Magnetic Measurements on Superconductors and Heavy Fermions.

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MAGNETIC MEASUREMENTS ON SUPERCONDUCTORS AND HEAVY FERMIONS

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Physics and Astronomy

by
Donavan Hall
B. S., University of Dallas, 1991
M. S., Louisiana State University, 1993
December 1997
Acknowledgments

Any experimental research project is a group effort; the work of many people came together to produce the results reported in this dissertation. This being the case, a list of acknowledgments are in order.

I wish to thank my advisor, Roy Goodrich, who has instructed me in the art of experimental physics and passed along as much of his wisdom as I could absorb. He has helped me learn the two cardinal virtues of experimental low temperature physics, patience and persistence. I owe an extra debt of thanks to him for bringing me to Louisiana. Our first meeting was during a visit he made to the University of Dallas. He told me about the promised land of the LSU physics department and his research efforts; it was a siren call I could not resist. The opportunity to do experimental physics and to work in a top class facility under the supervision of a man well respected in his field has been an honor and a privilege.

A number of my fellow graduate students deserve recognition. The afternoon brainstorming sessions at Highland Coffees with Alem Teklu contributed greatly to my understanding of the physics of electrons in metals and especially of superconductivity. We drank many cups of coffee and filled several trash cans full of equation-covered napkins in pursuit of our own theory of high $T_c$. Alem was also good enough to accompany me on a number
of trips to the National High Magnetic Field Laboratory in Tallahassee. He was an excellent assistant.

The necessary evil of any degree program is course requirements. The two years leading up to the general exams were years I will recall with an equal dose of terror and fondness. I firmly believe that it is a nearly impossible task to navigate successfully a full load of graduate physics courses on one’s own. Had it not been for my creative interaction with Russ Clark, Andrew Morse, Rob Nichols, and Erik Young, I would have learned only a tenth of the physics required of me. Learning works best as part of a process of dialog. During the summer I spent preparing for the general exams, I met every Saturday with Russ Clark and Ed Clayton for a day-long problem-solving session. Passing the general exams for me was a matter of team work. When one of would get stuck on something, usually the other two would have some clue as to what to do next.

Two former undergraduates deserve recognition for their contribution to the work reported herein. I had the opportunity to work with a number of undergraduate physics majors over the last six years, but two in particular did work that was outstanding and far surpassed that of the others. Angela Edens mastered the art of winding detection coils. I thank her for the many hours she spent preparing, winding, and balancing a custom detection coil for each sample we measured during 1992 and 1993. Steven Mitchell was a wizard of
computer programming. Steven and I worked together on the development of
the data acquisition and data analysis software used to procure and analyze
the data reported on in this dissertation. He handled the tedious task of
coding and debugging these vital systems. Steven was also good with his
hands, contributing to the research efforts of the lab through his manual
labor upon the construction of the vibration isolation and dewar support for
the new 1.5 K/18 T system installed in room 57. The next round of graduate
students will have a versatile system with which to make measurements.

The activity of laboratory research is not a demand only on the person
in the lab, but on his family. A special thanks should be extended to my
wife of the last three years who willingly has allowed me the time to spend
making measurements and to pursue my dreams.

For the last ten years I have been a student. This luxury has not been at
the expense of amassing a sizable debt. My father has been a willing source
of support, not only with respect to fiscal matters; he has been a source of
constant encouragement and inspiration. My earliest memories of my father
were of him reading. He always seemed to be reading or writing something. I
was a boy of seven or eight when my father completed his graduate education,
so I have vivid memories of his experiences. I suppose that to some extent
my early decision to pursue graduate studies in some field were inspired by
my father’s example. However, the choice of physics as a subject of study
was my own. He always allowed me the freedom to be myself and never tried
to control my destiny. He helped me develop a sense of confidence, without
which I probably would not have been able to enter physics, a field of study
which always seemed to me to be the ultimate intellectual challenge. When
I was an undergraduate, my father told me that when I choose my career,
I should find out what I really like to do and find some way to convince
somebody to pay me for doing it. At the time I did not know what the work
of an experimental physicist was, but I knew I enjoyed reading the popular
accounts of quantum mechanics, relativity, and astronomy. I decided that
I was going to find some way to get somebody to pay me to study physics.
My father gave me other choice bits of advice about graduate school. He
told me that the trick to finishing a Ph. D. is to stay in the program long
enough with the best professor you can find to direct you; if you do this you
are guaranteed to finish. There were points along the road when I wondered
if the end would ever come, but I stuck it out. I hope very soon to prove my
father's advice to be sound.

