Thermodynamics of the Magnetic-Field-Induced "Normal" State in an Underdoped High T$_c$ Superconductor

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THERMODYNAMICS OF THE MAGNETIC-FIELD-INDUCED “NORMAL” STATE IN AN UNDERDOPED HIGH $T_C$ SUPERCONDUCTOR

By

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ABSTRACT

High magnetic fields are used to kill superconductivity and probe what happens to system when it cannot reach the ideal ground state, i.e. what is the normal-state ground state? Early work in High-$T_c$, where the application of magnetic field destroyed the zero resistance state and recovered a resistivity value that connected continuously with the zero field curve, lead people to believe this magnetic-field-induced-state had fully driven the system normal, revealing the true underlying ground state, without any vestige of superconductivity. Many experiments done in this region of phase space have results interpreted as coming from the low energy ground state excitations. With the emergence of ultra-clean crystals in a unique family of hole doped high-$T_c$ superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, YBCO, a new and highly unexpected phenomena of quantum oscillations were discovered, and they followed the standard Lifshitz-Kosevich (LK) theory for a normal metal. The results suddenly made the problem of high-$T_c$ appear to be analogous to superconductivity in the organics, which is brought about by a wave-vector nesting and Fermi surface reconstruction. The only problem, it appeared, that needed to be reconciled was with Angle Resolved Photo-Emission Spectroscopy (ARPES) and Scanning Tunneling Microscopy (STM) data that claimed to see no such Fermi surface, instead only “arcs”, a set of disconnected segments in the Brillouin zone which quasiparticle peaks are observed at the Fermi energy, which in a mean field description does not allow for a continuous Fermi surface contour. These two discrepancies led to the “arc vs pocket” debate, which is still unresolved. The other kink in the quantum oscillation armor is that, to this date, quantum oscillations in the hole-doped cuprates have only been seen in YBCO, the only cuprate structure to have CuO chains, which conduct and are located in between two CuO$_2$ superconducting planes in the unit cell.
In an attempt to reconcile the “arc vs pocket” debate we measure specific heat on an ultra-clean de-twinned single crystal of underdoped YBCO 6.56 with a $T_c = 60$ K, up to fields twice irreversibility field, define as the onset of the resistive transition. The zero temperature extrapolation of the electronic contribution to the specific heat, $\gamma$, is the total quasiparticle density of states. For a two-dimensional system with parabolic energy bands, $\gamma$ is simply the sum of each pocket multiplied by its effective mass. Therefore, by determining gamma at high fields and using previously determined values for the effective mass from quantum oscillation transport measurements we can simply play a counting game to determine the number of pockets in the Fermi surface. Furthermore, at low fields the response to the specific heat as a function of magnetic field in a d-wave superconductor is known to have a $\sqrt{H}$ dependence, and we can look for deviations from this $\sqrt{H}$, which are expected to happen when the system is no longer in a superconducting state.

Results from our specific heat experiment shed new light on the true nature of the magnetic field induced “normal” state, and should force reinterpretation of many experimental findings. The specific heat measurements foremost show a smooth evolution of gamma from low to high magnetic fields which follows a $A_c\sqrt{H}$ dependence, with the prefactor, $A_c$, giving the correct magnitude for the anisotropy of the d-wave superconducting gap. This means with the application of magnetic fields strong enough to restore the resistive state, the superconducting gap still exits. Additionally, we see quantum oscillations that follow conventional LK formalism and can determine an effective mass uniquely, where no fitting parameters are required. Interestingly, these oscillations fit on top of the $\sqrt{H}$ finding. How can the $\sqrt{H}$ and quantum oscillation whose phenomena arise from very different physics be reconciled? Looking at our own zero field $\gamma$ value of 1.85 $mJ \, mol^{-1} \, K^{-2}$, which is intrinsic for YBCO, allows the pocket counting game to begin. Coupling bandstructure calculations, angle dependent quantum oscillation measurements, which determine the shape of the pocket, with the zero field $\gamma$ value leads to the simplest interpretation; quantum oscillatory phenomena is a manifestation of the CuO chain and BaO insulating layer orbital hybridization band and is likely not relevant to high temperature superconductivity.
CHAPTER 1
INTRODUCTION

“There are no more motivated people on the planet than surfers. We fall down a lot. We turn around, paddle back out, and do it all over again. Unlike anything else in life, the stoke of surfing is so high that the failures quickly fade from memory.”

-Gary Sirota (surfer)

1.1 Motivation

Superconductivity is the property of a material where resistance does not impede the flow of an applied current. In the Bardeen-Cooper-Schrieffer (BCS) model for superconductivity, this unique dissipation-less state arises from an electron-phonon interaction. The success of the BCS model, with a simple analytically solvable wavefunction the result was heralded as “The Theory of Superconductivity” [1]. Then in 1986 Muller and Bednorz discovered a family of superconductors with a $T_c$ greater than the liquefying point of nitrogen [2] [3] [4]. It was quickly discovered that superconductivity in this new class of materials, the cuprates-so called as they all contain CuO planes-was not electron-phonon mediated [5]. Some 25 years after the discovery of the cuprates, very little is understood about the nature of High-$T_c$ superconductivity.

The following is understood: the parent compounds of all cuprates, or high temperature superconductors, are antiferromagnetic Mott insulators. As holes are doped into the CuO$_2$ plane the Cu $d_{x^2-y^2}$ orbital is no longer exactly half filled, weakening the anti-ferromagnetic state, which gives way to the enigmatic pseudo-gap state [5]. Further introduction of holes
eventually leads to superconductivity at roughly 0.06 holes per copper atom. Maximum superconductivity happens around 0.16 holes per copper atom. Superconductivity disappears around 0.30 holes per copper atom and the system takes on the behavior of an ordinary metal. Doping below optimal doping is referred to as the underdoped regime, while doping above 0.16 is called the overdoped regime. Therefore, the number of holes per copper atom is the single most important tuning parameter, as it determines the properties of high-temperature superconductivity, HTS [6]. Figure 1.1 shows the typical schematic generalized phase diagram for the HTS.

YBCO is the easiest cuprate to create low disorder samples of, as it has a well-defined metal ion stochiometry, doping is controlled by oxygen content—which can be changed on the same sample, and large mass de-twinned single crystals are easy to grow [7]. With the development of ultra-clean YBCO single crystals this family of cuprates has garnered the most attention with regard to fundamental studies in high magnetic fields [6][8].

Perhaps the biggest obstacle in understanding the low temperature properties of the cuprates in the superconducting doping range is superconductivity itself, which effectively conceals the normal state at low temperatures. Measurements are made in a magnetic field-temperature phase space in which superconductivity can be suppressed. The resistive state at 1.5K is reached with fields of 25T. Thus, measurements at 1.5K in the 45T Hybrid magnet reach nearly twice the resistive transition at $H_{irr} = 25T$. The application of high fields and low temperatures, therefore, allows the underlying resistive state to be examined.

A prime motivation for the investigation of the magnetic-field-induced resistive state heat capacity in YBa$_2$Cu$_3$O$_{6-\delta}$ is the recent mapping of the Fermi surface topology from quantum oscillations in these high-temperature superconductors. A study of the electronic heat capacity $\gamma$ in high-temperature superconductors is challenging, given that the very high fields required to suppress superconductivity are only available in experimental conditions fraught with signal to noise problems. However, measuring of $\gamma$ is key to understanding whether the Fermi surface in its entirety has been uncovered by quantum oscillation measurements. Implications are widespread, and could potentially determine whether a Fermi
Figure 1.1: A schematic Temperature-Doping phase diagram for the cuprates [9]. For the parent compound the system is an AF insulator with an onset temperature of $T_N$. The dashed $T^*$ line represents the pseudo-gap phase and with optimal doping establishes the underdoped from overdoped regimes. The yellow dome represents the region in phase space where superconductivity occurs with the transition temperature labeled labeled $T_c$.

Surface reconstruction underlies the normal state in the underdoped regime of High-$T_c$ materials. Recent quantum oscillation measurements of a new thermodynamically dominant frequency in YBa$_2$Cu$_3$O$_{6.5}$ have claimed to reveal the complete normal-state Fermi surface in the YBCO high-$T_c$ material [60]. $\gamma$ measured in high magnetic fields would make the claim of a Fermi surface reconstruction completely definitive; in fact, it would perhaps secure the quantum oscillation discovery as one of the most important cuprate discoveries of the decade. $\gamma$ at high fields provides a comparison of the thermodynamic contribution of the observed Fermi surface pockets in YBa$_2$Cu$_3$O$_{6-\delta}$ with the linear temperature coefficient of specific heat. Resolution of this problem will prove critical to an understanding of the normal state in the entire family of high-$T_c$ superconductors.

The common interpretation from quantum oscillations in transport measurements is that, at low doping, the application of magnetic field destroys the d-wave superconducting
gap to uncover the Fermi surface of the competing state, that behaves like a conventional (i.e. Fermi Liquid) metal [9]. The competing viewpoint is that an applied magnetic field destroys long range phase coherence but the superconducting gap amplitude survives. Specific heat measurements on YBCO 6.56 determine the evolution of the quasiparticle density of states from the superconducting state well into the magnetic-field-induced-resistive state [10] [11]. At very high magnetic fields the specific heat exhibits both the conventional temperature dependence and quantum oscillations expected for a Fermi Liquid, and a magnetic field dependence that follows a $\sqrt{H}$. The $\sqrt{H}$ behavior persists right through the zero resistance transition, evidencing a fully developed d-wave superconducting gap over the entire measured magnetic field range.
“You can’t always get what you want, but if you try sometimes, you might just find, you [can extract] what you need”

- The Rolling Stones

There are six contributions to the heat capacity in a cuprate superconductor:

\[ C = C_{\text{electronic}} + C_{\text{phonon}} + C_{\text{Schottky}} + C_{\text{hyp}} + C_{d\text{-wave}} + C_{\text{vortex}} \]  

In this chapter we determine their nature, temperature and magnetic field dependence, followed by a functional form which can be used to subtract out each contribution.

2.1 Phonon contributions to the specific heat in a Fermi liquid

The \( T^3 \) specific heat law for a three-dimensional crystal can be calculated using the Debye model by starting with a linear dispersion relation, \( \omega = v_{\phi}k \) and constraining the total number of allowed phonon modes to \( 3Nl \), where \( N \) is the number of primitive unit cells, \( l \) describes the total number of atoms in the unit cell and \( v_{\phi} \) is the speed of sound. Now integrate over all possible frequencies \( \omega_D \):

\[ 3Nl = \int_{0}^{\omega_D} g(\omega)d\omega. \]
Applying the normal three dimensional density of states relation \( g(\omega) = A\omega^2 \), where \( A \) is a constant, \( \omega = v_\phi k \), and \( v_\phi \) is the speed of sound

\[
3Nl = \int_0^{\omega_D} A\omega^2 d\omega = \frac{A}{3} \omega_D^3 \Rightarrow A = \frac{9Nl}{\omega_D^3}.
\]  

(2.3)

Plugging in for \( A \) generates a density of states of

\[
g(\omega) = \frac{9Nl\omega^2}{\omega_D^3}
\]  

(2.4)

The total energy can now be calculated by integrating over the energy contribution due to each mode \( \hbar\omega \), from the density of states energy dispersion relation in the Bose-Einstein statistics framework.

\[
U = \int_0^{\omega_D} \hbar\omega g(\omega) \frac{1}{\frac{\hbar\omega}{k_BT} - 1} = \int_0^{\omega_D} \hbar\omega \frac{9n_l\omega^2}{\omega_D^3} \frac{1}{\frac{\hbar\omega}{k_BT} - 1}
\]  

(2.5)

taking the derivative in order to obtain specific heat

\[
C = \frac{dU}{dT} = \frac{9Nl\hbar^2}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^4}{k_BT^2} \frac{\frac{\hbar\omega}{k_BT}}{\frac{\hbar\omega}{k_BT} - 1} d\omega.
\]  

(2.6)

Making a straight forward substitution \( x = \frac{\hbar\omega}{k_BT} \) and \( \Theta_D = \frac{\hbar\omega_D}{k_BT} \) we have

\[
9Nl k_b \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.
\]  

(2.7)

So when \( \Theta_D \) is large (low temperature) the integral simplifies to

\[
C = \frac{12\pi^4 Nl k_b}{5} \left( \frac{T}{\Theta_D} \right)^3
\]  

(2.8)

giving again a \( T^3 \) phonon contribution to the specific heat.

2.2 Electronic contribution to the heat capacity in a Fermi liquid

The rigorous derivation for the Sommerfeld expansion determination of the electronic heat capacity in metals is readily available in any condensed matter textbook [12, 13].
goal for this section is to intuitively explain the physical origin of the electronic contribution to the heat capacity. Therefore, we start with the following assumptions:

1. The electron density is constant. Meaning $\epsilon_F$ is independent of temperature. (This is a central assumption of the Sommerfeld model).

2. The electron dispersion curve assumes parabolic energy bands, $\epsilon(k) = \frac{\hbar^2 k^2}{2m^*}$, which is reasonable unless $\epsilon_F$ is near $\frac{1}{2}$ filling, (i.e. near the Van Hove singularity).

3. Only electrons within $k_B T$ of the Fermi energy, $\epsilon_F$ take part in thermal processes.

From assumption two, it is possible to determine the electronic states within a particular energy range. As charge carriers are added, they fill the lowest energy states first followed by the next available lowest energy state and so on until all $N$ electrons are piled in. The total volume of electron energies in k-space is a sphere such that [13]

$$n = \frac{N}{V} = 2\left(\frac{1}{2\pi}\right)^3 \frac{4}{3} k_F^3 = k_F = (3\pi^2 n)^{\frac{1}{3}} \Rightarrow \epsilon_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{\frac{2}{3}}$$

where $\frac{4}{3} \pi k_F^3$ is k-space volume and $2\left(\frac{1}{2\pi}\right)^3$ includes the spin degeneracy and k-space normalization. We can now determine the density of states at the Fermi level

$$\frac{dn}{d\epsilon_F} = g(\epsilon_F) = \frac{3n}{2\epsilon_F}$$

which depends only on the number of electrons per unit volume and the Fermi energy. Now under assumption three the thermal energy of the system takes the form

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

and

$$C_{\text{simple}} = \frac{dU}{dT} = \frac{3nk_B^2 T}{\epsilon_F} \sim C_{\text{Sommerfield}} = nk_B^2 \frac{\pi^2 T}{2\epsilon_F}$$

We have derived rather intuitively, by calculating the density of states about the $T = 0$ ground state energy, the low temperature electronic specific heat, which is linear in temperature, and very close to the result of the full Sommerfeld derivation.
2.3 Schottky anomaly of a two level system

A Schottky anomaly is a contribution to the low energy specific heat arising from thermal excitations of discrete energy levels. There are many physical systems where the low temperature specific heat is readily described in terms of discrete energy levels; orbital or spin degeneracy in magnetic fields, crystalline electric fields, spin orbit coupling, or nuclear hyperfine interactions to name a few [14]. In the simple case of a two level system we can easily calculate the field dependence of the low temperature upturn in the specific heat.

We start by assuming a sample of volume $V$ contains $N$ atoms and any generic two energy levels, namely $E_{+1/2}$ and $E_{-1/2}$. We now write the internal energy per unit volume

$$< u > = \frac{N}{V} \left( \frac{E_{+1/2} e^{-\frac{E_{+1/2}}{k_B T}} + E_{-1/2} e^{-\frac{E_{-1/2}}{k_B T}}}{e^{-\frac{E_{+1/2}}{k_B T}} + e^{-\frac{E_{-1/2}}{k_B T}}} \right) = \frac{N}{V} \left( E_{-1/2} + \frac{\Delta E e^{-\frac{\Delta E}{k_B T}}}{1 + e^{-\frac{\Delta E}{k_B T}}} \right)$$

(2.13)

where $\Delta E = E_{+1/2} - E_{-1/2}$. From here, we simply take the derivative with respect to temperature and find the specific heat

$$C_{\text{Schottky}} = \frac{d < u >}{dT} = \frac{d}{dT} \left( \frac{N}{V} \left( E_{-1/2} + \frac{\Delta E e^{-\frac{\Delta E}{k_B T}}}{1 + e^{-\frac{\Delta E}{k_B T}}} \right) \right) = \left( \frac{N}{V} \right) \left( \frac{\Delta E e^{-\frac{\Delta E}{k_B T}}}{k_B T} \right) e^{-\frac{\Delta E}{k_B T}} \left( 1 + e^{-\frac{\Delta E}{k_B T}} \right)^{-2}$$

(2.14)

2.4 Schottky in relation to the cuprates

In High-Tc cuprate samples there are small concentrations of unpaired spin-1/2 magnetic copper moments associated with defects, chemical impurities, or chemical substitutions that are responsible for a field dependent Schottky anomaly of these residual paramagnetic centers [15, 16]. Since the contribution arises from spin-1/2 Cu moments we have a two level system where the contribution to the energy from the magnetic field term is given by $H_{\text{mag}} = \vec{\mu} \cdot \vec{B} = g \mu_B S_z B_{\text{eff}}$ where $B_{\text{eff}} = \sqrt{B_{\text{internal}}^2 + B_{\text{applied}}^2}$, $g$ is the gyromagnetic ratio, and $g S_z \approx 1.1$ [17]. The system can now be modeled by a simple two level Schottky anomaly [18, 17]. We solve for the Schottky anomaly found in High-Tc’s using the single particle partition function.
Figure 2.1: Schematic of the Schottky contribution to the specific heat in a two level system. In the low temperature limit where $k_BT \ll \Delta E$ the specific heat, $C/N \propto e^{-1/T}$ an exponential activation. In the high temperature regime $k_BT \gg \Delta E$ the specific heat is $C/N \propto \frac{1}{T^2}$, a power law dependence.

