T$ range included.

The temperature independence of $\Delta C_{\text{elec}}(H, T)/T$ can be interpreted in terms of the Sommerfeld expansion to conclude that the zero temperature limit must be more or less valid. In some sense,
Figure 5.26: $\Delta C_{\text{elec}}(H,T)/T$ versus $T$ at various values of $H$. Data for $H \leq 15$ T are from measurements in the (Oxford) superconducting magnet (SCM), and data for $H \geq 15$ T are from measurements utilizing a resistive magnet (res mag). $\Delta C_{\text{elec}}(H,T)/T$ increases nearly monotonically with field, but is essentially temperature independent. (* and **) The 1 T and 2 T data have substantial remaining temperature dependence because $C_{\text{Sch}}/T$ has an effectively field dependent $g$ below 3 T, which must occur for a finite $C_{\text{Sch}}(H = 0)/T$ as seen in fig. 5.19. *ad hoc* subtraction with arbitrary $g$ succeeds in removing the excess, but using fixed $g$ provides an honest demonstration of the power of the subtraction procedure. The red dashed line is an estimate of $H_R(T)$. [51] Sample mass for all data is 3.92 mg

this puts a lot of weight on the correctness of the subtraction procedure. As tempting as it may be to claim such a thing, the more reasonable assertion is that the particulars of the temperature dependence do not change with $H$. This is all the more likely given that the only field-dependence included in the subtraction procedure is well-defined within $C_{\text{Sch}}$ and reasonably constrained within the relatively unimportant $C_{\text{nuc}}/T$. This claim of unvarying temperature dependence becomes all
the more striking in light of the data feature visible in fig. 5.27, showing $\Delta C_{\text{elec}}(H, T)/T$ versus $H$ from 0 to 34.5 T. This feature appears to be an inflection point, with $\Delta C_{\text{elec}}(H)/T$ changing from negative to positive $\frac{\partial^2 C}{\partial H^2}$ before asymptoting to approximate linearity. The positive curvature asymptotes into a form quite nearly linear over a range of about 15 T, from 20 to 34.5 T, the maximum field measured.

![Graph](image)

Figure 5.27: $\Delta C_{\text{elec}}(H, T)/T$ versus $H$ from field-stepped run pattern. Data for $H \leq 15$ T was measured in a superconducting magnet (SCM), and data for $H \geq 10$ T was measured utilizing a resistive magnet (res mag). $\Delta C_{\text{elec}}(H, T)/T$ increases nearly monotonically with field, following a square root (green curve) before inflecting and finally saturating to follow a line (green line). While the subtraction of $C_{\text{nuc}}/T$ is significant, it is much less than $\Delta C_{\text{elec}}(H, T)/T$ for all data shown. Sample mass for all data is 3.92 mg.

As “Theoretical Background” discusses in part, a linear field dependence is a result of Zeeman splitting of the d-wave BdG quasiparticles (qps). Whether or not this is the explanation here,
this motivates a replotting (fig. 5.28) that separates Volovik scaling, entering as a constant, from Zeeman scaling, which enters as a sloped line. For constant $T$, SL scaling, which is simply the Volovik effect, manifests as a constant; Zeeman scaling shows up as a line of finite slope (and possibly finite intercept). In this particular case, $\Delta C_{\text{elec}}(H)/T$ is $T$-independent and so all data will fall on a single curve, within scatter. A point of interest is the initial deviation from the $H^{1/2}$ form established by fig. 5.24; this point is called $H' = 10\, \text{T}$ for the remaining discussion. The deviation for $H > H'$ is visible for measurements on both the full sample mass (5.98 mg, fig. 5.22 right panel) and with a smaller portion of sample (3.92 mg, fig. 5.27, e.g.) However, it only becomes clear through a combination of dynamic range and resolution, the latter in large part due to the field-stepped point density.