These last six years of graduate school have been especially demanding
of my mother who lives in the Seattle area. I have only been able to see her
a few times on rare holidays, but she has been a constant source of support
and encouragement. She too has allowed me the freedom to pursue my goals
and has done everything in her power to aid me in their attainment.
I will not draw out these personal acknowledgments too much further and test the patience of my reader, but this special acknowledgment must be included. Looking back along the train of events that has led to the composition of this dissertation, I can see many points where I could have pursued a different course or made a decision that would have taken me far from LSU and the past six years of study. One of those events seemed minor to me at the time, but in hindsight I figure that it played significantly in propelling me along the course I have chosen. For this event I wish to extend a special thanks to Father Ben, professor emeritus of physics at the University of Dallas. During my senior year at UD, Father Ben called me aside (I believe it was at my ΣΠΣ induction ceremony, but this might be a created memory) and told me that I would be wise to consider a profession in some other field than physics. He told me that, in his opinion, I would never survive graduate school and that my chances of ever gaining employment as a physicist were slim. Initially, my reaction was one of surprise and shock. But the more I thought about what he said, the more I wanted to prove him wrong. There have been many days when I wanted to throw down my soldering iron to become a philosopher, but those dreadful words would echo in my mind. To leave physics would be to prove Father Ben right.

In reality, my commitment to the study of physics cannot be summed up in a reaction to the words of a former teacher. My father suggested that
Father Ben was merely trying to encourage me and used the best motivation technique he knew of to ensure my success. Who knows? The real point to this story is that no one knows at the time what actions will influence a person. All the experiences of life and the people that we meet influence us in some way. I acknowledge all those who stirred within me the love of science. Some physicists might eschew the description of our field of study as romantic, but for some of us it is.

My romance with science began when I was young. I have long forgotten the name of a certain man and his wife who rented a house from my grandparents on our small farm in Oklahoma were I grew up. He was a geologist who worked for Conoco, I believe. He was an amateur astronomer with a telescope and a vast knowledge of the stars. Many an evening, my parents allowed me to stargaze with this man. I remember one night viewing the moons of Jupiter for the first time. Through his telescope the rings of Saturn were visible. These images sparked my imagination. He loaned me books about stars and planets; I read them all eagerly. One Christmas, he gave me a chemistry set. I was not quite sure what all the reactions were about, but the set was the occasion for me to ponder such questions as “why is this powder green?” and “why does it turn white when I dump this liquid on it?” I began to wonder about nature and I learned that such wondering could be fun. Somehow I have retained this romantic conception of my work
in physics. More than anything, it is this deep love for nature and all her works that compels me to discover her mysteries. I offer a hardy thanks to all my science teachers who taught me curiosity about nature.

One final acknowledgment is extended to the Reverend Charles A. Wood, formerly of St. Alban's Chapel. Our many conversations and lunch time philosophizing have helped tremendously to enliven my mind. Creative thinking is not done in a vacuum. A community of creative thinkers must be present to nurture the intellectual life of the whole. For their role in filling out my own creative thinking community, I would like to thank fellow students, Patrick Wood (soon to be a physician) and Steven Isaac (soon to be a historian). I have found that it is a rare thing to find deep thinking, intelligent individuals who can articulate their thoughts and express the relevance of their ideas in a compelling and stimulating way. To have found three such individuals within my small orbit around the LSU physics department is nothing short of a blessing.
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Abstract

Magnetization and de Haas - van Alphen (dHvA) measurements have been made on the high temperature superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$ and the heavy fermion CeB$_6$. First ever observations of the dHvA effect in Ba$_{0.6}$K$_{0.4}$BiO$_3$ are reported. Two dHvA spectrometers (pulsed field and field modulation) were used to measure two samples. Four frequencies are found in the field modulation data with the 11.6 kT orbit in good agreement with band structure calculations. The three lowest frequencies were measured with the pulsed field spectrometer. All dHvA measurements were made in the superconducting mixed state. These measurements indicate that Ba$_{0.6}$K$_{0.4}$BiO$_3$ has a Fermi surface. Magnetization measurements on Ba$_{0.6}$K$_{0.4}$BiO$_3$ suggest a superconducting to normal state phase transition of an order greater than two given that both the specific heat and susceptibility discontinuities across $T_c$ and $H_{c2}$ are zero. All thermodynamic critical fields exhibit a positive curvature as the temperature approaches zero. The present measurements suggest that the value of $H_{c2}(T=0)$ is higher than previously thought with the possibility that it diverges at zero temperature. Measurements on CeB$_6$ at temperatures as low as 25 mK and in fields as high as 50 T reveal that the dHvA frequency of the belly orbit in the $[100]$ direction changes as a function of field, decreasing in frequency with increasing applied field. This
is evidence that the Fermi surface of CeB$_6$ is polarized. Fermi surface polarization together with the observed magnetic field dependence of the cyclotron mass adequately account for the measured frequency shift. Additionally, the observed frequency shift can be modeled with a form of the Lifshitz-Kosevich equation modified to allow for the effects of strong correlations.
CHAPTER 1