\[ Z_1 = \sum_i e^{-\frac{E_i}{k_BT}} = e^{-\frac{gS\mu_B B_{eff}}{k_BT}} + e^{-\frac{gS\mu_B B_{eff}}{k_BT}} \] \hspace{1cm} (2.15)

By normalizing the spin-1/2 energy levels such that the lowest energy level is defined as $E = 0$, we can rewrite the partition function such that $E_{+1/2} = e^{-\frac{gS\mu_B B_{eff}}{k_BT}} \Rightarrow e^0 = 1$ and $E_{-1/2} = e^{-\frac{2gS\mu_B B_{eff}}{k_BT}} \Rightarrow e^{2gS\mu_B B_{eff}}$ yielding the familiar form

\[ Z = (Z_1)^N = \left( \sum_i e^{-\frac{E_i}{k_BT}} \right)^N = (1 + e^{-\frac{2gS\mu_B B_{eff}}{k_BT}})^N \] \hspace{1cm} (2.16)

And can calculate a specific heat from the free energy [15]
\[ C_{\text{magSch}} = -T \frac{\delta^2 F}{\delta T^2} = T \frac{\delta^2}{\delta T^2} N k_B T \ln(Z) = \frac{N \left( \frac{2g_S \mu_B B_{eff}}{k_B T} \right)^2 e^{-\frac{2g_S \mu_B B_{eff}}{k_B T}}}{(1 + e^{-\frac{2g_S \mu_B B_{eff}}{k_B T}})^2} \]

(2.17)

### 2.5 Nuclear Schottky

The magnetic dipole moment of a proton is much smaller than that of an electron because the strength of the moment is inversely proportional to the mass [19]. Therefore only at very low temperatures, i.e. low energies, will the nuclear hyperfine energy level spin splitting contribute to the heat capacity. The copper nucleus has a spin 3/2 and we apply the same method for solving for the heat capacity as in section 2.1.2, only now we have four energy levels instead of two.

\[
Z_1 = \sum_i e^{-\frac{E_i}{k_B T}} = e^{-\frac{g_N \mu_N B_{eff}}{2k_B T}} + e^{-\frac{g_N \mu_N B_{eff}}{2k_B T}} + e^{-\frac{g_N \mu_N B_{eff}}{2k_B T}} + e^{-\frac{g_N \mu_N B_{eff}}{2k_B T}}
\]

(2.18)

where is the \( \mu_N \) is the nuclear magneton and \( g_N \) is the nuclear gyromagentic ratio with the resulting specific heat of the form

\[
C_{\text{nucSch}} = T \frac{\delta^2}{\delta T^2} N k_B \ln(Z) = N \left( \frac{g_N \mu_N B_{eff}}{2k_B T} \right)^2 \left( \text{sech}^2 \left( \frac{g_N \mu_N B_{eff}}{2k_B T} \right) + 4 \text{sech}^2 \left( \frac{g_N \mu_N B_{eff}}{k_B T} \right) \right)
\]

(2.19)

### 2.6 Specific heat of a d-wave superconductor in zero magnetic field

Figure 2.3 shows that for a d-wave superconductor there are line nodes in the superconducting gap function, meaning it is possible to excite quasiparticles at very low temperatures. The electronic excitations near these gap nodes therefore govern the low-energy superconducting properties [22]. The gap nodes give rise to a quasiparticle density of states that rises linearly with energy at \( \epsilon_F \) for \( B = 0 \).
Figure 2.2: The Schottky anomaly for Copper $I = \frac{3}{2}$ nuclear spin at various effective field values. The high temperature regime is still characterized by $\frac{C}{N} \propto \frac{1}{T^2}$ while the low temperature regime is super-exponential because of the extra energy level transitions. The field dependence has two effects; a. spreading out the peak over a wider temperature range and b. moving the peak to higher temperatures.

\begin{equation}
g(E) \sim g_F \left( \frac{E}{T_c} \right)^{2-D}
\end{equation}

where $g_F$ is the normal metal density of states at the Fermi level and $D = 1$ is the dimensionality of the nodes. This leads to

\begin{equation}
C = \frac{d}{dT} T^2 g(E) \sim \frac{d}{dT} T^2 (\alpha T) \sim \alpha T^2.
\end{equation}

The specific heat picks up an $\alpha T^2$ nodal contribution, where $\alpha = \frac{\gamma_N}{T_C}$ and $\gamma_N$ is proportional to the normal-state density of states [22].
Figure 2.3: Top shows the single particle two dimensional Fermi surface for $s^-$ wave (dashed line) and $d_{x^2-y^2}$ symmetry (solid line) in two-dimensions. For $s^-$ wave there is an anisotropic gap in the Fermi surface at $T_C$, in which there are 8 nodes in the energy gap. For $d_{x^2-y^2}$ there are four nodes in the gap leading to a density of states of the form in the top panel. Notice the density of states only at the Fermi Energy is zero and increases linearly until the maximum gap value is reached. Figure taken from [21]

2.7 Specific heat of a d-wave superconductor in the mixed state

In a type II superconductor when the magnetic field is increased to the point where the Meissner effect breaks down, magnetic flux quanta penetrate the sample. When this happens, the density of states at $\epsilon_F$ becomes finite and the $\alpha T^2$ term becomes replaced by excitations both inside and outside the normal vortex core. Circulating around each flux quanta is a super-current. The super-current around a d-wave vortex leads to a small Doppler shift in the energy (because of the change in Fermi velocity) which strongly effects the low energy nodal excitations [23]. Volovik showed that the Doppler shifted energy $(E \rightarrow E + v_s(r) \cdot \hbar k_F)$ where $v_s$ is the super-current velocity around a vortex has important consequences around the nodes, i.e. when the Doppler shifted energy spectrum is comparable to the superconducting gap and leads to a density of states at zero energy with the
form [22]

\[ g(E = 0) \sim g_F \left( \frac{p v_s}{T_c} \right)^{2-D} \sim g_F \left( \frac{H}{H_{c2}} \right)^{1-D} \]  \tag{2.22}

where \( v_s = \frac{\hbar}{m_e R_v} \), and the vortex distance, \( R_v \sim \xi (\frac{H_{c2}}{H})^{\frac{1}{2}} \), where \( \xi \sim \frac{v_F}{T_c} \) is the coherence length. The vortex contribution to the specific heat takes a \( \sqrt{H} \) magnetic field dependence

\[ C = k_B \gamma_N T \left( \frac{H}{H_{c2}} \right)^{\frac{1}{2}} \]  \tag{2.23}

where \( \gamma_N \) is the normal state gamma value.
CHAPTER 3
MEASURING THE FERMI SURFACE VIA
QUANTUM OSCILLATIONS

“There is no limit to the ingenuity of [nature] if it is properly and vigorously applied under conditions of [magnetic field] and [temperature]”
- Winston Churchill

Fermi surfaces reveal the electronic properties of a material. While the Fermi surface can be predicted theoretically by a variety of numerical techniques, it can also be measured experimentally by probing a distinct behavior visible only in high magnetic fields, known as quantum oscillatory phenomena.

3.1 Electrons in a crystal

For a free electron where the dispersion curve, $\epsilon(k)$, is parabolic and continuous, the electron wave function can be written as a series of plane waves [19]. The electron can be defined as a superposition of plane waves, the group velocity with wave-vector $\mathbf{k}$ and energy $\epsilon$ can be written such that

$$\mathbf{v} = \frac{1}{\hbar} \mathbf{\nabla}_k \epsilon. \quad (3.1)$$

Putting the electron into a crystal imposes lattice translational symmetry defined by a set of vectors $\mathbf{T}$, such that the potential is now periodic.
\[ V(r) = 0 \Rightarrow V(r) = V(r + T) = \sum_{G} V_G e^{iG \cdot r}, \] (3.2)

where \( V_G \) are the Fourier components of a set of vectors \( G \) such that \( e^{iG \cdot T} = 1 \). The lattice translational symmetry destroys the parabolic nature of the dispersion curve as gaps appear in the spectrum of allowed energy states, which gives the formation of energy bands, see Figure 3.1 [13] [24]. Any applied external force is now depends on \( k \). To account for the concept of a \( k \)-dependent band an effective mass is introduced that depends only on the curvature of the band

\[ m^* = \hbar^2 \left( \frac{d^2 \epsilon}{dk^2} \right)^{-1}. \] (3.3)

Since \( k \) no longer defines the electron momentum (\( \hbar k \) is no longer an eigenvalue of the momentum operator), but instead the crystal momentum, the electron is now referred to as a quasiparticle as its mass depends on the imposed lattice translational symmetry. In other words, \( k \) is a quantum number describing the quasiparticle’s band state [13].

Figure 3.1: An example of the formation of an energy band when lattice translational symmetry is imposed. The dashed line represents the usual free particle dispersion relation. The solid line represents gaps in the allowed values of \( k \) enforced by the lattice.
3.2 Quantum oscillatory phenomena

A Landau Level’s, (LL) proximity to the Fermi energy is tuned by the applied magnetic field such that at zero temperature a completely filled level occurs when $\epsilon_F = (n + 1)\hbar\omega_c$, where $n$ is an integer. The quantized nature of the density of states has huge implications. The number of available k-states in two-dimensions are now delta functions given by $E_{LL}$. Thus thermodynamic and transport properties increase as step functions when a LL crosses the Fermi energy, see Figure 3.2. The presence of disorder effectively smears the LL, and the measured thermodynamic step function takes on an oscillatory nature. Basically, the delta functions become Lorentzians (or Gaussians, depending on which theorist you ask [25]). Temperature has the effect of smearing out the Fermi-Dirac distribution, playing a similar role as disorder. It should now be easy to understand that if $k_B T > \omega_c$, or if the system has large amounts of disorder the oscillations will be wiped out.

![Figure 3.2](image)

Figure 3.2: shows two Landau level’s separated in energy by the cyclotron energy. The line on top schematically plots the quantum hall phenomena.

From the density of states picture, it is clear how the measurements of quantum oscillatory phenomena can give the Fermi surface area. By applying a magnetic field the LL sweeps outward, and when it crosses the uniform two-dimensional Fermi surface
\[ n \frac{2\pi e B}{\hbar} = A_F, \]  

where \( A_F \) is the Fermi surface area perpendicular to the magnetic field in k-space. Increasing the magnetic field causes lower LL’s to \textit{“pop”} through the Fermi surface with a well defined periodicity:

\[ \Delta \frac{1}{B} = \frac{2\pi e}{\hbar} \frac{1}{A_F}. \]  

Now, plotting the oscillations as a function of \( 1/B \) determines the frequency and the area of the Fermi surface in the first Brillouin zone

\[ F = \frac{\hbar}{2\pi e} A_F \]  

where \( F \) is the frequency. It is easy to see from here that multiple components to the Fermi surface will simply add more frequencies to the measured quantum oscillations. In order to understand how to deduce the \textit{shape} of the Fermi surface from quantum oscillatory phenomena, a more formal Lifshitz-Kosevich formula will be needed.

Figure 3.3: Increasing the field from (a) to (b) finishes depleting one Landau level of quasi-particles and hence the free energy decreases. Upon further increasing the field, going from (b) to (c) causes the free energy to rise again until the next Landau level crosses the Fermi energy. This process repeats until all the quasi-particles are contained in the lowest Landau level.
3.3 Lifshitz-Kosevich Theory - Idealized thermodynamic potential

We start by calculating the thermodynamic potential $\Omega = F - N\mu$ for a system of Fermions with energy $\epsilon_i$:

$$\Omega = -k_B T \ln(Z) = -k_B T \sum_i \ln(1 + e^{\frac{\epsilon_i - \mu}{k_B T}}), \quad (3.7)$$

such that the thermodynamic potential takes on the familiar form of the Boltzmann free energy function where the partition function is simply the sum over all possible states. The allowed energy states for a quasiparticle in a magnetic field are determined the following ways:

1. The allowed values of $k$ in magnetic field determined by the LL quantization orbit given by the Onsager relation: $A_F(\epsilon, k_z) = (n + \zeta) \frac{2\pi e B}{\hbar}$ where $\zeta$ is a phase term related to the shape of the energy band. $\zeta = \frac{1}{2}$ for a parabolic band.

2. The degeneracy, given by the number of states on a section of Landau tube between $k$ and $k + dk$ such that $N_{\text{state}} = A_F dk \frac{V}{4\pi} = \frac{eBVd}{2\pi\hbar}$. Where $A$ is the annulus between adjacent landau tube states per unit volume in k-space.

Now that we can count up the number of available states the thermodynamic potential can be calculated:

$$\Omega = -k_B T \int dk_z \frac{e^{V B}}{2\pi \hbar} \sum_i \ln(1 + e^{\frac{\epsilon_i - \mu}{k_B T}}). \quad (3.8)$$

In the zero temperature regime, where there is no scattering as the quasiparticle orbits a LL gives three contributions [26]: a steady diamagnetic susceptibility term, a Pauli spin susceptibility term, and a term due to the $1/B$ oscillatory variation. From here we focus solely on the oscillatory contribution

$$\tilde{\Omega} = \left(\frac{e}{2\pi\hbar}\right)^2 \frac{T e h B^2}{m^* \pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} \cos[2\pi p \left(\frac{F}{B} - \frac{1}{2}\right) \pm \frac{\pi}{4}]. \quad (3.9)$$

Equation 3.9 represents the idealized oscillatory thermodynamic potential [27].
3.4 Lifshitz-Kosevich Theory - Smearing of the thermodynamic potential

Experimentalists study real systems where $T \neq 0$ and the mean free path is finite. There needs to be a way to incorporate these parameters into the oscillatory part of the thermodynamic potential.

Increasing temperature changes the probability of a quasiparticle occupying an energy state, $\epsilon$, given by the Fermi-Dirac distribution function:

$$f(\epsilon) = \frac{1}{1 + e^{\frac{(\epsilon - \mu)}{k_B T}}}.$$  \hfill (3.10)

As temperature is increased, the Landau level crossing is no longer a sharp cusp when $\epsilon_F = \left(n + \frac{1}{2}\right) \hbar \omega_c$, but is now smeared by the fact the quasiparticle has access to states within $\pm k_BT$ about $\epsilon_F$. Therefore, in two dimensions, the clearly defined Fermi surface circle becomes blurred since a finite temperature increases the total number of available states. The amplitude reduction factor for a finite temperature is given by \cite{27}

$$R_T = \frac{2\pi^2 p k_B T m^*}{\epsilon \hbar B} \frac{1}{sinh\left(\frac{2\pi^2 p k_B T m^*}{\epsilon \hbar B}\right)}.$$ \hfill (3.11)

The scattering of quasiparticles broadens the Landau level width by $1/\tau$. The amplitude reduction factor, $R_D$ associated with scattering is known as the “Dingle term”.

$$R_D = e^{-\frac{\mu_B}{\omega_c}}.$$ \hfill (3.12)

The term $R_D$ can be thought of as the square root of the fraction of electrons that have completed an orbit without being scattered. Simply put, with more scattering, fewer electrons complete an orbit. Disorder therefore increases the LL width and it evidently makes measuring quantum oscillations experimentally extremely difficult.

Another amplitude reduction factor occurs because of the energy level splitting for spin-$\frac{1}{2}$ particles in a magnetic field. The spin splitting energy levels, $\Delta \epsilon = \epsilon \pm g\mu B$ results in a phase difference of the spin up and spin down oscillations.
\[ \phi = 2\pi S. \quad (3.13) \]

Such that the reduction amplitude factor is:

\[ R_s = \cos(p\pi S) \quad (3.14) \]

Including the three reduction factors \((R_T, R_D, R_s)\) in the idealized thermodynamic potential gives \([27]\)

\[
\tilde{\Omega} = \left(\frac{e}{2\pi \hbar}\right)^3 2k_B T B^3 V \frac{d^2 A_F}{dk^2} \sum_{p=1}^{\infty} e^{\left(-\frac{2\pi^2 p m^* k_B T_D}{e \hbar}\right)} \cos\left(\frac{\pi p m^* g}{2}\right) \cos\left[2\pi p \left(\frac{F}{B} - \frac{1}{2}\right) \pm \frac{\pi}{4}\right] (3.15)
\]

where \(T_D\) is known as the “Dingle” temperature. Equation 3.15 shall now be referred to as the generalized Lifshitz-Kosevich formula.

### 3.5 Magnetic Breakdown

Magnetic breakdown is a phenomenon that happens when a quasiparticles cyclotron energy is large enough that tunneling in k-space from one section of Fermi surface to another is possible. A resulting higher frequency oscillation will appear that corresponds to a larger k-space orbit. Fig 3.4 gives a picture of magnetic breakdown in a simple two-dimensional Fermi surface.

### 3.6 Effective mass

Another important electronic property that can be determined from quantum oscillations is the effective quasiparticle mass. Remembering:

1. \(m^*\) depends only on the curvature of the energy band; \(m^* = \frac{d^2}{dk^2}^{-1}\)

2. At \(T = 0\) the amplitude of the oscillations depends only on the quantized density of states (\(\tau\) is fixed)
Figure 3.4: The top panel shows the typical low field semiclassical quasi-particle orbits for a Fermi surface with a one-dimensional line and small two-dimensional pocket. The bottom panel shows the high field magnetic breakdown limit where the quasi-particle can now tunnel from the one-dimensional line to the two-dimensional pocket and back, effectively creating a new frequency in the measure quantum oscillations.

3. As temperature increases only states within $\pm k_B T$ are important

The decrease in oscillation amplitude because of thermal broadening of the LL’s makes it possible to probe the band curvature around $\epsilon_F$ and hence $m^*$ as summarized in Fig 3.5. The effective mass of a semi-classical orbit $j$ in two dimensions with an applied perpendicular field $B$ is derived using the temperature and field dependence of the oscillation amplitude. From LK theory such that [27]:

$$A \propto \left[ \frac{\gamma_j T B^{-1}}{\sinh(\gamma_j T B^{-1})} \right] \left[ e^{-\gamma_j T D_j} \right] \left[ l^{n_1} q^{n_2} \right]$$

(3.16)

$$\gamma_j = \frac{2\pi^2 m^*_j p_j k_B}{m_e \hbar c}$$

$p_j$ is the $p$th harmonic.