![Figure 5.28: $\Delta C_{\text{elec}}/(TH^{1/2})$ versus $H^{1/2}$ from field-stepped run pattern. The color scheme is the same as fig. 5.27. The plot shows in stark terms the horizontal line consistent with Volovik scaling and the sloped line again follows $\Delta C_{\text{elec}}/T \propto H$. Sample mass for all data is 3.92 mg.](image)

Much of the lead up to this point of the discussion contains a motif of the fragility of the data and the struggle to produce and confirm robust results. For example, even within this section thermal cycling clearly produces dramatic effects. Yet, the three different sets of data in fig. 5.27,
represented by three different colors, each come from a fully distinct experimental time, separated by a warm-up and cool-down through room temperature as well as reconnection of instrumentation. While each one of these data sets utilizes its own zero-field subtraction ($\gamma(0)$, $\beta$, and $\beta_5$), they all use the same $C_{Sch}/T$ parameters as derived from the low field. Indeed, there are clear discrepancies outside of the simple statistical error bars. However, such discrepancies do not significantly cloud the features and even the functional form of $\Delta C_{elec}(H,T)/T$. Any such discrepancies are on full display as all redundant points from the various experimental times and modes in fig. 5.29.

Figure 5.29: $\Delta C_{elec}(H,T)/T$ versus $H$ comparison of redundant $(H, T)$ points from field-stepped and fixed field run patterns. The green line and $0.6\sqrt{H}$ curves are again guides to the eye. Sample mass for all data is 3.92 mg

Such repeatability, density, and resolution of data firmly establishes the essential features of the data. Because of the appearance of the linear region, the next natural question is the level to which Zeeman is responsible for such a phenomenon. Since the orbital effects are 2D phenomenon confined to the CuO$_2$ planes, a rotation of said planes to remove this effect removes such a complication and leaves Zeeman to drive the action at reasonably low field. Unfortunately, any additional experimental variables (in this case angle between the sample c-axis and $\vec{H}$) have the potential to
complicate as much as clarify. Both the present study and previous works[43] show an apparently negative $\Delta C_{\text{elec}}(H > 0, T)/T$. Fig. 5.30 shows fixed-field $\Delta C(H = 8 \, \text{T}, T)/T$ with $\vec{H} \perp$ to the crystal’s c-axis within about 20 degrees. The shape of the bump-like anomaly is qualitatively inconsistent with $C_{\text{Sch}}/T$, or any finite level system. There is no simple explanation for the form and assuming that the parameter $g$ from $C_{\text{Sch}}$ is isotropic yields no insight. Essentially, these “field-in-plane” measurements do not clarify, and it is further unclear whether the misalignment of the field with respect to the crystallographic axes plays any role. As such, no explanation of the field-in-plane data is forthcoming in the present study.

5.6 Further Discussion

Above, the points are mainly pertaining to the details of the data or well-accepted physics such as the Volovik effect/SL scaling and Zeeman effect. However, to put the present study into context, primarily with regard to YBCO6.47, some more speculative exploration is in order. Indeed, the question of the source of the linear-in-$H$ form of $\Delta C_{\text{elec}}(H, T)/T$ still remains. In the following, a summary of the implications of the data above ties the literature survey to the present study. Some of this includes a reiteration of the points above, but the main focus regards the complex story of the YBCO6.47 data as the outstanding message of this work.

The main story of the Hg1201 features two divergent parts: the lack of consistency between samples and the apparent saturation of $\Delta C_{\text{elec}}(H, T)/T$ versus $H$ above 30 T. Though different materials, the comparison between YBCO6.56 and Hg1201 strikes a few controversial points. The biggest contrast is that the resistive, LK state of Hg1201[9] shows the $\Delta C_{\text{elec}}(H, T)/T$ behavior naively expected (said saturation in the resistive state), while YBCO6.56, as published, shows a continuing square root of $H$ form in the LK region. Some comments on the source of YBCO ortho-II results claim the Cu-O chain layers make YBCO unique from many other cuprates; Hg1201 has no chains and thus makes the comparison all the more interesting. The chain layer is certainly not an explanation for the continuing d-wave form in fig. 5.16, but could house some confounding phenomena. One may speculate that the simpler structure of Hg1201 lends more clarity and thus
Figure 5.30: $\Delta C/T$ versus $T$ at 6 T with the field-in-plane ($\vec{H} \perp$ c-axis). The red curve is a free fit to $C_{Sch}/T$ and the green curve is a guide to the eye using $g=2.0$ and $n_S=.0032$ as determined by the $\vec{H}||$c-axis data set. Sample mass for all data is 3.92 mg

rules out the chains complication as a source of a Fermi liquid component. The question is whether the Hg1201 results do in practice clarify the picture given the “poor” sample repeatability. For example, the ease of drawing comparisons between the superconductivity between two different cuprates even for ideally pure samples is questionable. A lack of independent confirmation of the SdH oscillations for Hg1201 at the time of writing makes any immediate broad conclusions premature at best. The $\Delta C_{\text{elec}}(H,T)/T$ results must simply stand on their own and leave little more than confusion and an additional piece of the puzzle sitting on the table.