General Introduction

1.1 Fermiology

Explaining the response of electrons to externally applied fields in the context of their host materials is a complex task. Only by making simplifying assumptions and idealizing approximations can we begin to cast into our mathematical language the puzzling interactions which give rise to the varied properties of conducting materials. The actual motions of electrons are inferred from the measurement of various large scale or collective properties of the material in question. The experimentalist finds himself measuring quantities like resistance, magnetization, or specific heat. The solid responds to the alteration of its environment—the variation of temperature, pressure, and magnetic field. The response to changes in each of these system variables yields valuable information about how the electrons move and interact inside the material. By carefully quantifying the macroscopic or collective properties of a system, we can develop a concept or theory of microscopic phenomena.
The special emphasis of this study is how certain materials respond to the application of an applied magnetic field. That the motion of electrons (or any charged particle) is quantized in the presence of an applied magnetic field is well understood. This quantization produces an oscillatory behavior in not only the magnetization of the sample, but in all the thermodynamic quantities associated with the material. These oscillations in the magnetic susceptibility as a function of field are called the de Haas – van Alphen (dHvA) effect after the first experimentalists to observe the effect, W. J. de Haas and P. M. van Alphen [de Haas and van Alphen, 1930]. They measured the oscillations in the metal bismuth not long after L. D. Landau predicted that such oscillations should manifest themselves given the right conditions [Landau, 1930]. These events evince the amazing synchronicity of theory and experiment. The experimental observation of dHvA in bismuth was made without knowledge of Landau’s pioneering work. Landau was dubious about the prospects of experimentally measuring the effect, given the limitations of contemporary cryo-magnetic systems. It is a testament to the incredible magnitude of the effect in bismuth that de Haas and van Alphen were allowed to observe the quantum oscillations and, thereby, to spearhead the experimental study of what has come to be known as the Fermi surface.
A Fermi surface is the defining characteristic of a metal. A metal is a substance with a Fermi surface (FS). To know the FS of a metal is to hold the key to understanding and calculating the various properties of the material [Bohm et al., 1985]. A Fermi surface is defined as "a surface of constant energy in a space defined by components of the wave vectors of a system of half-integral spin particles" [Goodrich, 1987]. The space in which a Fermi surface has its being is not the position space of everyday reality, but a momentum or wave-vector space (also called phase space). Half-integral spin particles, also called Fermions (e.g. electrons), thrown together into a common environment (e.g. a lattice of ions) will distribute themselves in the available energy levels in such a way that only two particles will be in each level – one up spin and one down spin particle. This self-arrangement in available energy levels was first postulated in 1926 independently by Enrico Fermi and Paul Dirac [Fermi, 1926; Dirac, 1926]. They expressed their idea mathematically as

\[ f_{FD}(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}, \quad (1.1) \]

where \( k_B \) is Boltzmann’s constant. Assuming that only a finite number of unbound Fermions exist in a given system, the highest energy level occupied (at zero temperature) is called the Fermi energy (or Fermi level). At \( T=0 \), no free or quasi-free electrons exist above the Fermi level. The wave vectors

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of the Fermions having this highest energy define the shape of the Fermi surface.

The reason that the Fermi surface is the key to understanding the properties of a metal is that only the few electrons with energies near the Fermi level contribute to the properties. The reason for this is that the Pauli exclusion principle, that only one electron may occupy any given quantum state, locks electrons in lower energy states. Electrons in quantum states well below the Fermi level cannot be excited easily into unoccupied higher energy levels. Effectively, then, electrons in low lying quantum states do not contribute to the measurable properties of a metal in any direct way other than to support (by a sort of quantum pressure) the higher energy electrons at the Fermi level. Electrons at the Fermi level are free to interact with and respond to external stimuli and phenomena internal to the lattice; they are not locked into their quantum states due to the fact that higher energy quantum states are unoccupied. All of the conduction electrons in a metal reside near the Fermi level. Therefore, any experimental technique sensitive to the Fermi surface will provide important details about the conduction phenomena in any given metallic system.

The dHvA effect is only one incredibly sensitive method for probing the electrons at Fermi surfaces. Other methods for studying the FS are magneto-acoustic geometrical effects, magnetoresistance, anomalous skin effect, the
radio-frequency size effect, cyclotron resonance, acoustical geometrical resonance, and the Shubnikov-de Haas effect.* Other less direct methods of probing the FS include: photo emission, positron annihilation, the Kohn effect, and Compton scattering. The special concern of this work is the dHvA effect, therefore, we will focus on it, although magnetoresistance and specific heat measurements made on CeB$_6$ will be discussed in Chapter 4, and magnetization measurements on Ba$_{0.6}$K$_{0.4}$BiO$_3$ comprise the bulk of Chapter 6. Often I will compare dHvA results with those obtained through the other methods.

The frequency of dHvA oscillations directly gives a measurement of the extremal area of a FS. By making successive measurements at several crystal orientations with respect to the applied field, the entire FS geometry can be mapped out. The amplitude of the dHvA oscillations also yields valuable information concerning the FS. By measuring the temperature dependence of the amplitude, the cyclotron effective mass of the charge carriers at the FS can be measured. The field dependence of the amplitude provides information about the intrinsic scattering of the charge carriers. Harmonic content in the dHvA oscillations is rich with additional information. Comparison of the amplitude of two dHvA harmonics allows for the determination of the Lande g-factor of the electrons.