$T_D$ is the Dingle temperature.

$l^2 = e^{-\frac{B_0 j}{\hbar c}}, l$ is the probability tunneling between different parts of the Fermi surface.

$q^2 = 1 - l^2$
\( n_{1j} \) are to the number of magnetic breakdown points

\( n_{2j} \) are the number of Bragg reflection points

It is now possible from the amplitude of quantum oscillation measurements to determine the effective mass (first term), scattering rate (second term) and get an estimate of the magnetic breakdown (third term). While this formalism was derived for isotropic materials, it can be extended to very anisotropic materials given that the amplitude of the oscillations is small [28]. The first term shows that oscillations grow in amplitude as the temperature is lowered, while the second term includes the fact that the oscillations grow in amplitude as the magnetic field is increased (i.e. the Landau levels become better resolved). Equation 3.16 can now be simplified

\[
A \propto \frac{14.7m^*TB^{-1}}{\sinh(14.7m^*TB^{-1})} e^{\frac{\pi}{\omega_c \tau}}
\]  

(3.17)

Figure 3.5: How an experimentalist determines the effective mass from the temperature dependence of quantum oscillations. The left panel represents quantum oscillations at three different temperatures (black-\( T_0 \), red-\( \frac{1}{10} T_0 \), blue-\( \frac{1}{16} T_0 \)). The green dots represent a Dingle term that remains constant for the three temperatures. The middle panel represents a Fourier transform from \( 1/B \) space to frequency space (in Tesla). Notice the amplitude decreases as temperature increases. The right panel (black dots) plot the amplitude as a function of temperature. The red line is a fit from the LK formulae which determines the effective quasi-particle mass.
3.7 Oscillations in the specific heat

Consider a strictly two-dimensional system in an applied magnetic field perpendicular to the plane, with a Landau level spectrum

$$\epsilon_n = \hbar \omega_c (n + \frac{1}{2})$$  \hspace{1cm} (3.18)

where each Landau level has degeneracy \( D = \frac{\sqrt{2}}{\phi_0} \), where for spinless electrons \( g=1 \) and for spinfull electrons without Zeeman coupling \( g=2 \). The electronic flux quantum \( \phi_0 = \frac{hc}{e} \).

The thermodynamic potential for such a collection of Fermions is

$$\Omega = -k_B T D \sum_{n=0}^\infty \ln(1 + e^{-\frac{(\epsilon_n - \mu)}{k_B T}}). \hspace{1cm} (3.19)$$

$$\Omega = -k_B T D \int_0^\infty \sum_{n=-\infty}^\infty \delta(\epsilon_n - \epsilon) \ln(1 + e^{-\frac{(\epsilon_n - \mu)}{k_B T}}) \hspace{1cm} (3.20)$$

Remembering

$$\sum_{n=-\infty}^\infty \delta(\epsilon_n - \epsilon) = \frac{1}{\hbar \omega_c} \sum_{n=-\infty}^\infty \delta\left(n + \frac{1}{2} - \frac{\epsilon}{\hbar \omega_c}\right) = \sum_{p=-\infty}^\infty e^{2\pi i p (\frac{\epsilon}{\hbar \omega_c} - \frac{1}{2})}. \hspace{1cm} (3.21)$$

It is now possible to rewrite the summation over the \( \delta \)-functions such that

$$\Omega = -k_B T D \frac{1}{\hbar \omega_c} \sum_{p=-\infty}^\infty (-1)^p \int_0^\infty d\epsilon e^{2\pi i p \frac{\epsilon}{\hbar \omega_c}} \ln(1 + e^{-\frac{(\epsilon - \mu)}{k_B T}}) \hspace{1cm} (3.22)$$

The integral takes the form

$$\int_0^\infty d\epsilon e^{2\pi i p \frac{\epsilon}{\hbar \omega_c}} \ln(1 + e^{-\frac{(\epsilon - \mu)}{k_B T}}) = -\frac{\hbar \omega_c}{2\pi i p} \ln(1 + e^{-\frac{\mu}{k_B T}}) + \frac{1}{k_B T} \frac{\epsilon}{\hbar \omega_c} \int_0^\infty d\epsilon e^{2\pi i p \frac{\epsilon}{\hbar \omega_c}} \frac{e^{-\frac{(\epsilon - \mu)}{k_B T}}}{1 + e^{-\frac{(\epsilon - \mu)}{k_B T}}} \hspace{1cm} (3.23)$$

$$= -\frac{\hbar \omega_c}{2\pi i p} \ln(1 + e^{\frac{\mu}{k_B T}}) - \frac{1}{k_B T} \left(\frac{\hbar \omega_c}{2\pi i p}\right)^2 \frac{1}{1 + e^{-\frac{\mu}{k_B T}}} + \frac{1}{(k_B T)^2} \left(\frac{\hbar \omega_c}{2\pi i p}\right)^2 \int_0^\infty d\epsilon e^{2\pi i p \frac{\epsilon}{\hbar \omega_c}} \frac{e^{-\frac{(\epsilon - \mu)}{k_B T}}}{(1 + e^{-\frac{(\epsilon - \mu)}{k_B T}})^2} \hspace{1cm} (3.24)$$
where the last term in the integrand is the oscillatory component of the thermodynamic potential. Substitution such that \( \xi = \frac{\epsilon - \mu}{k_B T} \Rightarrow \epsilon = k_B T \xi + \mu \) and assuming \( k_B T << \mu \) such that the lower limit of the integral becomes \(-\infty\) the integral is reduced to

\[
-\frac{\hbar \omega_c}{2\pi ip} \ln(1 + e^{\frac{\mu}{k_B T}}) - \frac{1}{k_B T} (\frac{\hbar \omega_c}{2\pi ip})^2 \frac{1}{1 + e^{\frac{\mu}{k_B T}}} + \frac{1}{k_B T} (\frac{\hbar \omega_c}{2\pi ip})^2 e^{2\pi ip\frac{\mu}{\hbar \omega_c}} \frac{2\pi}{\sinh(2\pi^2 p\frac{k_B T}{\hbar \omega_c})} (3.25)
\]

such that the oscillatory component of \( \Omega \) is

\[
\Omega_{osc} = \frac{D\hbar \omega_c}{2} \sum_{p=1}^{\infty} \cos(2\pi p(\frac{\mu}{\hbar \omega_c} - \frac{1}{2}))f(x) \quad (3.26)
\]

where \( f(x) = \frac{x}{\sinh(x)} \) and \( x = \frac{2\pi^2 pk_B T}{\hbar \omega_c} \).

Finally, the oscillatory part of the specific heat can be calculated

\[
c_v^{osc} = \frac{C_v^{osc}}{L^2} = -T \frac{\partial^2 \Omega_{osc}}{\partial T^2} = -\frac{k_B^2 T g \pi}{2m^*} \sum_{p=1}^{\infty} \cos(2\pi p(\frac{\mu}{\hbar \omega_c} - \frac{1}{2}))f''(x). \quad (3.27)
\]

Therefore, in the clean case, the only temperature dependence comes from \( f''(x) \).

Now we solve this problem for the cuprate system, a quasi-two-dimensional system with weak interlayer hopping. The new dispersion is modified and takes the form

\[
\epsilon_n(k_z) = \hbar \omega_c(n + \frac{1}{2}) - 2t_w \cos(k_z c)
\]

where \( c \) is the lattice spacing in the \( z \)-direction. The thermodynamic potential for this collection of Fermions is slightly modified such that

\[
\Omega = -k_B T D L_z \int_0^{2\pi} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \ln(1 + e^{-\frac{(\epsilon_n(k_z) - \mu)}{k_B T}})
\]

where \( L_z \) is the vertical size of the system. The resulting specific heat can be obtained by simply shifting the chemical potential such that \( \mu \rightarrow \mu + 2t_w \cos(k_z c) \).

\[
c_v = \frac{C_v}{L^2 L_z} = -\frac{k_B^2 T g \pi}{2m^*} \sum_{p=1}^{\infty} J_0(4\pi p \frac{t_w}{\hbar \omega_c}) \cos(2\pi p(\frac{\mu}{\hbar \omega_c} - \frac{1}{2}))f''(x) \quad (3.30)
\]
where $J_0$ is a Bessel function of the first kind, such that the hopping term is finite [29].

As the temperature dependence contains the second derivative of a $\frac{x}{\sinh(x)}$ function, there must be an area in $(B, T)$ phase space where the function changes sign from positive to negative. The negative regime shown for the non-oscillatory part in Figure 3.6 corresponds to a phase shift of the specific heat quantum oscillations. The phase shift can be explained by understanding how the maximum in the specific heat oscillation will change as the Fermi Dirac distribution becomes smeared out with temperature to a point when more than one Landau level plays a role in the number of accessible states. When more than one Landau level crosses (i.e. when magnetic field tunes the Landau level spacing such that more than one can be accessed) the Fermi Dirac distribution, states can now be excited from one level to the next such that the peak in the density of states is no longer when the Landau level is centered about $\epsilon_F$, but instead when the Fermi energy is in between the Landau levels, leading to an overall phase shift. Not only is there a region where the non-oscillatory part of equation 3.30 is negative, but also the maximum temperature for the amplitude of the quantum oscillations is not at $T = 0$ and now depends on temperature and field! Remembering that the electronic part of the specific heat is linear in temperature (i.e. $C = 0$ when $T = 0$), it should not come as a surprise that maximum amplitude for the oscillations has to come when $T \neq 0$. Therefore, the magnetic field window used for taking the Fourier transform from the quantum oscillation data can greatly influence the resulting amplitude (see Figure 3.5), and great care must be taken when determining the effective mass by the usual LK formula.

The amplitude of quantum oscillations in the specific heat are small, usually a few orders of magnitude smaller than other measured quantities such as magnetization and transport. To demonstrate the relative magnitude we take the ratio of the oscillatory part of the specific heat to the oscillatory part of the magnetization [27].

$$\frac{\tilde{\Delta}C/C}{\Delta T/T} \approx \frac{x(x-2)}{(x-1)} \quad \text{for } x > 3$$

(3.31)

where $\tilde{\Delta}T = \frac{x}{c \cdot \sinh(x)} \frac{d}{dz} \left( \frac{x}{\sinh(x)} \right) \tilde{\Omega}$.
Figure 3.6: plots the non-oscillatory part of equation 22 in magnetic field and temperature phase space. For a constant effective mass as the temperature is increased the sign change of the function also increases linearly with magnetic field (as seen by the yellow line which indicates zero amplitude). The effective mass determines the slope in temperature verse magnetic field of where the sign change occurs. The max of the function occurs when $k_B T = \hbar \omega_c$.

Applying typical values for $x$, where $x = \frac{2\pi k_B T}{\hbar \omega_c}$ we see that the specific heat oscillations are generally 10 to 100 times smaller than the magnetization, making them quite difficult to detect [30]. It is important to note that the ratio vanishes for $x = 1.6$. We can use this fact to determine the node of the specific heat oscillation (and hence effective mass)

$$H_{node} = 9.19 m^* p T$$

Therefore measuring quantum oscillations of the specific heat in a material can determine the mass uniquely, that is, there is only one fit parameter, $m^*$, and ironically the mass in specific heat quantum oscillations is determined by not finding oscillations, quite counter-intuitive for a graduate student trying to figure out what is going on with the measurement.
The previous sentence (not the rambling on bit) has profound implications because most quantum oscillation measurements assume a temperature independent scattering rate and an “effective” magnetic field which is simply the average of the field range over which one fits the oscillations. While not completely arbitrary, as the magnetic field used is the value of the magnetic field halfway between the measured oscillations in $1/B$ space, the chosen field window for fitting the temperature dependence of the oscillations in torque or transport measurements can change the measured mass determination by up to 25 percent [31], a very large artifact that does not exist in specific heat measurements.
Figure 3.7: Note that the specific heat is zero at zero temperature and contains a node that cuts diagonally across the (B,T) plane. Therefore, the oscillation amplitude decreases at a finite temperature and field. The phase shift can be explained in the following way. Increasing the field increases the Landau level spacing, implying that at high field more smearing of the Fermi-Dirac distribution is required to have entropy contribution from multiple Landau level. This shifts the node to higher temperatures. The node is shown to shift down in temperature as \( m^* \) increases. The beat due to the warping term (the Bessel function in 3.30) is also affected by \( m^* \), moving up in field as \( m^* \) is increased.
CHAPTER 4

EXPERIMENTAL SET-UP

“I don’t know why they put all those fancy gauges in there. I am going to run it till it blows up anyway”

-Unknown motorcyclist

4.1 Measuring heat capacity - Relaxation method

Calorimetry is the measurement of the heat absorbed or generated in a substance as it undergoes a change from a well-defined initial state to a well defined final state [32]. Relaxation method calorimetry is a method in which a sample is heated with a short pulse of energy and the resulting temperature change is measured. If the system is in a steady state, the power, $P$, flows through the system. Cutting off the power causes the temperature of the system to decay back to the initial state temperature, $T_0$, with a time constant, $\frac{C}{k_{\text{block}}}$, where $C$ is the heat capacity and $k_{\text{block}}$ is the thermal conductance of the calorimeter to the heat reservoir. When raising the sample temperature, $T_1$, above the block temperature, the initial state temperature must remain fixed at $T_0$. The heat flow problem can now be solved for one-dimension (see Figure 4.1) where heat diffusion from the center of the sample towards the wires linking the calorimeter to the initial state (lateral diffusion) is much faster than heat diffusion from the wires to the bath (longitudinal diffusion) such that the heat balance equation becomes [33]

$$Power_{\text{intosample}} = power_{\text{out}} + \frac{\partial Q}{\partial t} \implies P = A\kappa \frac{\partial T}{\partial z} + C(T) \frac{\partial T}{\partial t} \quad (4.1)$$
where $Q$ is the amount of heat applied, $A$ is the cross sectional area of the wire, and $\kappa$ is the thermal conductivity. Heat flows only in one-dimension, here defined as the $z$-direction. Assuming the wire has no heat capacity and taking the thermal conductance of the wire to be $k(T) = \kappa(T) \frac{A}{l}$, with $l$ being the length of the wire, the heat capacity now takes the form

$$C(T) = \frac{d}{dt} \left[ P - A \int_{T_0}^{T} \frac{k(T')}{A} dT' \right] = \frac{d}{dt} \left[ P - \int_{T_0}^{T} k(T') dT' \right]. \quad (4.2)$$

For small temperature steps the integral in equation 4.2 reduces to

$$C(T) = \frac{d}{dt} \left[ P - k(T_{avg}) \Delta T \right], \quad T_{avg} = \frac{1}{2} (T + T_0), \quad \Delta T = T - T_0. \quad (4.3)$$

Keeping in line that $T_0$ is stabilized such that $\frac{dT_0}{dt} << \frac{dT}{dt}$, turning of the power and if the heat capacity is constant over the temperature step measured

$$C(T) = -\frac{k(T_{avg})}{\frac{d}{dt} (ln \Delta T)} \quad \text{constant} \quad \frac{d(\Delta T)}{dT} = \frac{-1}{\tau} = -\frac{k}{C} \quad (4.4)$$

making

$$\Delta T(t) = (T_1 - T_0) e^{-\frac{t}{\tau}} \quad \text{and} \quad C(T) = k\tau. \quad (4.5)$$

From equation (4.5) the heat capacity can now be determined by quantities that can be measured in the lab. Figure 4.1 shows the schematic drawing for the 1-dimensional heat flow model and for the relaxation calorimetry method. The relaxation method technique is a popular method as it is suitable for small samples (1mg-10mg), has simple procedures for mounting the sample to the calorimeter, can be used in a confined cryostat volume, and signal to noise ratio can be increased by averaging, $n$, number of data points. The relaxation method allows high sensitivity at low temperatures with small values of the heat capacity, $pJ/K$, and a few percent error in the absolute values at $0.6K$ [32]. The high sensitivity allows properties of spins, electrons, phonons, magnons, and other small thermal anomalies to be studied under magnetic field. The method is not good for characterizing phase transitions.
(even though they are easily detected by this method) because the limit that $C$ is constant over the temperature step breaks down.

Figure 4.1: (A) Schematic of relaxation calorimetry. The sample is attached with infinite thermal conductivity to the calorimeter which is attached via a weak link to the bath. All the heat flow is in one dimension. (B) Typical heating and cooling curve for the relaxation method. The bottom plot is an example of the heater power. At some time $t$ power is applied to the heater and the sample temperature increases by $\Delta T$. The exponential time constant is determined by fitting the curve and then the heat capacity is calculated; $C_p = \kappa \tau$. 