Returning to the YBCO front, beginning with $H = 0$, the effect of doping appears minimal between O6.56, 6.51, and 6.47 ($p=0.105, 0.095, \text{and } 0.085$.) This changes little for $H > 0$, where, within experimental/analytical error, the field dependence below 10 T appears nearly identical, except for the growth by 50% of the $n_s$ parameter. In light of the differences between refs.[43] and [52] it is possible that oxygen vacancies are acting to add paramagnetic impurities to the sample.

The implication of the $A_c$ is that $v_\Delta$ is doping independent within about 30%. This result is qualitatively and quantitatively consistent with some of the most recent ARPES on BSSCO, 0.1-
0.15 eV Å (see “Literature Survey”).[73, 71] By extension, these results require an essentially doping independent d-wave superconducting gap, a quite interesting fact in its own right given that the “strongly correlated” label of the cuprates implies that charge carrier density may play a significant role. The importance of this finding is, in part, drawing the similarity between one cuprate, BSSCO, desirable for its surface properties but maligned for its bulk disorder, and another, YBCO, for which the transpose is true.[42] Further, the determination of a set of universal properties within the hole-doped HTS cuprates is very likely to produce clues into the mechanisms of superconductivity in these materials.

On the other hand, the diversity of the cuprate phase diagram contributes to much of the interest in these materials. That theme features prominently in the following discussion of the high $H > H'$ portion of the YBCO6.47 data. Before this can be seen, however, the simplest explanations must prove untenable.

The first of these is a simple suppression of superconductivity by $H$ such that the coherence length approaches the magnetic length. Any hard look at the data reveals that such a scenario does not offer such a simple explanation. The notion that premises this simplicity is that all superconductors lose coherence and become “normal” at sufficiently high fields, such that the normal density of states must be recovered as well. Fig. 5.26 shows that almost the entire data set, and certainly all of the field-stepped data, are within the zero resistance regime. This fact by itself is not as telling as the completely uniform temperature dependence, viz. $\Delta C_{\text{elec}}/T$ is nominally $T$-independent for all $H$. Considering that superconductivity must weaken with increasing $H$ more rapidly at higher temperatures, both the position of $H'$ far below the resistive transition and the $T$-independence seems at odds with any understanding of classical phase transitions. If the Volovik explanation is correct for $H > H'$, then one can extract a $v_\Delta(H > H')$ by assuming that such an explanation continues to be correct but a changing superconducting gap gives rise to an additional field dependence. Solving eq. 4.24 $C/T = K \frac{\sqrt{H}}{v_\Delta}$ for $v_\Delta$ (where all $K$ combines all constants) yields

$$v_\Delta(H) = \frac{\sqrt{H}}{C/T} \eta$$ \hspace{1cm} (5.1)
Eq. 5.1 is plotted for the YBCO6.47 data in fig. 5.31. If this plot is physically accurate, it implies that the superconducting gap suddenly decreases at \( H' \) at a rapid rate and subsequently takes on the form \( \Delta_k(H) \approx (1/2) \frac{n}{0.17 \sqrt{H}} \) where the factor 0.17 mJ mol\(^{-1}\) K\(^2\) T\(^{-1}\) is determined by the linear slope of \( \Delta C_{\text{elec}}(H)/T \). This form has a positive curvature, \( \frac{d^2 \Delta_k}{dH^2} \), in contrast to the negative curvature that a mean-field gap exhibits. In fact, a mean-field-like gap suppression must produce the most rapid change where the gap vanishes. Since the data does not suggest a vanishing \( \nu_\Delta \) within the range of measurement, the way in which the gap actually dies must remain a mystery. The most straightforward choices are that a negative curvature eventually sets in or that the gap versus \( H \) function remains “long-tailed” following a weak inverse power law and dies very gradually. The former choice seems particularly odd for a case with a single tuning parameter, requiring the effect of \( H \) to be sudden at \( H' \), followed by a softening of the suppression up to 35 T, with a final rollover as the gap vanishes. Such a non-monotonic curvature strikes the author as altogether impossible in such a case. The latter scenario of vanishing gap seems more reasonable, though still altogether unexpected. In any case, there is no physical scenario to produce a sudden onset of gap suppression with subsequent long-tailed further suppression as magnetic field is increased.