*A number of these methods are discussed in the classic paper by Chambers [1956].
To measure the dHvA effect, experimental conditions and samples must meet a number of strict criteria derived from the requirement that the motion of an electron in a metal must complete a closed orbit and from the sharpness of the FS. Metals with a high scattering rate, such that electrons on the average are scattered out of their cyclotron orbits before completing a single circuit will produce weak or no observable signals. If the FS is broadened by high temperature then the resulting oscillations will be damped out by their mutual phase interference. Ideal observational conditions for the dHvA effect, therefore, are low temperatures, high magnetic fields, and high quality, single crystal samples. With sufficiently low temperatures and with the best samples, the dHvA effect can be observed easily in fields less than 10 T. However, the subject of this dissertation is the dHvA effect in heavy fermions (CeB$_6$) and high temperature superconductors (YBa$_2$Cu$_3$O$_7$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$). In heavy fermions, the large effective masses existing in this class of materials implies a low cyclotron frequency; therefore, more time is required to complete an orbit for a given scattering rate. Thus, in heavy fermions, it is more probable that the electron will scatter before an orbit is complete. Since cyclotron frequency is a function of electron effective mass and applied magnetic field, the probability to complete an orbit is increased with increasing field. We, therefore, employ high magnetic fields to study these materials. Steady fields of up to 32 tesla were used to study CeB$_6$. 

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High fields were necessary to study the high temperature superconductors (HTSc), but for other reasons that will be discussed later in the text (see Chapters 5 and 6). Both of the HTSc materials were studied in pulsed fields of up to 60 tesla.

Measuring the magnetic properties of materials requires the generation of high magnetic fields. The least expensive way to generate magnetic fields is with a superconducting magnet. Such a magnet consists of a series of coaxial solenoids wound with superconducting wire. The magnet is then cooled with liquid helium to below the critical temperature of the superconducting wires. Modest currents on the order of 150 amps can produce fields of up to 20 tesla in these types of magnets. Generation of steady fields higher than 20 tesla is an expensive endeavor. A number of state funded facilities around the world have water cooled resistive magnets capable of generating fields in excess of superconducting magnets. At the National High Magnetic Field Laboratory in Tallahassee, FL, one resistive magnet can produce a field of 33 tesla. The expense of these magnets comes in the amount of power required to sustain a field of 33 tesla. When fully energized the 33 tesla magnet at the NHMFL requires 34,000 amps at 16 megawatts. The bulk of the measurements presented in this dissertation were performed at the NHMFL using this 33 tesla magnet.
An alternative way of generating magnetic fields is to discharge a capacitor bank into a resistive solenoid cooled in liquid nitrogen. This discharge generates a field pulse which can reach fields of up to 60 tesla in a few milliseconds, decaying again on only a slightly longer time scale. Working with pulsed fields presents a wide range of experimental challenges not posed by steady field environments. The primary difficulty of using pulsed fields pertains to instrumentation and electrical circuitry. In Chapter 3, the advantages of pulsed fields will be discussed in comparison to steady fields. A series of pulsed field measurements were made on YBa$_2$Cu$_3$O$_7$ (YBCO) and Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO) at the Los Alamos division of the NHMFL.

Methods for measuring the magnetic properties of materials in a number of different scenarios will be discussed in the body of this thesis. One of the primary technical objectives of the work described here is the development of highly sensitive measurement techniques for probing the magnetic properties of materials in steady fields. The results of this effort and the physics we have learned in the process is the subject of this dissertation.

1.2 Overview

The following dissertation is an exposition of some recent work done in probing the magnetic properties of metals. The subject metals were selected primarily because of their intrinsic interest (i.e. not a lot is known about them
already) and the suitability of the materials to our experimental capabilities.

The primary focus of the body of measurements reported herein pertain to the de Haas - van Alphen effect. In Chapter 2, the theory of dHvA will be presented in a qualitative fashion, along with the most important mathematical relationships which describe the properties of the material's Fermi surface.

Chapter 3 contains a description of the experimental techniques employed to measure the dHvA effect. Details relating to the design of sensors and the measurement instrumentation will be revealed along with the many important techniques required to make successful, sensitive, and high quality measurements. Also, results of a magnetoresistance study of thick film ruthenium oxide based chip resistors is presented. These thick film chip resistors are important because they can be used for the determination of low temperatures at high magnetic fields. A phenomenological description of the magnetoresistive characteristics of these chips is presented to show their utility as low temperature (< 4 K) thermometers in magnetic fields.

Presentation of the results of a dHvA study of the heavy fermion compound, cerium hexaboride (CeB₆), comprise Chapter 4. Both field modulation and pulsed field techniques were used at low temperatures (0.025 - 2.5 K) and applied fields from 7 to 50 Tesla. This study was designed to provide accurate values of the orbit frequencies and cyclotron masses of the conduc-
tion electrons. The results reported here focus on the $\alpha_3$ orbit in the [100] direction. The dependence of the cyclotron mass on applied field for this orbit is extended in field range from previous results, and a field dependence of the dHvA frequency of the $\alpha_3$ orbit is observed. Evidence is given that the $\alpha_3$ orbit arises from a Fermi surface sheet having only one spin direction and that a modified form of the Lifshitz-Kosevich equation can be used to account for the data.

Chapter 5 is a preliminary report on our on-going efforts to measure the dHvA effect in the mixed state of patterned epitaxial single crystal films of YBa$_2$Cu$_3$O$_y$. The aim of this study was to determine the Fermi surface topologies, effective masses, and scattering rates for electrons in the normal state, and the interaction of normal electrons with flux vortices in the mixed state. Parameters determined from Fermi surface measurements in the normal state will place important restrictions on many theories of the mechanism of superconductivity.