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4.2 Measuring heat capacity - Dual slope

Dual slope calorimetry is a variation of the relaxation method where the heat capacity is determined by comparing the correlation of the heating and cooling curves without the need to take into account the thermal conductance between the sample and bath. Figure 4.2 shows a typical measurement cycle. Much like the traditional relaxation method, heater power, $\dot{Q} = \frac{P}{\Delta T} = \frac{IV}{\Delta T}$, is applied continuously to a thermally isolated sample. A temperature, $T_1$, is recorded. Heater power is then turned off and the sample relaxes back to its initial temperature $T_0$. The heating and cooling power balances such that

$$C(T) = \frac{dT_h(T)}{dt} = \dot{Q}_h - \dot{Q}_0(T) + \dot{Q}_p(T) \quad (4.6)$$

$$C(T) = \frac{dT_c(T)}{dt} = -\dot{Q}_0(T) + \dot{Q}_p(T) \quad (4.7)$$

where $\dot{Q}_0(T)$ is the power lost to the wires linking the calorimeter to the bath, and $\dot{Q}_p(T)$ is any type of parasitic heat loss (i.e. radiation). Assuming $\dot{Q}_0(T)$ and $\dot{Q}_p(T)$ do not vary with time and that the sample is in thermal equilibrium (an inherent assumption to all relaxation calorimetry methods) equations 4.6 and 4.7 can be reduced to

$$C(T) = \dot{Q}_h\left(\frac{dT_h(T)}{dt} - \frac{dT_c(T)}{dt}\right)^{-1}.$$ \quad (4.8)

In the limit of small intervals

$$C(T) = \dot{Q}_h\left(\frac{\Delta T}{\Delta t}\right)^{-1} = \frac{IV}{\Delta T}\left(\frac{\Delta T_w}{\Delta t_w} - \frac{\Delta T_c}{\Delta t_c}\right)^{-1}. \quad (4.9)$$

In the traditional relaxation method technique, around a phase transition the exponential behavior of the heating and cooling traces breaks down as the heat capacity is no longer constant over the temperature interval. Since the dual slope method simply measures the slope of the two traces, deviations from an exponential form will not affect the calculation of the specific heat value, making it a good method for measuring phase transitions. One issue with the way this method is implemented for the NHMFL system is the need for one
Figure 4.2: Typical dual slope data trace. The sample is heating adiabatically over a long time period. The slope of the heating and cooling curves are taken over some interval in temperature. The heat capacity is then calculated such that
\[ C(T) = \frac{IV}{\Delta T} (\frac{\Delta T_h}{\Delta T_c} - \frac{\Delta T_c}{\Delta T_h})^{-1} \]

cooling and one heating curve per data point which effectively cuts in half the number of data points that can be determined (as the program only uses the point where the warming and cooling slopes are equal). Normally, the dual slope method will provide a continuous measurement of the heat capacity for one heating and cooling curve. In order for this to work, there must essentially be no thermal link from the bath to the sample. Traditionally type one superconducting wires are used as they have effectively infinite conductivity and zero thermal conductivity. The calorimeter is then suspended from the wires in a vacuum. Obviously this type of wiring is impossible in a high magnetic fields as the critical field values for type one superconductors is inherently small. (For YBCO 6.56 measurements maganin wires were used to connect the bath to the calorimeter only at a single point). When \( T_c = T_h \) any thermal link problems are cancelled and the absolute value of the heating slope and warming slope are identical. Figure 4.3 demonstrates the use of the dual slope mode in our specific heat set-up.

### 4.3 \( \tau_2 \) Effects

The most common problem associated with relaxation calorimetry involves the introduction of other relaxation times such that
Figure 4.3: A typical dual slope trace for small signal samples. The sample is heated over a small temperature step and then allowed to cool over a short time interval.

\[
\Delta T(t) = (T_1 - T_0)(e^{\frac{-t}{\tau_0}} + e^{\frac{-t}{\tau_1}} + e^{\frac{-t}{\tau_2}} + \cdots + e^{\frac{-t}{\tau_{n-1}}})
\]  

(4.10)

The addition of any extra time constants makes determining the \( \tau \) of the sample and therefore the heat capacity difficult to resolve as the sample and calorimeter are no longer at the same temperature. Figure 4.4 gives a schematic example of a so-called "\( \tau_2 \)" effect. The two most encountered experimentally are, the distributed \( \tau_d \) effect and the lumped \( \tau_l \) effect. The distributed \( \tau_d \) effect happens when the sample is a poor thermal conductor and causes the heat flow from the leads to be comparable to that reaching the sample. To avoid this different wires are chosen to attach the calorimeter to the holding puck (i.e. the
bath heat reservoir). For extreme cases, calorimeters have been designed with a hole in each corner and sputtered NiCr thin glass wires are implemented in order to provide low thermal conductivity, rigid support of the calorimeter, and allow the wires to be used as electrical contacts for the calorimetry. The lumped $\tau_1$ effect is when the sample is a good thermal conductor but contact to the calorimeter is bad. Commonly this is caused by poor thermal conductivity of the grease used for adhesion or ineffective surface area covered by the adhesive. To overcome this simply make sure a thin coat of adhesive is applied to the sample and that the adhesive has a large thermal conductance.

While complex analysis can be used [33] to take into account the contamination of additional time constants, the resulting data contain large errors. When looking for minute field induced changes in small mass samples the author found it more effective and far less ambiguous to pull the probe, change the wires or re-mount the sample to ensure a single time constant for the measurement.

The typical ultra-clean YBCO sample is currently limited to a mass of approximately 7 mg, while the average is 3-4mg. The change in $\gamma$ as a function of field (when the field step is roughly 2T) is on the order of a few percent. The combination of small sample mass (which is proportional to the signal) and small change in $\gamma$ necessitates consistency checking of the data. For these reasons all YBCO heat capacity measurements are made by taking full
advantage of both relaxation calorimeter and dual-slope techniques. The dual slope method is applied to the data on the fly in order to save on processing time as fitting an exponential to the data is more computationally intensive. The relaxation method is applied after the experiment and the two methods are compared. Under optimal conditions scatter from the dual slope and relaxation method are comparable and are limited to roughly half a percent each.

4.4 First Generation calorimetry

The first generation calorimeter is of the basic design discussed by reference [34]. A Cernox thermometer and chip resistor are attached to sapphire platform. The chip resistor is used as a heater. The sapphire platform is used as it is an insulator with effectively perfect thermal conductivity. Therefore the heat flow from the heater to the sample is infinite, while the zero temperature heat capacity from the calorimeter is zero. Figure 4.5 shows a traditional relaxation calorimeter.

4.5 Second Generation calorimetry

The second generation calorimeter is the type used for the YBCO 6.56 heat capacity measurements. The new calorimeter is based on the traditional first generation design as it uses a Cernox for thermometry. The major improvement resulted from working with Lakeshore Cryogenics on a custom design which is likely to become commercially available. In this new design the thermometer is the calorimeter. Lakeshore deposited their Cernox thermometers onto a 4mm x 4mm sapphire substrate with four gold contacts in each corner. A NiCr heater is then sputtered on using a mask made by the FSU physics micro-machine shop. Manganin or NiCr leads are used as electrical contacts that also link the stage to the bath. Different metallic contacts and geometries are used to control the thermal link of the block to the calorimeter. Figure 4.6 shows an example of typical second generation calorimeter. The advantage of using the thermometry as the stage is twofold: it allows for a larger surface area while decreasing the addenda (4 times larger area than a PPMS
calorimeter with a factor of 5 less addenda at 10K) and there are no additional $\tau_2$ problems associated with the thermometer and heater being attached to a sapphire stage.

### 4.6 Third Generation calorimetry

The third generation calorimeters are currently under development. They will consist of a RuO deposited thermometer and the same second generation sputtered NiCr heater. RuO will be an improvement over Cernox because the magneto-resistance is roughly two percent different at 45T than at zero field [35]. The RuO and NiCr heater will have a new pattern so as to minimize the loop area and decrease induced voltages from vibration of the high magnetic field from the water cooled magnet. Finally holes will be drilled into the sapphire substrate to minimize the damage done to the calorimeter caused by torque applied to the sample during magnetic field sweeps (and magnet trips, i.e. when the magnet goes from
Figure 4.6: Left hand panel shows a typical second generation calorimeter. For the lower temperature ranges needed to measure the small YBCO samples NiCr wires worked best as the thermal link to the bath. The right hand panel shows the calorimeter attached to the puck. The wires double as supports for the platform.

field to zero in a matter of milliseconds). Figure 4.7 shows the first schematic for the new calorimetry design.

4.7 Probe and cryogenics

The heat capacity instrumentation consists of two main components. The first component is a custom built helium-3 probe with an indium vacuum seal. The probe is placed into a custom built helium-3 vacuum jacket that uses mechanical pumping from already existing NHMFL gas handling systems to help regulate low temperature stability and the thermal link to the bath. The probe frequently reaches base temperatures of $0.650\, \text{K}$. A picture of the probe is in Figure 4.8. The top of the probe uses a cylindrical conical piece with Lemo connectors connected via a KF50 flange. The KF50 flange allows for easy access into the probe for repair while also providing a simple vacuum tight seal. Lemo connectors are used as they provide excellent vacuum by means of a compression o-ring seal. Lemos also support two, four or six wire cables, where each cable consists of individual shielded twisted pairs, making single point cable grounding straight forward. The probe wiring is specifically designed for low noise in high magnetic fields where vibration is an issue. 0.005 TP gauge PhBr twisted pair wires are threaded through 0.0300 inch OD diameter SS
Figure 4.7: Schematic drawing for the third generation calorimeter. The platform is either sapphire or diamond with dimensions 3mm x 3mm x 0.25 mm. Holes are cut into the corners such that the wires can be woven through them to produce much stronger support. A RuO thermometer will be applied along with a sputtered NiCr heater. The geometry will allow for smaller loop areas.

tubes. The SS tubes serve as an electrical isolation shield for the twisted pairs and have a single point ground to the probe. The single point ground is located at the bottom of the probe, doubling as a vacuum seal for the sample space. Each SS tube is covered in shrink wrap and multiple spacers are place throughout the length of the probe to ensure that there is no electrical touch and, thus, a proper single point ground. The phosphor bronze wires are coated in low temperature Stycast epoxy while being threaded through the SS tubes. Once the Stycast sets the wires are rigid and mechanically stable from vibration, which would otherwise be a source of noise. Twisted pair wiring is used in the balance pair operation, also known as differential mode transmission, where each wire carries equal and opposite signal. This reduces crosstalk from stray or nearby wires and reduces pick-up from electromagnetic interference coming from outside sources (cell-phones, walkie-talkies, radio stations etc).

The bottom of the probe is defined as the volume encapsulated by the indium seal and consists of two regions. The bottom part of the probe is machined from coined silver. Coined silver is used as it has low electrical conductivity (to abate eddy current heating in high fields) and high thermal conductivity. High electrical conductivity and high thermal
conductivity typically go hand in hand. Therefore, finding the right construction material for a low temperature high field probe is always a compromise. In the region outside the radiation shield, the PrBr wires come out of the SS tube electrical shielding and are wound around a coined silver shaft. The wires are wound so that a large amount of the surface area is touching the shaft (block). This gives the wires extra cooling power by linking them to the block temperature. Two 50 Ohm resistors are in series and epoxied with Stycast into two holes machined on the block and used as a heater for block temperature regulation.

The coined silver radiation shield helps thermally isolate the sample from the bath and creates a uniform temperature surrounding the sample. The radiation shield is screwed onto the probe and seats tightly with the top flange. The tight seal helps to thermally anchor the shield to the block such that the inner chamber and block temperature are coupled. The

Figure 4.8: a. displays the bottom portion of the probe. b. shows the bottom portion of the probe with the indium sealed vacuum can on. c. demonstrates the probe once it is placed into the helium-3 vacuum jacket.
wires are again wrapped around the coined silver for thermal anchoring until the bottom is reached and then soldered to the connector. At the center of the support shaft, in the inner chamber, a flat is filed. On this flat a Cernox thermometer is attached with thermally conductive epoxy. This thermometer measures and controls, in a PID feedback loop, the block temperature stability. The construction of the bottom portion of the probe, and the careful attention to the details of making low temperature high-field-resistive-magnet measurements, have allowed micro-Kelvin stability at helium-3 temperatures in fields up to 45 T.

The probe is vacuum sealed with indium and leaked checked. Afterwards the probe is placed into a double wall vacuum jacket. The jacket is pumped out. Once pumped out the jacket can be filled with helium-3 gas. The volume and pressure of the gas can be controlled in order to help regulate the temperature stability. The helium-3 exchange gas temperature couples the probe temperature to the surrounding helium-4 environment. A double wall design is used as it weakens the link of the outside environment to the probe and sample space by having an additional vacuum between the inner and outer walls of the jacket. The vacuum is made by filling a small part of the inner and outer region with charcoal which then passively pumps on the jacket walls as it is cooled.

4.8 Noise reduction

There are a few essential noise reduction techniques required to reduce the scatter in specific heat data to less than one percent. The most important of these is proper grounding: (a) Electrically isolate the cryostat from the magnet by using the in house NHMFL cryostat rig and properly aligning the tail so it does not touch the inside of the magnet (b) Secure electrical isolation of the pumping lines with the use of plastic o-ring supports and clamps (c) Power all equipment using the isolation transformer located in each cell (d) Ground the probe cable shielding to the cryostat (e) Isolate the GPIB/USB computer interface with the National Instruments isolator located in each cell (f) Finally, attach equipment to the rack to the single point clean ground strip located in each cell. Figure 4.9 shows a typical
control thermometer waveform before and after proper grounding. All cables between the probe and equipment rack should be twin-ax, which carry the signal via a twisted pair of wires inside a common shield that should be grounded to the front panel of the particular electronics to which it is connected on the rack. The absence of ground loops must be confirmed using a Megger ground meter designed for ground loop detection and ground resistance measurements. These are located on a noise crash cart in the instrumentation room.

An additional noise source inherent in resistive magnets is the vibration from cooling water being pumped through the magnet. Secure all stainless steel pumping lines with sandbags to reduce noise resulting from vibration. Use stiff wire on the calorimeter to minimize vibration. Use twisted pair wires to help remove area-turns that would pick up voltages due to vibration with a non-uniform magnetic field. Finally, look the signal on an oscilloscope, fast FFT in order to see the remaining noise spikes from RF, radio stations, etc., and choose an excitation frequency accordingly!

Figure 4.9: Left hand panel displays the control thermometer waveform before connecting the current-source and platform thermometer current-source cable shields to ground. Right hand panel: after proper grounding the 500 mK waveform is killed resulting in sub mK temperature stability.
4.9 Digital lock-in

All lock-in amplifiers, analog and digital, operate on the concept of phase sensitive detection. Phase sensitive detection is the demodulation or rectification by mixing of an input AC waveform signal, which is locked in phase and frequency to a reference waveform signal of known amplitude. Therefore a phase sensitive detector only responds to signals which have the same frequency and phase with that of the reference waveform and rejects everything else. Figure 4.10 shows the schematic for a general phase sensitive detection device.

![Phase Sensitive Detection Schematic](image)

Figure 4.10: Upper panel is a schematic of a typical phase sensitive detection device adapted from ref [36]. An input waveform passes through an inverting and non-inverting amplifier to produce in-phase and out-of-phase versions of the signal. The signal is then rectified by means of mixing with a reference signal and then output. The average value of the output signal now has a non-zero value. The lower panel shows how the mixing works. Assuming both the input and reference signals are sinusoidal, the multiplier output will contain components at frequencies $\omega_s + \omega_r$ and $\omega_s - \omega_r$ where $\omega_s$ is the signal frequency and $\omega_r$ is the reference signal. Such that, when $\omega_r = \omega_s$ the output will be a DC voltage that is proportional to the signal: $V_{total} = V_sV_r\sin(\omega_st + \theta_s)\sin(\omega_rt + \theta_r) = \frac{1}{2}V_sV_r\cos(\theta_s - \theta_r)$. 

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The NHMFL-designed digital lock-in is a synchronous lock-in where the signal is a integer multiple of the clock. As the phase is constant in a synchronous lock-in, it allows the amplitude of the oscillation signal to be determined within one period. That is, there is no aliasing or RC time constant. Aliasing is when the clock and the signal are not in phase and when they are mixed, a beat occurs. Finding the maximum of the beat would require more averaging, increasing the RC time constant and slowing the data collection rate. The digital lock-in also saves all the raw sine wave signals of the inputs and clock. This allows complete flexibility to post-process the data with different filtering windows, and averaging over different number of sine waves. Finally the NHMFL digital lock-in allows for a more precision measurements without needing to spend the instrumentation time to offset and expand about some value in order to increase smaller changes about that value.

4.10 Experimental set-up

Temperature stability is controlled with a Cernox thermometer mounted on the block via a LKS 340 temperature controller. The calorimeter experimental set-up is shown in Figure 4.11. The set-up consists of three different standard 4-wire measurements completed on two circuits; one circuit is for the heater resistor and the other circuit for the thermometer resistor. Voltage measurements are made differentially with inputs on the digitizer component of the digital lock-in.

The heater circuit uses a Keithley 220 programmable constant current source to supply a constant current to the nichrome heater on the calorimeter. The resulting voltage is put through a differential SRS low noise pre-amp where the signal is then fed into an input channel on the digitizer. The thermometer circuit voltage is generated using a SRS 840 lock-in with the sine wave frequency being synchronized to the digital lock-in. The voltage is input to a constant current transformer which supplies a constant current over the frequency and thermometry magneto-resistance range used. A test resistor is put in series which measures the supplied voltage to ensure that it stays constant over the time period of the measurement. The voltage across the thermometer is put through a differential
SRS low noise pre-amp with appropriate band-pass filtering and the signal feed into an input on the digitizer.

Figure 4.11: Block diagram of the heat capacity set-up.

When using the constant current transformer there are a few things to remember: (a) Make sure the calorimeter thermometer’s resistance value is not close to the value of the load resistor or some current will be lost to the primary coil (b) To prevent current loss through the primary coil change the load resistor to a higher resistance on the secondary coil (c) If the transformer is not labeled and the turns ratio is unknown use a known resistor in place of the sample and measure the output voltage to determine the current. Because driving up the excitation frequency increases the impedance on the transformer there is a limited range of frequency over which a transformer can work. Other factors that affect the frequency range of the transformer: (a) permeability of the magnetic coil can become complex at high frequency (b) increasing the excitation voltage changes the inductance thereby changing the frequency response via $I\omega L$. Obviously in the DC limit the transformer will not work as the current induced in the coil is $V_1 = L_1 \frac{dx}{dt} - m_1 \frac{dx}{dt}$, where $m_1$ is the mutual inductance of the coil. For DC, $\frac{df}{dt} = 0$.