In light of the abrupt changes in both the data and the calculated \( \nu_\Delta \), any successful understanding must incorporate some kind of crossover in place of a single regime of physical parameters tuned by magnetic field. As shown in “Theoretical Background,” the Zeeman effect gives a linear-in-\( H \) DOS the eventually overtakes the orbital effect, completely neutralizing it at high field. The result is a relatively small crossover window with \( \sqrt{H} \) behavior below and linear behavior above. The details of the size of the crossover region, as well as the behavior of DOS within this region are beyond the scope of this work. Instead, working backwards from the assumption that the two behaviors are Zeeman and orbital physics, one may appreciate the merits of such a picture without much calculation.

In order to include the Zeeman splitting in the discussion, a note that the value of the parameter \( \nu_F \) cannot be directly determined by the specific heat, but comes in the form of a product \( \frac{g}{\nu_\Delta \nu_F} \) where \( g \) is that of the BdG qps. \( \Delta C_{\text{elec}}(H)/T \) can determine \( \nu_\Delta \) with justifiable assumptions, but this still leaves the quotient \( g/\nu_F \) as a single parameter. Electron magnetic resonance (EMR)
Figure 5.31: \( v_\Delta(H) \) as determined by eq. 5.1. The units are nominally \( 10^4 \) m/s.

measurements very precisely measure \( g \) factors and can provide further perspective in the determination of \( v_F \). None of the literature suggests a measurable field dependence of the BdG \( g \)-factor, however, the minimal literature on YBCO6.47 leaves much to the imagination, meaning that very little can be ruled out. For the sake of the following discussion, the \( g \)-factor is assumed constant with a value of 2, which is consistent with the literature.[41]

Using eq. 4.25, the slope 0.17 mJ mol\(^{-1}\) K\(^2\) T\(^{-1}\) gives \( v_F = 1.8 \times 10^4 \) m/s. This compares quite unfavorably to \( v_\Delta = 2.4 \times 10^4 \) m/s in the sense that the Volovik treatment requires \( v_F \gg v_\Delta \).[71, 33] Instead, some assumptions must be wrong, or \( g/v_F \) must depend oddly on \( H \). Further, the Zeeman portion of the \( \Delta C_{elc}(H)/T \) extrapolates back to the origin. This is an expectation of the simplest semi-classical picture, with Zeeman abruptly taking over from the orbital effect such that the Zeeman and Volovik regions do not know anything about the other. Nonetheless, that simple picture cannot stem the shortcoming the violation of \( v_F \gg v_\Delta \).

So, again, in order to find a reasonably simple explanation, more complication is necessary,
this time in terms of the influence of a phase boundary, whether as a sharp crossover or an actual phase transition. Fortunately, the complexity of the present phase diagram of YBCO seems to give ample opportunity to find an appropriate phase. Unfortunately, there are no other measurements in this region of the $H-T-p$ phase diagram, nor do measurements at higher and lower dopings suggest a decent explanation. For example, in the resistive state near $H=55$ T and $T = 1.5$ K, strong indications of a metal to insulator transition very near YBCO6.47 exist in the form of a sign change in $\frac{d\rho}{dT}$ versus $p$ and the vanishing of SdH oscillations that may indicate a diverging cyclotron effective mass $m^* \rightarrow \infty$. As stated above, if $m^*$ is in fact greatly enhanced to the level of the SdH interpretations for this sample, but $v_\Delta$ is much less sensitive to doping, this ensures a much larger $\alpha$ than for nearby dopings. The Zeeman slope is intimately connected to $\alpha$, as the Zeeman energy scale is analogous to the thermal scale that gives rise to $C/T \sim \alpha T$. Again, assuming a field-independent g-factor, the measured slope 0.17 mJ mol$^{-1}$ K$^2$ T$^{-1}$ implies $\alpha \approx 0.4$ mJ mol$^{-1}$ K$^{-3}$. This value is quite large and given that it must only exist for $H \rightarrow 0$ in the clean limit, including it would require a field-dependent phonon term as well, that just happens to result in parallel traces of $C/T$ versus $T^2$ at $H = 0$ and 34.5 T in YBCO6.47, as well as for 0T and 45 T in YBCO6.56. Given these constraints, the strict upper bound on $\alpha$ from the temperature dependence is $\alpha < 0.2$ mJ mol$^{-1}$ K$^{-3}$, at least a factor of 2 too low to match the Zeeman slope. This inconsistency suggests a caveat to the mass enhancement scenario: the enhancement is field-induced.