Continuing the study of normal electrons in high temperature superconductors, the material, Ba$_{0.6}$K$_{0.4}$BiO$_3$ is the subject of Chapter 6. Extensive measurements of the magnetization of several superconducting single crystal samples of Ba$_{0.6}$K$_{0.4}$BiO$_3$ have been made using SQUID and force magnetometry at temperatures ranging between 1.3 to 350 K and in magnetic fields from near zero to 27 T. Hysteresis curves of magnetization versus field
allow a determination of the thermodynamic critical field, the reversibility field, and the lower and upper critical fields. The results from these crystals show high critical fields, and interesting thermodynamic properties including a critical point and a "fishtail" behavior below the reversibility field at low temperatures. Some observations concerning the thermodynamic order of the superconducting transition are given.

The final chapter, Chapter 7, will serve as a summary of the research program outlined in this dissertation, coupled with some commentary about the importance and relevance of these results.
CHAPTER 2

Theory

The following chapter is a discussion of the physical and mathematical models that describe the magnetic phenomena presented in this dissertation. The main subject of this chapter is the de Haas - van Alphen effect (dHvA). I will first discuss the canonical formalism of the dHvA effect, the Lifshitz-Kosevich (L-K) theory and then discuss the various modifications to this theory in the case of heavy fermions and superconductors. The reader in need of a more complete discussion of magnetic oscillations in metals is urged to consult the masterful work by D. Shoenberg [Shoenberg, 1984].

2.1 Electrons in Metals

2.1.1 Introduction

In the introduction I stated that a metal is defined as a material with a Fermi surface (FS). The FS is made up of free electrons, that is, electrons that are not localized or bound to an ion. These free electrons, called conduction electrons, are free (or at least quasi-free) to move throughout the metal. Left to themselves the electrons in a metal move in such a way that there is no net transport of energy. If we pretend for a moment that electrons are hard
spheres, then we can imagine the hard spheres moving in all directions, with no general tendency for the population of electrons to move in a preferred direction. Only under some external influence such as a temperature gradient or applied electric field does any net transport of energy occur."

The simplest model for electrons in a metal is called the free-electron approximation. In this approximation, we pretend that the electrons are like the non-interacting particles of an inert gas; we even call a system of electrons treated in this way an electron gas. The only interaction which the electrons observe is the restriction imposed by Fermi-Dirac statistics. From the Schrödinger equation, we can show that the energy of the electrons at the Fermi level in this free-electron gas is given by

\[ E_F = \frac{\hbar^2 k_F^2}{2m}, \]  

(2.1)

where \( k_F \) is the electron wave vector and \( m \) is the electron mass. All of the available energy levels up to \( E_F \) are filled at zero temperature with electrons. The free-electron gas yields the simplest possible Fermi surface geometry; the wave-vector \( k_F \) describes the radius of a sphere. The surface of this sphere is the surface of constant energy called the Fermi surface. In this simplest

*For an excellent basic introduction to electrons in metals, see C. M. Hurd's book [Hurd, 1975]. The information in the book is dated, but for basic, phenomenological explanations (models) of the workings of physical processes in condensed matter, it is an excellent starting place.
case we can call it the Fermi sphere. Additionally, the density of states for a
free-electron gas is

\[ g(E) = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2}. \]  

(2.2)

The number of electrons per unit volume in a small energy range \( \Delta E \) is

\[ n(E) \Delta E = g(E)f(E) \Delta E, \]  

(2.3)

where \( f(E) \) is the Fermi-Dirac distribution, given in Equation 1.1. Using
the number density and the density of states, the Fermi energy for a three di-

dimensional electron gas (for \( T=0 \)) can be evaluated analytically to yield

\[ E_F = \frac{\pi^2 \hbar^2}{2m} \left( \frac{3N}{\pi V} \right)^{2/3}, \]  

(2.4)

where \( N \) is the total number of electrons and \( V \) is the volume of the Fermi
sphere.

Before launching into a discussion of the effects of allowing electrons to
interact with the lattice, let us first apply a magnetic field to our free electron
gas. Because a magnetic field can do no work on a charged particle, no net
transport of energy occurs when an external magnetic field is applied to a
metal. The classical model of the electron as a little hard sphere (assumed
above) breaks down at this point. A quantum mechanical treatment of elec-
trons in metals shows that even though there is no net energy transport due to the application of the field, the motion of the electrons is affected and the available energy levels that the electrons can occupy in the material are quantized. This quantization is a consequence of the Lorentz force experienced by a charged particle in a magnetic field,

$$\vec{F} = \vec{F} = -\frac{e}{c} (\vec{v} \times \vec{B}).$$  \hspace{1cm} (2.5)

Landau [1930] was the first to solve this problem (a problem which is now taught and solved in every undergraduate quantum mechanics class). What Landau showed was that the motion of an electron in a magnetic field could be separated into a parallel and a perpendicular component. Motion parallel to the direction of the applied field is unaffected, while motion perpendicular to the field is subject to a constant redirection such that the path traced out by the electron would be circular. Landau solved the Schrödinger equation for an electron in a magnetic field and found that the solution to the perpendicular motion part was that of a simple harmonic oscillator. Hence, an electron will circulate in a magnetic with a frequency give by \(\omega_c = eB/m_c\), the cyclotron frequency, where \(e\) is the charge of the electron, \(B\) is the magnetic field, and \(m_c\) is the cyclotron mass. I should point out that Landau solved this problem for an electron in free space, not an electron in a metal. Solving
the Schrödinger equation for an electron in a metal (called a Bloch electron) is a difficult problem which has no analytic solution due to the fact that the crystal potential couples the parallel and perpendicular solutions of the motion equations. Therefore, it is the custom to solve the problem of electron motion in a metal in the semi-classical approximation.