Raw sine wave voltage measurements from the thermometer and heater on the calorime-
Figure 4.12: The experimental set up. Notice how happy the author is that it actually works and his twenties were not merely an exercise in futility (as displayed by the thumb up). Second notice the large rusted steel pipe, found on the ground by Albert Migliori. The application of such shielding technology reduced the noise by a factor of two.

Data are streamed via the digitizer to the computer. Raw data is saved and may be operated on later. “On the fly” lock-in processing is implemented in LabView on the two channels. The processed data is then fed into a program used to calculate the heat capacity. Figure 4.14 shows a flow chart for a typical heating and cooling pulse (which yields one heat capacity point).

4.11 Calibration of a Cernox calorimeter in high magnetic fields

Magneto-resistance is the change in resistance of a material with the application of an applied external magnetic field. At low temperatures, magneto-resistance is greatly enhanced as the primary mechanism responsible for scattering is quasiparticle-quasiparticle scattering. For Cernox ZrN thin films, the temperature range in which magneto-resistance is greater than one percent for fields up to $45T$ is roughly $25K$. Therefore, for all temperatures less than $25K$, the magneto-resistance of the calorimeter’s thermometry must be taken into
account for the correct temperature to be calculated for heat capacity measurements in high magnetic fields.

As the LKS calorimeters are a special design developed in collaboration for this thesis, they must be thermally cycled before calibration. The sapphire substrate and ZrN thin film have different coefficients of thermal contraction. Without thermally cycling to allow for an equilibrium relaxation between the surfaces to be reached, the room temperature resistance value can change by up to ten percent. Calorimeters are thermally cycled by repeated dunking in liquid nitrogen and then being placed onto a 360K hot plate. Thermal cycling is complete once a repeatable stable resistance at both 77K and 360K has been reached. Usually resistance stability is reached around 20 temperature cycles. The temperature-resistance curve will then be stable over the lifetime of the calorimeter (on the order of years, or months depending the graduate student handling the calorimeter). Figure 4.15 shows a typical thermal cycling plot for a LKS calorimeter.

After thermal cycling, the calorimeter’s thermometry needs to be calibrated in zero magnetic field. The zero field measurement is very important as it will be used to determine the starting pulse temperature during magnetic field calibration (explained later). Therefore, zero field measurements are conducted on a probe in which the calibrated thermometer is in direct thermal contact with the calorimeter. The calibration is done at 17 Hertz using a
Figure 4.14: **ADD THIRD PART OF ANALYSIS LABVIEW PROGRAM**
Flow chart of the raw data as processed by the LabView runtime software routines. The raw sine wave is processed and sent to the second module which plots (in red) the heater voltage as a function of time and the thermometer voltage (in units of temperature, white) as a function of time. The two traces are synchronous waveforms such that the software puts an array marker on the exact point in time when the heater is turned off and on. Now that a cut-off has been established the heat capacity can be extracted from the data trace

resistance bridge. A resistance bridge is used so that any of the inherent problems associated with the constant current transformer are absent, which allows for a cross check during pulsed field calibration. The temperature is swept both cooling and warming, slowly, at roughly 0.5 K per minute, making sure there is no hysteresis.

The resistance of the calorimeter’s thermometer at base temperature will determine the probe used for pulsed magnetic field calibration. If the resistance is less than 5kΩ, the low noise probe can be used. If the resistance is higher than 5kΩ, the low capacitance probe must be used. The low capacitance probe has individual wires separated by fiberglass shields which lower the high capacitance inherent in twisted pair wires. Lowering the capacitance results in a lower RC time constant allowing more resistive-or-higher resistance samples to be measured during the short width of the magnetic field pulse. Both probes are constructed with as little metal as possible to minimize eddy current heating: As a magnetic field pulse generates a large $dB/dT$, even small eddy current heating can make maintaining constant temperature over the pulse duration difficult if not impossible. Figure 4.16 shows the bottom
connector parts of both probe styles.

The experimental set-up mimics that for the calorimeter’s thermometer circuit as shown in the specific heat block diagram in figure 4.11. The only discernable difference is the data sampling rate, which is roughly 12 Mega-samples per second, as expected since all the data for the field sweep are taken in a window of 400 milliseconds. The constant current frequency and load resistor effects must also be taken into consideration. Ideally, the load resistor and excitation frequency used for pulsed field calibration will be identical to the one used in the DC magnetic field heat capacity experiment.

There is only one pulsed field available at the Los Alamos NHMFL site that has a pulse width long enough to measure resistivity at an excitation frequency around $3 - 5KHz$, the typical frequency used for a DC magnetic field heat capacity experiment. The NHMFL 50T "Mid-Pulse" magnet has a 400 ms pulse width allowing for roughly 17 sine waves per Tesla to be measured in the range of $3 - 5KHz$. The bore size of the "Mid-Pulse" is 15 mm, providing plenty of room for the 8 mm diameter calorimeter puck. The "Mid-Pulse" magnet takes around roughly one hour to cool down after a 35T shot, with a typical pulse
Figure 4.16: The left hand panel shows the low capacitance probe used by the NHMFL pulsed field facility. The probe separates the pairs of wire in fiberglass sleeves to reduce the RC time constant. The right hand panel is the low noise probe, which uses twisted pairs that are stycast into mechanically secure ss tubes to electrically shield and mechanically isolate the wires, increasing noise reduction.

Before each pulse, the resistance is checked with a resistance bridge and compared with the zero field calibration. It is not uncommon for the temperature reading of the Cernox thermometer mounted on the probe to slightly differ from the calorimeter temperature. The difference between both thermometer readings on the pulsed field probes comes from the fact they are not in direct contact and a small thermal gradient is present. The thermal gradient will disappear at 1.7 K when the exchange gas is pumped and the He-4 becomes superfluid. The resistance is then doubled checked for consistency with both a resistance bridge, and in the constant current transformer experimental set-up modes. Now, if the two readings on the calorimeter are different, it is known that there is some current leakage from the secondary to primary coil on the constant current transformer. Changing the load resistor or excitation frequency, or both, remedies this problem. It should now be obvious the importance of a good zero-field calibration before doing any pulsed field shots. A typical plot for checking the resistance bridge and constant current transformer lock-in technique
Once thermometry and the experimental set-up are understood, the magnet can be pulsed. Each magnetic field pulse gives a resistance versus magnetic field profile at a single temperature. As heat capacity calibration curve requires a resistance versus temperature at a single magnetic field, the idea is to build a large array of fixed temperature points such that the resistance-magnetic-field-temperature matrix is large and little interpolation between temperatures is required. Figure 4.19 shows a typical data set for a magnetic field calibration. The total amount of time needed to complete a data set can be reduced if one takes advantage of the linear behavior of the magneto-resistance above 25T. The pulsed magnet takes roughly 1 hour to cool down after a 35T shot and 1.5 hours to cool down after a 42T shot. Therefore, pulsing to 35T and then linearly extrapolating the data to 45T greatly reduces the total time needed to collect a full data set.

The completed data set is put into a LabView program which takes the resistance versus magnetic field traces and outputs a resistance versus temperature curve at a fixed magnet field. Figure 4.20 shows the front panel display of the program, as well as a curve for 20 T
and the polynomial fit to the data points. It is important to understand the temperature range in which the calibration is relevant. As the polynomial fit is done on a log-log scale, there is more weight put on the fit at low temperature. The pulse field data at lower temperatures (usually \( T < 1K \)) has more noise, so it is often better when measuring at higher temperatures to only include magnetic field pulses around the temperature being measured. In the case of YBCO 6.56, the heat capacity experimental set-up can only reach 0.80\( K \) in the 25\( T \) – 35\( T \) resistive magnets, while the pulsed field experiment can get down to 0.30\( K \). Therefore, only using calibration shots with \( T > 0.75K \) is prudent.

There are a few problems associated with transport measurements in high magnetic fields. The most common is temperature stability. If the sample is in thermal equilibrium throughout the entire up and down sweep of the magnetic pulse, the starting and ending temperatures should be identical. Any hysteresis is a cause for concern. Figure 4.21 shows a typical pulse where heating occurred. Heating can arise from too high current, too little exchange gas, eddy current heating, poor probe design, and/or from a ‘soft fridge’ (i.e. soft vacuum). A Cernox at base temperature has a resistance value of \( \sim 4k\Omega \). Therefore, a
Figure 4.19: The left hand panel is a complete resistance as a function of field data set for a LKS calorimeter. The green traces are $10T$ shots that overlay the $45T$ shots. The $10T$ shots are used to check for heating. The right hand panel shows the percentage change caused by an applied field at three different temperatures. In the low temperature regime the resistance can change by 20 percent.

Current of 5 micro-amps is commonly used with the resulting heat load to the system of 700 nW. Any higher than this can cause heating. To check, simply reduce the current and monitor any temperature change. In the case of exchange gas, helium-4 has a high thermal conductivity and the simple act of over pressuring gas into the fridge should allow any local heating to be quickly dispersed. Helium-3, with its weak thermal conductivity can cause a large temperature gradient if too much is used. Not enough helium-3 can allow for local heating as it has little cooling power. The use of helium-3 requires some experience as every cryogenic system is different. A soft fridge is the result of Helium gas bleeding into the porous G-10 tails of the vacuum jacket. If the tail becomes contaminated with Helium the vacuum separating the sample from the bath is lost and temperature stability becomes nearly impossible as the bath will essentially become a large heat sink.

4.12 Other issues in high magnetic fields

A major issue with measuring heat capacity in a resistive magnetic is the induced EMF from vibration. There are a few ways to reduce the induced EMF. The first; use sandbags
to damp any mechanical oscillations coming from vacuum hoses. Use the NHMFL cryostat isolation cage and make sure the tail is not touching to reduce the vibrations coming from the water cooling housing around the resistive magnet. Finally, reduce the open loop area of your calorimeter wiring. Figure 4.22 shows two calorimeters, one with a much lowered loop area resulting in higher signal to noise.

As the sample is in vacuum, and the probe construction uses a lot of metal, both stainless steel and coined silver, sweeping the field no faster than a rate of 4 T/min will reduce eddy current heating. At high fields, it takes a long time for a sample in vacuum to cool down as there is no cooling power (i.e. the sample is well isolated from the bath) and any induced heating only exasperates this problem. Another non-intuitive problem arises from the diamagnetic nature of Helium-3. At approximately 27 T, the diamagnetic force exerted on Helium-3 is stronger than the force of gravity. The result is a vacuum bubble around the sample at field center. The bubble isolates the sample from the exchange gas, and essentially there is no cooling power that can reach the sample. Ramping the field below 27 T collapses the bubble and cooling power is restored. Therefore, one must be
careful that a base temperature is reached below 27 T, the field is ramped at a slow ramp rate to reduced eddy current heating, to reduce the time one must sit at high fields and wait for the sample to reach the desired low temperature (which is on the order of hours).

4.13 Experimental procedure for measuring YBCO single crystals

Heat capacity measurements were made on a home-built in house system designed by the NHMFL for its user community. On-the-fly measurements use the dual-slope method [18] for speed. Post-analysis uses the relaxation method as a cross check [19]. The sample was placed on a 3 mm x 3 mm NHMFL custom designed calorimeter built in collaboration
with Lakeshore Cryogenics. The sample is attached to the calorimeter by means of silver paint. It is then put under vacuum, placed into the magnet, and allowed to cool. Depending on the temperature step, once temperature stability (usually $\pm 1mK$) is reached, a heat pulse is applied to the sample and the temperature step recorded.

The heat capacity of the calorimeter is measured with no sample (the addenda). Results of such an addenda measurement are shown in Figure 4.23. The signal from a 6 mg YBCO 6.56 sample, in the temperature range measured, is about a factor of 10 greater than the addenda. The custom designed calorimeter has an addenda which is smaller than that of a Quantum Design PPMS at 50K by more than a factor of two. All the YBCO 6.56 data presented in the following chapter have had the addenda subtracted.

The calorimeter thermometry has been calibrated in magnetic field to compensate for magneto-resistance [37, 38]. At each new field, the YBCO 6.56 sample was brought above $60K$ (zero field $T_c$) and allowed to field cool. For the oscillation data, the $C(H)$ sample was brought to $60K$ at $27T$ allowed to cool and then the field was swept. To check for hysteresis the $1K$ oscillation data was done sweeping field up from $30T − 45T$ then down from $45T − 30T$. The two data sets lay on top of one another with no hysteresis being detected. Thermometry settings for field sweeps assumes a fixed magnetic field of $35T$. 

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Post analysis finds the actual field values and corrects each $\Delta T$ of the heating and cooling curves to account for the magneto-resistance of the thermometry. The oscillations are visible to the eye pre and post analysis. The magnetic field is applied parallel to the c-axis of the single crystal YBCO 6.56 sample.

![Graph](image.png)

**Figure 4.23:** Addenda as a function of temperature for the NHMFL custom calorimeter (blue squares) and the Quantum Design calorimeter (red circles).

### 4.14 Review - how to make a good heat capacity measurement

The accuracy of heat capacity measurement is critically dependent on the accuracy of the current, voltage, time and temperature measurements. There must be good thermal equilibrium within the calorimeter, and the calorimeter must indicate the correct temperature, especially in the presence of high magnetic fields. Heat exchange between the sample and bath must be minimized to allow for temperature stability, which needs to be roughly
±1mK. Below about 10K, heat conduction happens via electrical connections, and attention must be paid to the thermal link of the bath to the calorimeter via the calorimeter wires. The addenda must be minimized; ideally the sample signal is at least 10 times greater than the addenda, especially at low temperatures. The use of simple cryogenic, easy to remove, and easy to re-use calorimetry is essential as it greatly reduces the risk of damage, and the need for re-calibration for high magnetic fields.
CHAPTER 5
RESULTS

“I have a theory that the truth is never told during the nine-to-five hours”
-Hunter S. Thompson

5.1 Experimental determination of $\gamma$ and $\frac{C(1K)}{T}$

Specific heat is a bulk thermodynamic measurement that probes all excitations in a system. In order to extract the excitations arising only from the electronic quasiparticle density of states, all other contributions to the specific heat need to be subtracted out. There are five contributions to the temperature and magnetic field dependence of the specific heat in YBCO:

$$C(T, B) = C_{\text{electronic}} + C_{\text{phonon}} + C_{\text{Schottky}} + C_{\text{hyperfine}} + C_{\text{oscillatory}}. \quad (5.1)$$

The data analysis done here does not consider the expected zero field term from a gap with line nodes; $C_{\text{node}} = \alpha T^2$, where $\alpha$ characterizes the shape of the nodes. The $C_{\text{node}}$ term does not need to be incorporated into our data in order to obtain reliable and physically motivated fits. For YBCO, $C_{\text{node}}$ is often hard to detect and early magnetic field studies of the specific heat found $\alpha$ to be negative [39]. The difficulty arises in the very narrow range of temperature in which $\alpha$ contributes any meaningful percentage of the total specific heat [16]. Since $\alpha$ scales with the slope of the line nodes in the d-wave superconducting gap, an estimate of $\alpha$ can be determined for YBCO 6.56. Previous measurements on YBCO 6.95 give $\alpha = 0.11 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [16]. Assuming an anisotropy from thermal conductivity
measurements where, \( \frac{v_{F,0.99}}{v_{F,0.54}} \sim 2 \), would yield an \( \alpha \sim 0.05 \text{ mJ mol}^{-1} \text{ K}^{-2} \) for YBCO 6.56 [40]. As the purpose of this experiment is to study the high field evolution of the specific heat, the value of \( \alpha \) being small, a zero field manifestation, and difficult to detect in YBCO 6.56, it is not taken into account when extracting values for \( \gamma \) [2].

The term describing the lattice phonon excitations, \( C_{\text{phonon}} = \beta T^3 \), is a field independent quantity where the pre-factor \( \beta = \frac{12 \pi^4 R}{5 \Theta_D^4} \) and \( \Theta_D \) is the Debye temperature. For the sample measured, the Debye temperature is 395 K. When global fits are done to extract \( \gamma \), and \( \beta \) is allowed to be independent for each \( C(T) \) at fixed field, rather than a global fit parameter, values for \( \beta \) range from \( \beta = 0.392 - 0.420 \). Figure 5.1 shows the specific heat divided by temperature as a function of \( T^2 \) for zero and 45T magnetic fields. The slopes of these two lines are identical, where the high temperature data is fit to the following equation

\[
\frac{C}{T} = \gamma + \beta T^2.
\]  

(5.2)

The constant value for \( \beta \) over the field ranges measured establishes \( \beta \) as a field independent quantity. The temperature dependence is also linear over the temperature range measured; implying in the low field and very high field limits the only significant high temperature contribution from the specific heat is a result of phonon excitations. The phonon contribution can now reliably be subtracted away and is no longer considered.