Otherwise, somewhat comparably, the constraint of field independence on the g-factor may be relaxed. However, the invocation of an extra field dependence in the g-factor requires the Zeeman effect to play a major role. The main reasons to consider the Zeeman effect are (1) it is irrevocably a part of any system of charged, spinful particles in a magnetic field (2) it explains, without any further complications, $\Delta C_{\text{elec}}(H)/T \sim H$. At the point where extra field dependence is included, such simplicity breaks down. Including Zeeman in a phase transition/crossover scenario maintains some simplicity if there is a transition region and then an asymptotic form such that for much of the $H$ range, $\Delta C_{\text{elec}}(H)/T \sim H$ while all relevant parameters are essentially fixed.

The current phase diagram (fig. 5.18) of YBCO suggests a virtual melee of phases that are relevant to $H$ tuning. The most tempting comparison is to the NMR sourced claims of “field-
induced charge order,"[82] but x-ray measurements utilizing sharp time resolution claim the onset and boundaries of this order are far from well-defined.[27] Perhaps the most immediate disqualification of charge order origins comes from the many indications from the cited NMR and x-ray measurements that fig. 5.16(right panel) is deep within the charge ordered phase yet lacks any demarcation within the data similar to $H'$. Turning to lower dopings, a suggestion of an $H$ dependent Lifshitz transition[48] provides another possible connection. In this case the boundary follows a non-monotonic curve in the $H$-p plane, all within the present region of interest near O6.47. Unfortunately, the scenario of ref. [48] requires the multiple Fermi pockets picture that does not fit with the current experimental landscape, especially the high-field specific heat,[54] given eq. 4.6.

![Figure 5.32: Comparison of $\gamma(H) - \gamma(0)$ for YBCO6.56 (purple dots) with guide to the eye following $0.47\sqrt{H}$ (purple curve)[54] and $\Delta C_{\text{elec}}(H)/T$ for YBCO6.47 (present study, red points) versus $H$. The green line and curve are the same guides to eye as fig. 5.27 and represent $0.6\sqrt{H}$ and 0.17 $H$. The two y-axes are essentially equivalent given the temperature independence of $\Delta C_{\text{elec}}(H)/T$ for YBCO6.47.](image)

To demonstrate this last point, fig. 5.32 shows an overlay of the YBCO6.47 $\Delta C_{\text{elec}}(H)/T$ on top of the analogous $\gamma(H) - \gamma(0)$ for YBCO6.56. Riggs et al and SdH measurements both suggest that $m^* \approx 1.4$ for YBCO6.56[54, 58]. Using eq. 4.6, which requires only 2D Fermi liquid parabolic bands to be applicable, the LK $m^*$ for each sample (assumed to simply be $\gg 1$ for YBCO6.47) rules out

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any scenario including more than one Fermi pocket. This is more difficult to verify for YBCO6.47, for which the superconducting state is robust and there have been no successful measurements of any quantum oscillations. Nonetheless, the clear indication is that the YBCO6.47 $g(\epsilon_F)$ is at least twice that for the resistive state of YBCO6.56, consistent with an enhancing high-field mass.

Without a clear connection to prior studies, it stands out as a reasonable possibility that the physics behind $H'$ may not be a simple corollary to a known mechanism but as something all together new. This possibility deserves proper consideration, but is well outside the scope of this study. Instead, the answer is left open including the question of the relevance of the Zeeman effect and the precise nature of the order or phase at play.
APPENDIX A

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[1] Mun Chan, Univ. of Minn., private communication.


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Jonathon Kemper attended high school near Chicago, Illinois. He completed a Bachelor of Science degree from Tulane University in 2005, followed by brief graduate work at the University of Alabama in Huntsville while working at NASA Marshall Space Flight Center as a research assistant in aerospace propulsion research. He left Alabama to pursue a doctorate in physics at Florida State University.