2.1.2 Quantization of Electron Motion

The quantization of electron motion is the physical cause of the dHvA effect. A model of electron motion in a magnetic field can be constructed by using the Bohr-Sommerfeld quantization rule for periodic motion:

\[ \oint (\hbar \vec{k} - e\vec{A}/c) d\vec{R}' = (r + \gamma)2\pi\hbar, \]  

(2.6)

where \( \hbar \vec{k} \) is the momentum vector, \( e \) is the electron charge, \( \vec{A} \) is the magnetic vector potential, \( c \) is the speed of light, \( R' \) is the position variable, \( r \) is an integer, and \( \gamma \) is the phase. From this it can be shown that the area of the electron orbit in phase space is given by

\[ a = (r + \gamma)2\pi eH/c\hbar, \]  

(2.7)

where \( H \) is the applied magnetic field. This result was derived independently by Onsager [1952] and Lifshitz and Kosevich [1954]. In practice the value of
γ can be taken as \( \frac{1}{2} \), but Roth [1966] showed that γ differs slightly from \( \frac{1}{2} \) depending on energy and applied field.

This result gives us a way of conceptualizing the dHvA effect. If we imagine some surface (e.g. the Fermi sphere mentioned above) in phase space, a surface of constant energy, the quantization of electron motion produces orbits of electrons, Landau tubes (a three dimensional extension of the familiar Landau levels), that intersect the Fermi sphere and run parallel with the applied field as shown in Figure 2.1 (for the case of an ellipsoidal FS the tubes need not be parallel with the applied field). As the applied magnetic field is changed, the diameter of the Landau tube changes. As this happens the density of states changes at the extremal area of the sphere. As successive Landau tubes pass through the Fermi sphere the density of states rises and falls—the density of states oscillates periodically with inverse field. This leads to an oscillation in all thermodynamic properties associated with the density of states. The oscillations that arise in this way are called Landau quantum oscillations (LQO). The dHvA effect is the oscillation of the magnetization of a metal as the applied magnetic field is changed. LQO is the more inclusive term; whereas dHvA refers to the oscillation in the magnetization, Shubnikov-de Haas refers to the oscillation in resistivity, etc.
Figure 2.1: This is a Fermi sphere showing intersections with Landau tubes. The dependence of the tube radius on applied magnetic field gives rise to the de Haas - van Alphen effect.

Each Landau tube is associated with a quantum number, \( r \). The energy difference between Landau tube \( r \) and \( r + 1 \) is given by \( \hbar \omega_c \) or \( \beta H \), where \( \beta = e\hbar/mc \) is the Bohr magneton.

2.1.3 Lattice Effects

So far I have treated electrons as independent bodies acting only under the limitation of Fermi-Dirac statistics. Electrons in metals are not really free in the sense given above, but only approximately free. Several limitations are placed on the real electrons in a metal. First, the electrons are confined to the spatial extent of the lattice of metallic ions in which they reside. However, sample sizes are usually so large compared to the size of the electron that an
infinite lattice approximation is usually a good one. Second, the electrons interact with the electromagnetic fields of the lattice ions. The ion potential distorts the Fermi sphere, in some cases even opening up gaps in the energy level spectrum. Third, the periodicity of the ion lattice and the wave nature of electrons leads to Bragg reflection of the electrons at the boundary of the Brillouin zone (the Wigner-Seitz primitive cell in the reciprocal lattice).

Interesting Fermi surface geometries result when the radius of the Fermi sphere is larger than the Brillouin zone. The resulting crossing points result in Bragg reflection where the wavevector of the reflecting electron changes direction. This effectively breaks the Fermi surface into several sheets. It is also possible to have sheets of holes. In a paper on the Fermi surfaces of polyvalent metals, Harrison [1960] outlines a method for constructing Fermi surfaces by a simple geometric method. Experimentally determining the shape of the Fermi surface from the dHvA effect is a straightforward procedure. Extremal areas are determined from a measurement of the dHvA frequency. Fermi surface curvature can be derived from measurement of the electron wavevectors. In practice, experimental results make use of detailed energy band calculations for assistance in determining complicated Fermi surface geometries.
2.1.4 Other Interaction Effects

Ion potentials and Bragg reflection do not exhaust the possible influences experienced by an electron in a metal. Indeed, the extent of the number of effects that bear on electron motion in a metal is in part what drives interest in the study of metallic systems. After a discussion of the Lifshitz-Kosevich theory of the dHvA effect, I will outline the effects that electron-electron and electron-phonon interactions, and a host of other many body interactions, have on the conduction electrons at the Fermi surface.