In the low and intermediate field ranges there is "Schottky-like" contribution of the form \( C_{\text{Schottky}} = \frac{N e^2 z^2}{(e^2 + 1)^2} \) where \( z = \frac{2 g \mu_B H_{\text{eff}}}{k_B T} \) with \( H_{\text{eff}} = \sqrt{H_{\text{applied}}^2 + H_{\text{internal}}^2} \) [16] and it needs to be subtracted out. In the high temperature regime where \( k_B T << \Delta_s \) the specific heat, \( C \propto \frac{e^x}{T} \) giving way to exponential activation. In the high temperature regime \( k_B T >> \Delta_s \) the specific heat, \( C \propto \frac{H_{\text{eff}}^2 T}{T^2} \), yielding a power law or "upturn" behavior in the temperature dependence. These limiting behaviors work for any \( n > 1 \) level system. An applied magnetic field has the effect of decreasing the amplitude, moving the peak up in temperature and increasing its width in temperature. At very high fields the Schottky term becomes negligible as it merges into the background. The nature of the Schottky term is not well understood [18] and is currently ascribed to residual paramagnetic centers.
Figure 5.1: \( \frac{C}{T} \) as a function of \( T^2 \) for zero field (yellow circles) and the highest field measured, 45 T (blue triangles) with the field applied parallel the c-axis. For this sample \( \beta = 0.395 \frac{mJ}{\text{molK}^2} \) while [41] found \( \beta = 0.392 \frac{mJ}{\text{molK}^2} \) and [16] found \( \beta = 0.305 \frac{mJ}{\text{molK}^2} \). In both of these regimes the specific heat looks Fermi liquid like as the only contributions appear to be from a phonon and electronic term. The phonon term is field independent as shown by the same value of the linear slope for all fields measured.

associated with unpaired copper spin-1/2 moments [16]. In zero field, \( H_{\text{eff}} \) must be small since the moments are ordered only by internal interactions. While the data can be modeled well with this formalism, \( H_{\text{eff}} \) is a fit parameter which is itself a function of the applied field and temperature such that it essentially allows for equivocation. Thus, the data are analyzed two ways in regards to the low magnetic field electronic Schottky anomaly. First is the traditional manner where \( H_{\text{internal}} \) is allowed to be a fit parameter over the range of 0T-16T where the Schottky-like anomaly plays a role, and second all data taken for YBCO 6.56 assume \( H_{\text{internal}} = 0 \) making \( H_{\text{eff}} = H_{\text{applied}} \) and no longer a fit parameter. Fits to
the specific heat are done globally as described in table 5.25 - 5.32 and over field regions which have physical meaning (and will be explained throughout this section).

The low field limit is then defined as the field range where only the high temperature limit of the electronic Schottky term contributes and the total specific heat takes the form

\[ C_{LFL} = C_{\text{electronic}} + C_{\text{HighT Schottky}} = \gamma T + \frac{N z^2}{T} \] (5.3)

\[ \gamma \] and \[ \frac{C(1K)}{T} \] can now be determined in low fields by two independent fitting procedures. First a linear fit only over the high temperature regime, like that done in Figure 5.1, for the trace where the phonon pre-factor is fixed, leaving only one fit parameter, \( \gamma \). The second is shown in Figure 5.2 where equation 5.3 is used to globally fit the family of curves over the entire temperature range. The resulting values for \( \gamma \) are plotted in Figure 5.6.

The intermediate field limit is defined when the full form for the Schottky term must be included into the specific heat formula.

\[ C_{IFL} = C_{\text{electronic}} + C_{\text{Schottky}} + C_{\text{hyp}} = \gamma T + \frac{N z^2 e^z}{(e^z + 1)^2} + \frac{P \Delta^2_{\text{hyp}} H_{\text{applied}}^2}{T^2} \] (5.4)

Figure 5.3 shows the field range of \( 2T - 8T \). The \( 2T \) data overlaps the low and intermediate field ranges and is used as a consistency check. From equation 5.3 the only parameters which are allowed to float in the fit are \( \gamma \) and \( N \). \( z \) is a global fit parameter which gives the best fit of \( z = \frac{2gS \mu_B H_{\text{applied}}}{k_B T} \approx 1.37 \frac{H_{\text{applied}}}{T} \). Such that \( z = \frac{2gS \mu_B H_{\text{applied}}}{k_B T} = 1.37 \frac{H_{\text{applied}}}{T} \) which is close to the experimental determined value from muon experiments of \( gS \approx 1.03 \) [17]. When the field value reaches \( 8T \) equation 5.4 no longer works well in the low temperature region as the nuclear Schottky anomaly begins to play a role.

In the high field regime \( H \approx 10T - 16T \), the Schottky-like anomaly can easily be observed by following its quick suppression as field increases from \( 6T \) to \( 14T \). The high field regime overlaps the intermediate field regime in the \( 6T \) and \( 8T \) traces where there is a small but non-negligible nuclear Schottky term.

\[ C_{HFL} = C_{\text{electronic}} + C_{\text{Schottky}} + C_{\text{hyp}} = \gamma T + \frac{N z^2 e^z}{(e^z + 1)^2} + \frac{P \Delta^2_{\text{hyp}} H_{\text{applied}}^2}{T^2} \] (5.5)

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Figure 5.2: Specific heat with the phonons subtracted out as a function of temperature for the low field regime. The low field determination of gamma is shown using equation 5.3 where with $H_{\text{eff}} = H_{\text{applied}}$ the upturn of the Schottky-like behavior is well modeled. The zero field data with an upturn is shown although the data is not used for the global fit in this regime as $H_{\text{applied}} = 0T$.

Where P is the number of nuclear spins. Equation 5.5 has the largest number of fit parameters. The low field Schottky-like behavior is suppressed at such a fast rate that small changes in the fit parameters have a large effect on $\gamma$, as the $C_{\text{Scottky}}$ term still has an exponential and power law response. Global fitting of the data at fields lower and higher than this regime are therefore important as it allows constraints to be made on the fit parameters. Further complicating this regime is the effect of magneto-resistance in the calorimeter. At 20$T$ the magneto-resistance of cernox thermometers reach a local maximum and changes sign [37] [38] implying that any miscalibration will be amplified in the $15T - 25T$ regime as $\frac{dR}{dT}$ is large. Finally, the full contribution of the hyperfine term is rarely observed [18] because the nuclear-spin-relaxation time is longer in regions that are
Figure 5.3: Specific heat as a function of temperature for fields in the intermediate field range. The Schottky-like contribution is largest in this field regime. At 8T the Hyperfine term begins to play a role as the data deviate upward from the equation 5.3 fit.

superconducting versus regions that are in the field induced normal state; hence, those nuclei do not contribute to the specific heat. High field measurements therefore quasi-constrain $\Delta_{hyp}$, while low and intermediate fields constrain $z$, leaving only $N$ and $\gamma$ as fit parameters. Once high enough fields are reached, $B \approx 20T$, $\Delta_{hyp}$ is found to essentially be constant. At lower fields, the full value of $\Delta_{hyp}$ is not yet reached.

The very high field limit is defined by the vanishing of the low temperature Schottky anomaly such that it no longer contributes to the specific heat ($\sim 20T - 45T$). In this regime the only subtraction needed to determine the electronic contribution comes from the $C_{hyp}$, the interaction of copper nuclear magnetic moments with the applied magnetic field [18]. As the copper moment is few orders of magnitude smaller than the electronic moment the
Figure 5.4: Specific heat with phonons subtracted out as a function of temperature in the high field limit. The Schottky-like anomaly is quickly suppressed from $6T$ to $14T$ while the hyperfine contribution grows rapidly with increasing field.

density of states contribution will only play a role at high fields and low temperatures.

$$C_{VHFL} = C_{hyp} = \gamma T + \frac{P\Delta_{hyp}^2 H_{applied}^2}{T^2}$$ (5.6)

The very high field limit fit is much like that of the low field limit since can be checked by using equation 5.6, and by fitting over the higher temperature region using an equation of the form like that in 5.2. In equation 5.6, the second term is caused by the hyperfine interaction, and, the only fit parameter is $\gamma$, as $\Delta_{hyp}$ can be globally determined and found to be nearly constant in this field regime from both $C(T)$ for different fields and (as shown in the next section) $C(B)$ at fixed temperature.

The different ways of fitting the $C(T)$ as a function of magnetic field data are shown in Figure 5.6 with the fit parameters given in figures 5.25 - 5.32. $\gamma$ values in the results section

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Figure 5.5: $C_s$ as a function of $T^2$ for 40$T$ and 45$T$. In the very high field limit the only contribution to the specific heat that must be subtracted is the Hyperfine contribution. $\gamma$ is the only fit parameter and can be calculated by either equation 5.2 or equation 5.6 as shown in the inset. The temperature in which the $C_{osc}$ component can be seen in the raw data is at roughly 4$K$.

use fitting procedures over different field windows for the following reasons: for 0$T$ − 2$T$ and 20$T$ − 45$T$ the fits are based on equations 5.2 and 5.6. Using equation 5.3 the fit has only one unknown fit parameter, $\gamma$, as $\beta$ is known. Fits in the range 2.5$T$ − 16$T$ are explained in the figure 5.25 - 5.32. Fits are done comparing both $H = H_{eff}$ and $H = H_{applied}$ because some small non-zero upturn exists at zero field. Currently the only way to explain this zero-field upturn at low temperatures is by a small internal field caused by disorder [18] [42]. The true nature of the Schottky-like anomaly and $\gamma(0)$ are unknown, yet appear weakly linked as the strength of effect increases with $\gamma(0)$ [18] [42]. Verifying the $\sqrt{H}$ dependence under a plethora of constraints only demonstrates the robust nature of the effect.

The 0$T$ − 16$T$ traces where done in an Oxford cryogenic magnetic in a home built He-3 system. The 30$T$, 40$T$, 45$T$, and $C(H)$ measurements were made in the Hybrid magnet. A He-4 system was adopted and temperature measurements were made from 1.5$K$ to 10$K$ while using equation 5.6 to extract $\gamma$ for 20$T$, 20.5$T$, 222$T$, 24$T$, and 28$T$ fields.

The scatter from the higher field data (which used equation 5.2 and equation 5.6 to extract $\gamma$) is correlated to the oscillation amplitude. In Figure 5.5, the small contribution coming from the oscillatory part of the specific heat, $C_{osc}$, can be seen with the eye. Deviations upward or downward are then expected in $\gamma$. From figure 5.11 the field in which $C_{osc}$ begins to play a role is roughly 23$T$. Using the Shoenberg model for specific heat oscillations the $C_{osc}$ component can be subtracted out. Subtraction of the $C_{osc}$ can be complicated because any slight misalignment in the platform creates small phase shifts in the oscillations. Thus, matching the phases of oscillatory data derived from fixed field $C(T)$
Figure 5.6: $\gamma$ calculated by equations stated in the text and figures 5.25 - 5.32 as a function of applied magnetic field. The line is a $\gamma(B) = A_c \sqrt{B}$ fit through all the data.

traces with that from fixed temperature $C(H)$ traces is difficult, as the $C(T)$ and $C(H)$ data were taken during different magnet runs. Assuming the magnetic field through the two-dimensional CuO plane is $B_{internal} = B_{applied} \cos(\theta)$ and a $\pm 10$ deg platform tilt angle the internal magnetic field can vary by around three percent. This variation in field range is used for subtraction of $C_{osc}$. The best fit to the $C_{osc} \sqrt{H}$ values in this field range are used with the resulting values for $\gamma$ shown in Figure 5.7.

5.2 Estimating the Dirac cone anisotropy ratio

Start by calculating the total energy, $<\epsilon>$, of $n$ particles about the Fermi energy

$$<\epsilon> = \sum_n \epsilon n n_F(\epsilon_n) = \int dV \int \frac{d^2k}{(2\pi)^2} \epsilon_k \frac{1}{e^\frac{\epsilon_k}{T} + 1}$$

(5.7)
Figure 5.7: $\gamma$ with the residual and the oscillatory component of the specific heat subtracted out as a function of $\sqrt{H}$. The slope of the straight line gives the value for the Dirac cone anisotropy.

where $\epsilon_n$ is the energy of the $n$th particle and $n_F$ is the distribution of particles about the Fermi energy. From here we can calculate the specific heat

$$
\int \frac{d^2 k}{(2\pi)^2} \frac{\epsilon_n^{\frac{3}{2}}}{(\epsilon_n^{\frac{3}{4}} + 1)^2} \left( \frac{\epsilon_n}{T^2} \right) = \int \frac{d^2 k}{(2\pi)^2} \left( \frac{\epsilon_n}{2T} \right)^2 \frac{1}{\cosh^2 \left( \frac{\epsilon_n}{2T} \right)}.
$$

Changing variables such that $\epsilon_n = \sqrt{v_F^2 k_x^2 + v_\Delta^2 k_y^2} = \sqrt{\xi_x^2 + \xi_y^2}$ the formula for specific heat can be rewritten as

$$
C = \frac{1}{v_F v_\Delta} \int \frac{d\xi_x d\xi_y}{(2\pi)^2} \frac{\epsilon(\xi)^2}{4T^2} \frac{1}{\cosh^2 \left( \frac{\epsilon(\xi)}{2T} \right)} = \frac{v_F}{v_\Delta} \frac{1}{v_F^2} F_\alpha(T, H).
$$

This shows the specific heat to be roughly linearly dependent on the anisotropy ratio $\frac{v_F}{v_\Delta}$ [29]. In the high field YBCO 6.56 data there is no detectable sign of a vortex melting
thermodynamic phase change in either $C(T)$ at fixed field or $C(B)$ at fixed temperature in the ranges measured. This is important to point out because when the system reaches $H_c2$ (defined as the field needed to suppress the d-wave superconducting energy gap), the specific heat should no longer have a $\sqrt{H}$ dependence, and a thermodynamic signature is expected. Theoretically little is known about the vortex physics in the crossover regime. The experimental data imply that the $\sqrt{H}$ and subsequent physics relating to the specific heat are unaffected in this regime.

Figure 5.8: The value of $\gamma$ after subtraction of the residual is plotted as a function of magnetic field for YBCO 6.56 and $YBa_2Cu_3O_7$ from ref [15]. The data for $YBa_2Cu_3O_7$ was done up to magnetic fields of $16T$. The value is extended up to $45T$ where $A_c = 1$. The pre-factor of the $\sqrt{H}$ in YBCO 6.56 directly demonstrates that $\gamma$ up to $45T$ is measuring a fully developed d-wave superconducting gap. The pre-factor, $A_c$ was fit over 5 different field ranges ($0T - 16T$, $30T - 45T$, $16T - 30T$, $0T - 45T$, and the quantum oscillation $30T - 45T$ ) with each fit giving a value of $A_c = 0.45 \pm 4\% \frac{mJ}{molK^{5/2}}$. 
5.3 Extracting Background information from the $C(H)$ quantum oscillations

For very high magnetic fields, it is possible to generalize the nuclear Schottky anomaly due to the copper nucleus with a spin-$3/2$ to a four level system. The high temperature limit still contains the $\frac{\Delta B^2}{T^2}$ dependence with only the low temperature activation having additional contributions. After subtraction of the phonon term, only the high temperature part of the nuclear Schottky term, which contributes a temperature dependence, needs to be subtracted out. The data are therefore fit in the low temperature regime $C(T, B = 40T)/T$ to the following equation

$$\frac{C(T, 40T)}{T} = \gamma + \frac{B_T}{T^3}$$

(5.10)

where $B_T = \Delta^2 B^2 = 18.7$ is the Schottky coefficient at fixed magnetic field.

Next we hold the temperature constant and examine the magnetic field dependence of the specific heat. The magnetic field component to the specific heat is fit to a modified form from equation [14] in ref [15]

$$\frac{C(1K, B)}{T} = \gamma(B, T = 1K) + B_H B^2 + A_c \sqrt{B} + \alpha T$$

(5.11)

where $\gamma(0)$ is $2\text{mJ}/(\text{molK}^2)$ in our case, $\alpha$ is zero in our fit and $B_H$ is the nuclear Schottky coefficient at fixed temperature. From the fit $B_H = \frac{\Delta^2}{\gamma} = .0108$, and $A_c = 0.434$.

Comparing the two data sets provides a consistency check.

$$B_H T^3 = \frac{B_T}{B^2} \implies 0.0108(1)^3 \approx \frac{18.7}{40^2} = 0.0117 = \Delta^2 \implies \Delta = 0.106 \pm 0.002$$

(5.12)

The values for the nuclear Schottky energy gap are the same in two different specific heat parameter sweeps: One as a function of temperature in fixed magnetic field, the other as a function of magnetic field at fixed temperature. Also, the value for the $\sqrt{H}$ pre-factor, and $A_c$, closely match the calculated (0.464) value from the $\gamma(B) - \gamma(0)$ as a function of field plot, Figure 5.6. With the consistency check, it becomes possible to subtract out
contributions other than the electronic part of the specific heat. After subtracting away these components, the oscillations fit on top of the $\sqrt{H}$ background as seen in Figure 5.11. Interestingly, the specific heat as a function of field can be fit to a formula where the only physics needed to capture the data are the electronic, nuclear Schottky and d-wave gap contributions.

5.4 Electronic Schottky anomaly

The electronic "Schottky-like" anomaly in cuprates is attributed to chemical impurities on the copper sites that induce a local moment [18]. A simple example is the case of Zn or Cr substitution onto Cu sites where Zn actually removes a Cu spin-1/2 moment.
Specific heat on Cr substituted $YBa(Cu_{1-y}Cr_y)_3O_7$ has a low field contribution that is well modeled by a two level Schottky system with a g-factor of 2 [18]. The Zn and Cr specific heat measurements were the motivating factor attributing the electronic Schottky seen in YBCO as a result of paramagnetic centers arising from disorder [18].

In zero field the internal interactions order the moments, resulting in an internal magnetic field. For YBCO 6.56 at 0T, the data are well described with an internal field of 1T. Application of a magnetic field orders the internal moments such that at 12T the internal field is effectively zero, and the Schottky anomaly can be well characterized by only using the applied magnetic field value such that $B_{\text{eff}} = B_{\text{applied}}$. Therefore, at roughly 12T for the sample measured, the internal interactions arising from defects no longer play
Figure 5.11: The magnetic field dependence of $\gamma$ (closed circles) and 1K quantum oscillations (blue curve). The cyan line is a fit to $\gamma$. The oscillation is a fit to the equation (with the fit parameters described in the text): $C(T = 1K, B) = A_c\sqrt{H} + AJ_0(4\pi \frac{\omega_c}{\omega})\cos(2\pi(\frac{H}{m^*} - \frac{1}{2}))$

a significant role to the magnetic part of the heat capacity as the system is well described by a paramagnetic spin-1/2 Schottky anomaly. Figure 5.12 shows the Schottky anomaly in YBCO 6.56 and the model from a simple spin-1/2 two level Schottky system. As the electronic Schottky anomaly gets suppressed with field, $N$ should also decrease because the number of spin-1/2 paramagnetic centers is suppressed with increasing applied field. When $B_{eff}$ is constrained to equal $B_{applied}$, $N$ will increase because $B_{eff}$ is suppressed, forcing $z$ to be slightly smaller than its actual value. At 10T $N$ is nearly saturated while at 12T $N$ becomes saturated; therefore, one can think of this as the value for which $B_{int} = 0$. 

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Figure 5.12: The left hand panel is a contour plot of $C_{elect Schottky} = (C_{total} - \beta T^3 - \gamma T) T^{-1}$, the electronic Schottky specific heat for YBCO 6.56. The right hand side is a model of a 2-level spin-1/2 Schottky system with a g-factor of 2 and $N(B) = \frac{1}{B^\alpha}$, where $\alpha = 0.5$ to capture the tendencies. The model fits well using $B_{eff} = B_{applied}$. Deviations at higher fields from the two contours are caused by the formation of the nuclear Schottky anomaly.

5.5 Residual electronic term: $\gamma(0)$

The residual gamma term, $\gamma(0)$, is thought to arise solely from disorder as the value of $\gamma(0)$ increases with decreasing doping, and is larger in untwined YBCO versus twinned YBCO [18]. Furthermore, the larger $\gamma(0)$, the smaller the magnitude of the specific heat anomaly at $T_c$ even though the location of the transition temperature is unaffected. This suggests disorder destroys superconductivity and leads to the existence of normal state regions around these impurities, implying $\gamma(0)$ is related to the “volume fraction of superconductivity” [18]. High field Nernst effect measurements [10] [11], magnetization [43], NMR [14], STM [15,16] and the $\sqrt{H}$ dependence of the electronic part of the specific heat all support the idea of local superconductivity (phase separation) in the underdoped cuprates.

The intrinsic $\gamma(0)$ for YBCO is 2 $mJ mol^{-1} K^{-2}$ [18]. For LSCO in the underdoped regime $\gamma(0)$’s of 0.44 $mJ mol^{-1} K^{-2}$ have been achieved. Even though LSCO is known from transport to be inherently more disordered, the lower value of $\gamma(0)$ in LSCO compared to YBCO has been attributed to extra disorder due to Ba spin impurities for YBCO. While disorder undoubtably plays a role, by smearing out the d-wave gap node, the fact oscillations have been seen in YBCO down to 20$T$ and have yet to be seen in $LaSrCuO_{4+\delta}$,
La$_{1.80}$Sr$_{0.20}$CuO$_2$, or La$_{1.84}$Sr$_{0.16}$CuO$_2$ \cite{44} up to 85\,T with $T_c$ transition widths as narrow as 500\,mK suggests the difference in $\gamma(0)$ for LSCO and YBCO is too large to be explained from disorder only. A $\gamma(0)$ of 2\,mJ\,mol$^{-1}$\,K$^{-2}$ is on the order of copper, which is quite large. Among cuprates for which intrinsic $\gamma(0)$ has been measured, YBCO has the largest value and is the only cuprate to contain chains. It is possible that the additional density of states orginates from the chains. A definitive experiment to determine the chain contribution to $\gamma(0)$ would be a measurement of $\gamma(0)$ on a detwinned YBCO 6.51 sample where the chains are ordered othro-I then ortho-II.

### 5.6 Pocket counting

The effective mass $m^*$, is related to the curvature of the dispersion curve
Figure 5.14: Blue curve plots a clean d-wave superconducting gap. For a clean d-wave gap there is a single nodal point. The dotted line is an example of a d-wave gap in the presence of disorder. Disorder plays the role of removing the node and creating a small but finite contribution to the density of states.

\[ m^* = \frac{1}{\frac{d^2E}{dk^2}} \tag{5.13} \]

About \( \epsilon_F \) the Fermi surface effective mass relates to the specific heat for a two-dimensional system, where the density of states is constant, such that

\[ C = \frac{\pi^2 k_B^2}{3} g_{2D}(\epsilon_F) = \frac{\pi^2 k_B^2 N_A a^2}{3h^2} \sum_i m_i = 1.48m_Jmol^{-1}K^{-2} \sum_i \frac{m_i}{m_e} \]

\[ \Rightarrow \frac{C_{\text{total number of pockets}}}{T} = 1.48 \sum_i n_i \frac{m_i}{m_e} \tag{5.14} \]

where \( g(\epsilon_F) \) is the density of states, \( N_A \) is Avogadro’s number, \( a \) is the lattice spacing and \( m_e \) is the electron rest mass.

It is important to remember when counting the number of pockets in equation 5.14, the number of pockets is giving per CuO\(_2\) plane, and there are two planes per unit cell in YBCO. The pocket counting for various proposed YBCO Fermi surfaces is discussed in Figure 5.15.
From 5.13 it can be seen that the effective mass is one over the curvature of the band. Therefore, for an anisotropic two-dimensional Fermi surface pocket, the mass will be different in the x-direction and the y-direction. The mass that enters into the thermodynamic potential in LK formalism is then the geometric mean of the Fermi pocket anisotropy coming from the x-direction versus the y-direction. The energies of the Landau levels, $E_n = \hbar \omega_c (n + \frac{1}{2})$, are given by the cyclotron frequency, $\omega = \frac{eH}{(m_1 m_2)^{\frac{1}{2}}} c$, for an anisotropic pocket, such that the LK fitting determines a mass that is actually the geometric mean effective mass. Figure 5.16 plots the change in effective mass as the pocket becomes more anisotropic.

### 5.7 Sample preparation

$YBa_2Cu_3O_{7-\delta}$ is grown by the self flux method. The $Y_2O_3 - BaO - CuO$ melt is very reactive, leading to high levels of disorder caused by dissolved chemicals from the crucible. Most samples are grown in commercially purchased $Y_2O_3$ stabilized $ZrO_2$ crucibles (YSZ) [6]. During the $Y_2O_3 - BaO - CuO$ melt these crucibles corrode which yields a solid $BaZrO_3$ resulting in impurities as well as disturbing the growth. Furthermore, these crucibles are only 99 percent pure and can contain other impurities such as: $Al_2O_3$, $MgO$, $SiO_2$, $TiO_2$, and $Fe_2O_3$. The key to the clean samples from the UBC group has come from the use of hand fabricated $BaZrO_3$ crucibles that are inert and insoluble in the $Y_2O_3 - BaO - CuO$ melt. The UBC crucibles used for $YBa_2Cu_3O_{7-\delta}$ sample growth have resulted in ultraclean low disorder samples with $T_c$ transition widths of 0.200K and extremely sharp rocking curves of $\text{FWHM} = 0.007$ degrees, roughly 25 times sharper than $YBa_2Cu_3O_{7-\delta}$ grown from YSZ crucibles [6].

Above 400K on the underdoped side of the phase diagram $YBa_2Cu_3O_{7-\delta}$ goes through a tetragonal to orthorhombic structural phase transition which leads to the formation of twin boundaries. A twin boundary is the boundary between two grains with a-axis and b-axis exchanged. Figure 5.17 shows a twin boundary for an underoped cuprate. The twin boundaries are a large source of disorder. As such, for these studies twinned $YBa_2Cu_3O_{7-\delta}$
is put under pressure and allowed to cool below the structural phase transition, forcing a preferred direction of the orthorhombicity to form, thus de-twinning the sample.

\(YBa_2Cu_3O_{7-\delta}\) has two different copper sites; the chains or ribbons Cu(1) and the planes Cu(2) [6]. Figure 5.18 shows the structure of \(YBa_2Cu_3O_{7-\delta}\). Knowing the carrier density involves understanding how the holes get distributed amongst these two sites. Furthermore, in certain areas of phase space the density holes also depend on the oxygen ordering on the chain sites. In the phase space of YBCO 6.56, measuring the \(T_c\) by means of magnetization gives a reliable value for the doping. Also, in this phase space the oxygen ordering of the chains does not play a role in the calculated carrier density. A good method for determining the doping of \(YBa_2Cu_3O_{6+x}\) in the range of \(0.52 \leq x \leq 1\) is by measuring the superconducting transition temperature and comparing it with the established phase diagram as shown in Figure 5.19. The \(T_c\) value for YBCO 6.56 has been measured after initial growth and after the specific heat experiment (approx 1 year apart) and \(T_c\) (i.e. doping) has not changed. Figure 5.20 shows the values of \(T_c\) after the experiment, displaying the robustness of the UBC samples even after significant exposure to the high levels of humidity in Florida.

5.8 Additional experimental results

Figure 5.21 shows the Fourier transforms of the specific heat oscillations in which a single peak is observed at 530T. The effective mass can also be determined from the Fourier peak amplitude as a function of temperature [50]

\[
\phi(y) = 2y \frac{\cosh(y)}{\sinh^2(y)} - y^2 \frac{1 + \cosh^2(y)}{\sinh^3(y)}
\] (5.15)

where \(y = \frac{rT}{T_H}\), \(T_H = \frac{e^H}{2\pi^2k_Bm^*}\) and \(r\) is the rth harmonic. Figure 5.22 shows the effective mass value by fitting the experimental data to equation 5.15 where a value of the midpoint in \(1/H\), which happens to be \(H = 37.5T\), is used as the magnetic field value. The best fit is when \(m^* = 1.35m_e\), the same value determined from the simple node observation.

When low Landau level’s are reached the density of states can no longer be approximated with cosine function and higher order terms are expected to appear which will cause the
LK formalism to become invalid. In YBCO, experimentally these higher order terms have not been observed, and traditional LK theory correctly maps the Fermi surface. In the organic superconductor \((BEDT-TTF)_2Cu(NCS)_2\) with a similarly small Fermi surface pocket of 622T, for instance, no deviations in LK theory have been seen up to 60T, which corresponds to approximately 10th Landau level. In YBCO 45T reaches the 12\text{th} Landau level as seen in Figure 5.23.

Resistive measurements [52] on LSCO x=0.08 with a zero field \(T_c = 20K\) shows that the vortex melting line (defined as when the system has a finite resistance) happens at fields less than 15T at 1.5K. Specific heat in LSCO has been reported up to 12T in doped samples of x=0.069, 0.075 with superconducting transition temperatures of 12K and 15.6K. Neither of these cuprate superconductors-LSCO and YBCO-give any evidence of a thermodynamic phase transition at the vortex melting transition. The high field YBCO 6.56 data is consistent with the LSCO data where there is no detectable sign of a vortex melting thermodynamic phase change in either \(C(T)\) at fixed field or \(C(B)\) at fixed temperature in the ranges measured. It is important to point this out because when the system reaches \(H_{c2}\) (defined as the field needed to suppress the d-wave superconducting energy gap) the specific heat should no longer have a \(\sqrt{H}\) dependence, and a thermodynamic signature is expected. Theoretically little is known about the vortex physics in the crossover regime. The experimental data imply that the \(\sqrt{H}\) and subsequent physics relating to the specific heat are unaffected, and starting with a vortex lattice to model Landau level mixing not only greatly simplifies the problem but is physically motivated.

With the YBCO 6.56 sample in the superconducting state, and in a vacuum sitting at pumped He-4 temperature \(\sim 1.75K\) with good thermal contact with the calorimeter, the magnetic field is swept at a rate of 2T/min. Magnetic flux avalanches into the system causing a huge spike in the temperature. The temperature spike decreases linearly with applied magnetic field, reaching zero once the vortex melting transition is reached, as show in Figure 5.24. For at \(\sim 1.75K\) the vortex melting transition is around 25.5T. The flux jumps: (A) tell the sample is still well attached to the calorimeter, (B) indicate the sample
is superconducting, and (C) set the field starting value in which $C(B)$ measurements can reliably be measured.
Figure 5.15: Panel A is the unreconstructed CuO$_2$ plane cuprate Fermi surface in the very overdoped regime. For YBCO 6.56 with the effective mass as calculated from specific heat would yield a $\gamma_{\text{isotropic}} = 3.82mJ/(molK^2)$. Panel B is the proposed chain + BaO hybridization pocket from band-structure calculations [45]. The shape of the CuO+BaO pocket matches the shape determined from angular dependence quantum oscillation measurements [46]. The panel B scenario gives a $\gamma_{\text{isotropic}} = 1.91mJ/(molK^2)$. Panel C is the proposed ($\pi/2, \pi/2$) AF reconstructed Fermi surface in the CuO$_2$ plane. C1 assumes the specific heat measured mass comes from the electron pocket, while the hole pocket effective mass is taken for YBCO 6.51 from ref [47] and would propose a $\gamma_{\text{isotropic}} = 26.2mJ/(molK^2)$. C2 assumes the heavier mass is now the electron pocket, while the measured specific heat pocket comes from the holes, giving a $\gamma_{\text{isotropic}} = 18.8mJ/(molK^2)$. C3 assumes the specific heat mass is coming from the electron pocket while the hole pockets now follow the same MIT mass divergence scaling as the electron pocket from ref [48] so that the hole effective mass can be deduced for YBCO 6.56. The resulting gamma for C3: $\gamma_{\text{isotropic}} = 15mJ/(molK^2)$. The $\gamma_{\text{anisotropic}}$ column refers to the reduced value of gamma that would come from a 10:1 ratio non-isotropic pocket as explained in the text.
Figure 5.16: A plot of the change in effective mass as a function of the anisotropy in a two-dimensional Fermi surface pocket. A pocket with an anisotropy of 10:1 from a fully isotropic pocket reduces the $\gamma$ value by 42 percent. The blue circle represents a fully isotropic surface. The blue ovals are schematic representations of what amount of anisotropy needed to reduce the effective mass from the fully isotropic case.
Figure 5.17: The left hand picture shows a $CuO_4$ plane in the tetragonal state where $a = b$. Upon cooling in the underdoped region the system becomes orthorhombic, $a \neq b$ as shown in the center panel. Thermodynamically there is no preferred direction of twinning, that is $a > b$ or $a < b$ such that equal amounts of both orientation occur. The right hand panel depicts when two sections of $a > b$ and $b > a$ meet; the formation twin boundary.
Figure 5.18: The atomic structure of $YBa_2Cu_3O_{7-\delta}$. $YBa_2Cu_3O_{7-\delta}$ is a layered Perovskite structure, where layers of $CuO_2$ planes are separated by Yttrium atoms. Perpendicular to the planes are $CuO$ ribbons or chains. Barium atoms separated the planes and chains. The figure is taken from ref [49].
Figure 5.19: $T_c$ as a function of doping phase diagram for $YBa_2Cu_3O_{6+x}$. In the region of $x = 6.3 - 6.52$ the oxygen ordering of the chains changes $T_c$ and doping. Above $x = 6.52$ chain ordering no longer plays a role and $T_c$ can reliably be used to determine the chemical doping. The figure is taken from ref[6].

Figure 5.20: Magnetization plot as a function of temperature for YBCO 6.56 taken on Dec 10 2009 after the specific heat experiments, where $T_c = 60K$. 


Figure 5.21: Fourier transforms of the specific heat quantum oscillations in YBCO 6.56, after the background subtraction. Here it is assumed $B = \mu_0 H$. A single peak is observed at a frequency of $530T$. 
Figure 5.22: The Fourier transform amplitudes of the YBCO 6.56 specific heat oscillations as a function of temperature. The zero amplitude references the node. Fits to the data were done using equation 5.15. The best fit is when $m^* = 1.35 m_e$, the same mass determined from the oscillations model.
Figure 5.23: Filling factor as a function of $1/H$ for YBCO 6.56. At $45T$ the twelfth Landau Level has been reached.
Figure 5.24: The YBCO 6.56 sample is adiabatically separated from the bath at \( \sim 1K \). As the field is swept at 5\( T \) per min vortex avalanches greatly affect the temperature (by up to 9\( K \) visible from the inset) until the vortex melting transition is seen to occur at \( \sim 23T \), which is consist with transport measurements [51].
Figure 5.25: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)^2 e^{\Delta H}}{(1+e^{\Delta H})^2}$ from $2T - 5T$ (phonon term has been subtracted out). In the table $\gamma = g$, and $\Delta = d$. Fit parameters with *’s are globally fit. For this particular fit $H = H_{appplied}$, $\Delta$ is a global fit parameter and $N$ is a local fit parameter. The results for $\gamma$ in the $2T - 5T$ range closely match those in figure 5.26 when $H = H_{eff}$. 

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Figure 5.26: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)^2 e^{\Delta H}}{(1+e^{\Delta H})^2}$ from $2T - 5T$ (phonon term has been subtracted out). In the table $\gamma = g$, and $\Delta = d$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{eff}$, $\Delta$ is a global fit parameter and $N$ is a local fit parameter.
Figure 5.27: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)}{(1 + e^{\Delta H/2T})^2}$, from $2T - 5T$ (phonon term has been subtracted out). In the table $\gamma = g$, and $\Delta = d$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{eff}$, $\Delta$ is a global fit parameter and $N$ is a global fit parameter. $\gamma$ is somewhat higher than in figure 5.25 and 5.26 when $N$ is a global fit parameter. In the case of a Schottky anamoly the total number of paramagnetic spin $\frac{1}{2}$ arising from disorder would be expected to change as the magnetic field is increased and the spins become aligned to the field. Therefore, $N$ should be a local fit parameter and unconstrained.
Figure 5.28: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)}{(1+e^{\Delta H/T})^2} e^{\Delta H}$ from $2T - 5T$ (phonon term has been subtracted out). In the table $\gamma = g$, and $\Delta = d$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{applied}$, $\Delta$ is a global fit parameter and $N$ is a global fit parameter. Now $N$ is a global but $H = H_{applied}$. Again the result is a slightly larger $\gamma$. 