2.2 The de Haas - van Alphen Effect

The Onsager relation given above (Equation 2.7) can be rewritten in terms of the frequency, $F$, of the oscillations.

$$\Delta \left( \frac{1}{B} \right) = F = \frac{\hbar A}{2\pi e}. \tag{2.8}$$

The dHvA oscillations are periodic in $\frac{1}{B}$.

Assuming the nearly free electron approximation, Lifshitz and Kosevich [1954] (see also [Lifshitz and Kosevich, 1956]) developed a detailed theory of dHvA oscillations. The principle equations which represent the oscillatory

*A clear discussion of the dHvA effect has been given by Gold [1968].
magnetization are given by

\[
\tilde{M}_\parallel = - \left( \frac{e^8}{2\pi^5\hbar} \right) \frac{B^{1/2} F}{m^*|A^\eta|^1/2} \sum_{r=1}^\infty R_r \sin \left( 2\pi r \left( \frac{F}{B} - \gamma \right) \pm \frac{\pi}{4} \right),
\]

(2.9)

and

\[
\tilde{M}_\perp = - \frac{1}{F} \frac{\partial F}{\partial \theta} \tilde{M}_\parallel,
\]

(2.10)

where

\[
R_r = \frac{R_T(r)R_D(r)R_s(r)}{r^{3/2}},
\]

(2.11)

and \( r \) is the harmonic index of the magnetization oscillation. \( \tilde{M}_\parallel \) and \( \tilde{M}_\perp \) are the components of the oscillatory magnetization in directions parallel and perpendicular to the applied magnetic field respectively.

The quantity \( R_r \) contains all the pertinent reduction factors, factors which reduce the amplitude of the dHvA oscillations. First, \( R_T \) is the reduction due to the broadening of the FS by temperature. It is called the finite temperature effect and has the form

\[
R_T = \frac{ZTr}{\sinh (ZTr)},
\]

(2.12)
where $Z = \frac{2\pi^2 k_B}{\beta H}$. Next, $R_D$ is the reduction due to the finite scattering time, a measure of the intrinsic electron scattering in the metal having the form

$$R_D = e^{-Z\pi r}, \quad (2.13)$$

where $x = \frac{A}{2\pi k_\tau}$ is called the Dingle temperature. Finally, $R_s$ is the spin reduction factor

$$R_s = \cos \left( \frac{\pi}{2} pg \frac{m}{m_0} \right). \quad (2.14)$$

Two other reduction factors are due to sample and field inhomogeneity. If the sample has an inhomogeneous composition, the the single frequency amplitude is reduced by the factor

$$R_{\Delta F} = e^{Z x' r}, \quad (2.15)$$

where $x' = \frac{\beta (\Delta F_0)}{\pi k}$, and $\Delta F_0$ is the spread in frequency. If the applied magnetic field is inhomogeneous across the sample, the signal is reduced by

$$R_{\Delta H} = \frac{\sin(Z'\tau)}{Z'\tau}, \quad (2.16)$$

where $Z' = \frac{\pi F_{\Delta H}}{H^2}$, and $\Delta H$ is the field inhomogeneity.
LK theory has been tested experimentally and found to be an excellent description of the dHvA effect in a number of normal metals at low fields where the quantization number of the occupied Landau levels is large. Two effects lead to a deviation of the dHvA effect from the LK description: magnetic breakdown (MB) [Shoenberg, 1960; Cohen and Falicov, 1961; Blount, 1962; Priestley, 1963; Stark and Falicov, 1967; Falicov and Zuckerman, 1967; Kishigi et al., 1995] and the Shoenberg effect or magnetic interaction (MI) [Shoenberg, 1962]. Magnetic breakdown occurs when electrons tunnel from one FS sheet to another (the electrons fail to Bragg reflect) giving rise to orbits which are sums and differences of primary FS orbits; hence, new frequencies appear in the dHvA spectrum [Shoenberg, 1984, Chapter 7]. Magnetic breakdown is the magnetic equivalent of Zener breakdown in insulators and semimetals where the electric force $eE$ is replaced by the Lorentz force $e v H / c$. Blount [1962] formulated MB in these terms and showed that the condition for its observation is

$$\hbar \omega_0 \geq \frac{\epsilon_g^2}{E_F},$$  \hspace{1cm} (2.17)

where $\epsilon_g$ is the energy gap between orbits. The applied field at which MB occurs is calculated to be approximately

$$H_{MB} \sim \frac{mc}{\hbar k} \frac{\epsilon_g^2}{E_F} = \frac{H}{\hbar \omega_c} \frac{\epsilon_g^2}{E_F}.$$  \hspace{1cm} (2.18)
Thus the criterion for the observation of magnetic breakdown is that $H$ be greater than or, at least, equal to $H_{MB}$.