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Figure 5.29: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)^2 e^{\frac{\Delta H}{(1+e^{\frac{\Delta H}{T}})^2}}}{P(\Delta_{hyp} H)}$ from $6T - 15T$ (phonon term has been subtracted out). In the table $\gamma = g$, $\Delta = d$, and $\Delta_{hyp} = c$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{applied}$, $\Delta$ is a global fit parameter, $\Delta_{hyp}$ is a global fit, $N$ is a local fit parameter, and $P$ is a local fit parameter. This is the fit used in the conclusions section of the paper for fields 6T-15T. This fit makes it the most physically motivated as it sets the electronic Schottky and hyperfine Schottky anomaly energy scales as a fixed constant, while letting the amplitude change and only uses the applied magnetic field as an input parameter, not a value which is allowed to float.
Figure 5.30: Table of fit parameters for the equation $C = \gamma T + \frac{N (\frac{\Delta H}{T})^2 \Delta H}{(1 + e^{\frac{\Delta H}{T}})^2} + P(\frac{\Delta_{hyp} H}{T})^2$ from $6T - 15T$ (phonon term has been subtracted out). In the table $\gamma = g$, $\Delta = d$, and $\Delta_{hyp} = c$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{eff}$, $\Delta$ is a global fit parameter, $\Delta_{hyp}$ is a global fit, $N$ is a global fit parameter, and $P$ is a local fit parameter. Again forcing $N$ to be a global fit parameter slightly increases the calculated value of gamma.
Figure 5.31: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)^2 e^{\Delta H}}{(1+e^{\Delta H})^2 + \beta T^3}$ from $0.5T - 5T$. In the table $\gamma = g$, $\beta = b$, and $\Delta = d$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{\text{applied}}$, $\Delta$ is a global fit parameter and $N$ is a local fit parameter. The fit is done over a larger range and the phonon term is allowed to float. It is well established that the value of $\beta$ resulting from fits of the individual data sets in non-zero field, where the $\alpha T^2$ term is suppressed, can be significantly lower [16]. The value for $\beta$ changes by only a few percent.
Figure 5.32: Table of fit parameters for the equation $C = \gamma T + \frac{N(\Delta H)^2 \Delta H}{(1 + e^{\Delta H \beta})^2} + P(\Delta_{hyp} H)^2 + \beta T^3$ from $6T - 15T$. In the table $\gamma = g$, $\Delta = d$, $\beta = b$, and $\Delta_{hyp} = c$. Fit parameters with *'s are globally fit. For this particular fit $H = H_{eff}$, $\Delta$ is a global fit parameter, $\Delta_{hyp}$ is a global fit, $N$ is a local fit parameter, and $P$ is a local fit parameter. Again beta is allowed to float, and similar results as to figure 5.31, where beta varies only by a few percent across the entire magnetic field range. While these small changes in beta may be because of the $\alpha T^2$ term as described in ref. [16], another alternative could be the interpolation procedures when correcting for the magneto-resistance of the cernox. Never-the-less these changes are small and do not change the fact $gamma$ sits on a sqrt(H) background.
"Everything’s got a moral, if only you can find it."

-The Duchess

The nature of the magnetic-field-induced resistive state in high temperature cuprate superconductors remains a mystery. One interpretation is that at low doping the application of magnetic field destroys the d-wave superconducting gap to uncover the Fermi surface of the competing state that behaves like a conventional (i.e. Fermi Liquid) metal [9]. Another view is that an applied magnetic field destroys long range phase coherence but the superconducting gap amplitude survives [10, 11]. By measuring the specific heat of ultraclean YBCO 6.56 we have determined the evolution of the quasi-particle density of states from the superconducting state well into the magnetic field induced normal state. We have found that at very high magnetic fields the specific heat exhibits both the conventional temperature dependence and quantum oscillations expected for a Fermi Liquid. On the other hand, the magnetic field dependence of the quasi-particle density of states follows a $\sqrt{H}$ behavior that persists right through the zero resistance transition, evidencing a fully developed d-wave superconducting gap over the entire magnetic field range measured.

Specific heat of a material is a measure of heat necessary to raise the temperature of a given amount of material, typically a gram or a mol, by 1 kelvin. Near absolute zero, this bulk thermodynamic quantity is a sensitive probe of the low energy excitations of a complex quantum system. Such low energy excitations contain useful information about the nature
of the ground state. For the canonical example of an ordinary (so-called ‘Fermi liquid’) metal, the electronic (charge-carrying quasiparticles) component of specific heat vanishes linearly with temperature and the lattice vibration (phonon) component vanishes as $T^3$. The two different power-laws ultimately arise from the different quantum statistics of electrons (fermions) and phonons (bosons). With the application of an intense magnetic field $H$, the electronic orbits are quantized in a Fermi liquid metal, resulting in oscillations that are periodic in $1/H$ in many physical quantities, including magnetoresistance, magnetization and specific heat. In superconductors, specific heat probes the low energy excitations governed by the magnitude and symmetry of the superconducting energy gap.

In order to gain insight to the nature of the magnetic-field-induced normal state, the specific heat in an underdoped, high-quality, high temperature superconductor YBCO 6.56 has been measured as a function of temperature and magnetic field up to $45T$. Samples in this doping range are of particular interest, as the level of disorder is small enough for the observation of quantum oscillations in the resistive state [9] [47] [53] [54]. One of the motivations of the specific heat measurements reported here is to probe the evolution of the system’s low energy excitations with increasing magnetic field from the low field nodal d-wave superconducting state well into the high field low temperature resistive state. The nature of this low temperature, field-induced, resistive state in underdoped cuprates is a subject of intense attention [10, 11, 55, 56, 52, 57, 58] that is undergoing a resurgence [9] [47] [53] [54] [59] [60] [43] because understanding the resistive state is essential to understanding high temperature cuprate superconductivity, arguably the greatest challenge in condensed matter physics today.

At low $T$ and magnetic field $H$ of order a few Tesla, well below that needed to suppress superconductivity, it is established that the system is a nodal d-wave superconductor [61] [62] in the vortex state and that its low energy excitations behave as BCS quasiparticles. Previous measurements on optimally doped YBCO [16] [63] [41] [15] performed at magnetic fields up to $\sim 16T$ observed a low temperature $T$-linear coefficient to specific heat, $\gamma(H)$, that grows as $A_c \sqrt{H}$. The field independent coefficient $A_c$ was found to be in the range $0.88 - 1.3 \text{ mJ mol}^{-1} \text{ K}^{-2} \text{ T}^{-\frac{1}{2}}$. More importantly, such $H$-dependence is understood to be
a signature of the low field d-wave scaling [64]. In this regime, the energy associated with Landau-level quantization, \( \hbar \omega_c = \frac{\hbar e H}{m^* c} \), and the d-wave gap \( \Delta_0 \), satisfy \( \hbar \omega_c \ll \Delta_0 \). Here \( m^* \) is the effective mass and \( c \) is the speed of light. As a result many Landau levels are thoroughly mixed by the pairing term [65] [66]. At the semiclassical level, the \( \sqrt{H} \) increase of the electronic contribution to the specific heat is ascribed to the Doppler shifted d-wave quasiparticles [67] [68]. It is the magnetic-field-induced superconducting vortices which give rise to the additional low lying quasiparticles that contribute to the specific heat. While important for understanding the nature of the superconducting state, such small magnetic fields do not suppress superconductivity altogether and are insufficient to place the sample well into the resistive state at temperatures near 1K [16] [63] [41].

Here we perform specific heat measurements over the magnetic field range from 0 to 45T, which crosses through the irreversibility field \( (H_{irr} \approx 23 \pm 4T \text{ at } 1.5K) \) where vortex motion causes the superconductor to become resistive [48]. Such high fields provide a unique ability to track the evolution of low energy electronic excitations in YBCO continuously through the resistive transition. Our results in Figure 6.1 show two distinct components to the electronic specific heat: a high field oscillatory contribution atop a \( \sqrt{H} \) component that extends unperturbed to twice the magnetic field at which the resistive transition occurs as determined by both the disappearance of vortex flux jumps and transport measurements [48].

The remarkable persistence of the \( \sqrt{H} \) behaviour across \( H_{irr} \) suggests that the underlying physical reason for the magnetic field dependence of the electronic specific heat is the same in both the low field superconducting and the high field resistive regimes. Furthermore, for underdoped YBCO 6.56 we find \( A_c \), the prefactor of the \( \sqrt{H} \) contribution, to be 0.47 \( mJ \ mol^{-1} K^{-2} T^{-\frac{1}{2}} \), roughly half the value obtained from the low field measurements in the optimally doped samples [16] [41]. This is consistent with previously-reported thermal conductivity experiments [40] that estimate a factor of two decrease of the Dirac cone anisotropy from \( \approx 15.5 \) for optimally-doped YBCO 6.99 to \( \approx 7.9 \) for underdoped YBCO 6.54. Thus both the functional form and magnitude of the \( \sqrt{H} \) dependence indicate a fully
developed d-wave superconducting gap unperturbed by the superconducting transition from zero resistance at $H = 0$ to the resistive state at $H = 45T$.

The high field oscillatory contribution, visible at fields above $H_{irr}$ in Figure 6.1, is isolated and plotted in the Figure 6.2 for closer study. In standard Fermi Liquid metals, these oscillations result from quantization of electronic orbitals into so-called Landau energy levels. Similar quantum oscillations have been reported in YBCO from magneto-transport and magnetization measurements [9] [47] [53] [54]. Specific heat measurements provide an important additional advantage in that they probe the nature of the low energy excitation continuously across $H_{irr}$, below which both transport and magnetization signals are overwhelmingly dominated by the superconducting condensate. In a clean quasi two-dimensional Fermi Liquid the oscillatory component of the specific heat due to Landau level quantization of the orbits is given by the Lifshitz-Kosevich (LK) formula

$$\Delta C_v(T, H) = -AT \sum_{p=1}^{\infty} J_0(4\pi p \frac{t_w}{\hbar \omega_c}) \cos(2\pi p \frac{\mu}{\hbar \omega_c} - \frac{1}{2}))f''(x)$$

where $A$ is a constant, $\hbar \omega_c = \frac{\hbar e H}{mc}$, $x = \frac{2\pi^2 p k_B T}{\hbar \omega_c}$, $f''(x) = x \frac{1+ \cosh^2(z)}{\sinh^4(z)} - \frac{2 \cosh(z)}{\sinh^2(z)}$, $J_0$ is a Bessel function of the first kind $a t_w$ is the c-axis hopping energy, resulting in a small warping of the two dimensional Fermi surface.

The frequency of the oscillations is determined by the cross-sectional area of the Fermi surface or equivalently by the chemical potential $\mu$. In a disordered case, an additional Dingle term should also be included [27], but there is no evidence of a Dingle term in our data over the field ($30T - 45T$) and temperature ($1K - 5.5K$) ranges over which we measure. Quantum oscillation transport measurements find a Dingle temperature of 6.4K for YBCO 6.59 [31]. Even with a Dingle temperature as high as 12K, the effect of the Dingle term would be negligible in the temperature-magnetic-field phase space we measure specific heat quantum oscillations. The oscillations shown in Figure 6.2 were measured while sweeping the magnetic field. The data are fit between 30-45 T to the first harmonic ($p=1$ term) of the LK formula. Note that the function $f''(x)$ changes sign near $z = 1.6$, which accounts for the $\pi$-phase shift that is clearly visible between 1.7K and 5.5K. This node determines
an effective mass $m^* \approx 1.3 \pm 0.07m_e$. The frequency of the oscillations $F = 531 \pm 3$, the warping term $t_w = 15.7T$ and the amplitude $A = 8.5 \pm 1mJ\text{mol}^{-1}K^{-2}$ are fitted to our $T = 1\text{ K}$ data, for which the signal to noise ratio is the highest. The resulting formula is then compared with the data at higher temperature without further fitting, as shown in Figure 6.2.

Figure 6.1: Electronic component of the specific heat, $C(T, H) = \gamma(H)/T$, as a function of magnetic field for YBaCuO6.56. Red circles are extracted from $C(T)$ measurements. The red oscillatory data are from the $C(H)/T$ trace at $T = 1K$ after subtraction of well-characterized background terms [16] [63] [41] [15]. The line is a fit to $A_c\sqrt{H}$ where the pre-factor is determined to be $A_c = 0.47mJ\text{mol}^{-1}K^{-2}T^{-1/2}$. The cyan oscillation trace is $C(T = 1K, H) = A_c\sqrt{H} + AJ_0(\frac{\sqrt{H}}{2\alpha})\cos(2\pi(F(H) - \frac{1}{2}))$ with the fit parameters described in the text. The inset $\gamma(H) - \gamma(0)$ plotted as a function of $H^{0.5}$ with the oscillatory fit subtracted from quantum oscillation data.

The detailed agreement of specific heat data with LK formalism is compelling evidence that conventional Fermi Liquid quasiparticles exist at high magnetic fields in underdoped
YBCO. However, the novel and most interesting revelation of our specific heat data is the simultaneous presence of the $\sqrt{H}$ background that indicates the persistence of the low field d-wave superconducting gap that remains unmodified well into the resistive regime.

Figure 6.3 shows the linear temperature dependence of $C_v/T$ at $H=0$ and $H=45$ T up to 10 K, revealing an $H$ independent slope and an intercept that grows with increasing $H$. The $T^3$ contribution to $C_v$ originates from phonons, a term that is naturally $H$ independent. The finite intercept at $H=0$ indicates a finite density of states at low energy, a remarkably large value of $\gamma(0) \approx 1.85 \text{ mJ mol}^{-1} \text{ K}^{-2}$, although a similarly large value has been measured in clean optimally-doped $YBa_2Cu_3O_7$ samples [15] [18]. It has been proposed that this large value for $\gamma(0)$ originates from a disorder-generated finite density of quasiparticle states near the d-wave nodes, although the measured value is larger than in LSCO, a material that is considered to be significantly more disordered [39]. Alternatively, the data of Figure 6.3, the large value of $\gamma(0)$ and the quantum oscillations of Figure 6.2 would be consistent with the existence of a Fermi surface in YBCO that is unaffected by the presence of superconductivity.

For a two dimensional system with parabolic bands, where the density of states is constant, the total contribution to the specific heat is simply the sum of the number of pockets multiplied by the mass of the pocket.

$$\gamma_{total} = \gamma' \sum_i m_i n_i$$  \hspace{1cm} (6.2)

Where $\gamma' = 1.46 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Therefore, a single pocket per CuO2 plane (that is $n = 2, m* = 1.35m_e$) would yield $\gamma_{total} = 3.8 \text{ mJ mol}^{-1} \text{ K}^{-2}$, while a single pocket per unit cell ($n = 1, m* = 1.35m_e$) would yield $\gamma_{total} = 1.9 \text{ mJ mol}^{-1} \text{ K}^{-2}$. In the antiferromagnetic Fermi surface reconstruction scenario, where there is one pocket in the CuO2 plane at $(\pi, 0)(0, \pi)$ with $m* = 1.35m_e$ and two pockets at $(\pi/2, \pi/2)$ with an $m* = 3.8m_e$ [4]) would yield $\gamma_{total} = 26 \text{ mJ mol}^{-1} \text{ K}^{-2}$.

Coexistence of a Fermi surface with the robust d-wave pairing gap suggests, prima facie, existence of at least two distinct closed Fermi surfaces, one of which is d-wave gapped while the other is not. Recent band-structure calculations [45] [69] find that large Fermi surfaces...
derived from the CuO2 planes can coexist with a small pocket arising from the hybridization between CuO chains and orbitals of the BaO layer, which has a similar mass and frequency as the quantum oscillation measurements. If this were the case in YBCO6.56, then strong d-wave pairing originating in the CuO2 planes could give rise to a tiny proximity-induced gap on the small pocket, arising from weak interplane hopping. Such an explanation may account for every aspect of our specific heat data, but it is not without a complication: the same band structure calculations [45] [69] find that the small pocket does not exist in YBa2Cu4O8, a material in which quantum oscillations have been reported as well [53].

Most importantly, our measurements place a clear and strong constraint on any theory of the resistive state in underdoped YBCO. Specifically, since we find that the d-wave superconducting gap persists well into the high field resistive state, theoretical and experimental arguments claiming the existence of electron pockets in the anti-nodal directions - where the superconducting gap is at its maximum - appear to be effectively excluded.
Figure 6.2: (A) Model of the quantum oscillatory phenomenon in specific heat using the LK formula and fitting parameters discussed in the text for a single 531 ± 3T pocket with a warping of 15.7 ± 0.9T. The location of the node in C(T,H) phase space only depends on m*. For YBCO6.56, we find $m^* = 1.3 ± 0.07$ me. (B) Oscillatory part of the specific heat data (scatter plots) with profile traces from the 3D model (solid black) superimposed. The vertical dashed line serves as a guide to show the II phase shift between trace II and IV. (C) Color density plot of (A). Lines I,II,III,IV show the location in the temperature-field plane of the corresponding data (color) and profile trace (black) from (B).
Figure 6.3: $C/T$ as a function of $T^2$ for zero field (yellow circles) and the highest field measured, 45 T (blue triangles) with the field applied along the c-axis. In both the zero-field superconducting state and the high-field resistive state, the temperature dependence of the specific heat looks Fermi liquid like, as the only contributions appear to be from a (linear) electronic and (cubic) phonon term. The phonon term is field independent as shown by the unchanged value of the slope, $\beta = 0.395 mJ mol^{-1} K^{-4}$, consistent with previous reports [63][16]. The upper left are schematic Fermi surface representations of the $\Gamma$ and $(\pi, \pi)$ points, the only location closed pockets can formed in the Brillouin zone for YBCO, yielding a $\gamma_{total} = 3.8 mJ mol^{-1} K^{-2}$. The lower left inset is a schematic representation of a Fermi surface reconstruction giving one electron pocket and two hole pockets per CuO$_2$ plane, resulting in $\gamma_{total} = 26 mJ mol^{-1} K^{-2}$. 
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[30] S. C. Riggs. Ask Scott, it only took him what four years?


[36] 225 lock-in amplifier, Pamphlet.


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