Magnetic interaction occurs because the electron responds to the total field $B$, not simply the applied field $H$ [Shoenberg, 1984, Chapter 6]. When the LK equation was derived, the oscillatory part of the magnetization $\tilde{M}$ was treated as a function of $H$, a consequence of the independent electron approximation. However, the experimental work of Shoenberg [1962] and the theoretical work of Holstein et al. [1973] (and a subsequent simpler derivation by Pippard [1980]) showed that $B$ is the correct field seen by the electrons. This adds an extra term to the LK equation above (Equation 2.9). The LK equation modified for the Shoenberg effect is

$$\tilde{M}' = \tilde{M} + 4\pi M \frac{d\tilde{M}}{dH}. \quad (2.19)$$

When $4\pi \frac{d\tilde{M}}{dH} \approx 1$, the magnetic interaction effects are important and this term must be included in the LK expression. The effect is largest when the oscillatory part of the magnetization nearly corresponds to the period of a single oscillation, $\Delta(1/B) = H^2/F$. The signature of the Shoenberg effect is an increase in the harmonic content of the dHvA signal and a modification of the temperature and field dependence of the signal amplitude due to modulation by $\tilde{M}$. The most harmonic content is achieved when the modu-
lation field amplitude is small. In this case none of the harmonics is reduced because of over modulation. Both MB and MI will be discussed later in the context of the measurements made on HF's and HTSc's.

2.3 Modifications to LK Theory

The subject materials of this dissertation exhibit interactions which lie outside the simplifying assumptions made in the formulation of LK theory. Many body effects in heavy fermions and in high temperature superconductor challenge the conceptual applicability of LK theory to these materials. In this section I will examine how LK theory might be modified when many body effects are included in the mathematical description of the dHvA effect.†

2.3.1 Many Body Effects

LK theory was developed in the independent electron interpretation with the crystal lattice supplying an arbitrary dispersion relation. A strong Coulomb interaction between conduction electrons invalidates this approximation because the electrons in such a metal cannot be treated as if they were independent of each other. In addition to the Coulomb interaction, other interactions are important in heavy fermions and high temperature superconductors. In heavy fermions, the charge carriers interact strongly with the d and f electrons associated with a rare earth ion. Electrons in HTSc interact with fluxons.

†This discussion is drawn primarily from [Shoenberg, 1984, pp. 73 - 82]. See also [Haanappel, 1992, pp. 12 - 13].
Clearly, it would seem that the independent electron approximation would leave out important features of the dHvA effect in these materials.

The existence of a FS is assumed in LK theory. The FS is defined as a surface of constant energy in phase space which separates the occupied energy levels from the unoccupied at T=0. Many body theory dispenses with the concept of the electron in favor of an entity called a quasiparticle. A quasiparticle is not an individual particle, but it is an entity which is arbitrarily objectified (individuated) from a unified (interacting) system. More specifically, a quasiparticle is an electron plus all of its interactions with other constituents of its contextual system. The many body nature of electrons in metals stems from the fact that each electron interacts in some way and to some extent with all other electrons and perhaps with other phenomena in the lattice. Since all the parts of this system are interacting, it is impossible to isolate a single electron and affect its motion without influencing the motions of other electrons in the system. The collective, many body effects of a large number of electrons interacting can give rise to a number of new phenomena which cannot be anticipated through an analysis of the interactions of only a few electrons (e.g. plasmons and superconductivity).

To make calculations on many body systems, a number of techniques were developed. Landau's Fermi liquid theory [Landau, 1957a; Landau, 1957b; Landau, 1959] dispenses with attempts to describe the microscopic
motion of electrons in order to focus on a description of the whole system of electrons. Such a shift of focus allows for a great simplification of the mathematical description of the whole system. In Fermi liquid theory, a system of strongly interacting electrons can be treated as a system of weakly interacting quasiparticles allowing for a one-to-one correspondence between electron and quasiparticle states. In this picture, quasiparticles are electrons with renormalized masses. Luttinger [1960] showed that because the distribution function of the quasi-particles has discontinuities at $T = 0$ for certain momentum values, the resulting constant energy surface in phase space is different from a FS of non-interacting particles that does not have such discontinuities. As it turns out in the non-spherical case, the FS for interacting and non-interacting particles have equal volumes. Therefore, it seems that a FS is possible in many body systems. Thus LK theory is still valid when applied to the calculation of dHvA frequencies and FS extremal areas in many body systems.

Further work by Luttinger [1961] and by Bychov and Gorkov [1962] showed that the electron-electron (e-e) interaction does not change the form of the LK equation (Equation 2.9), but that other parameters, such as the g-factor* and cyclotron effective mass, might differ from the functional forms given. But in the case of possible mass enhancement, the effect is small,

---

*The Landé g-factor is the ratio of $\mathbf{S} \cdot \mathbf{L}$ along $\mathbf{J}$ to the angular momentum vector $\mathbf{J}$.
usually on the order of $10^{-2}$. The modification of the g-factor might be more significant; e.g. the g-factor for potassium goes from 2 to 2.8 [Shoenberg, 1984, p. 78]. Thus, the frequencies and amplitudes of the dHvA oscillations remain unchanged in the many body case. The difference between the interacting case and the non-interacting case is the phase.

It was shown by Fowler and Prange [1965] and by Engelsberg and Simpson [1970] that the electron-phonon (e-p) interaction modifies the LK equations only at low temperatures and high magnetic fields. The finite temperature reduction factor remains the same except that the cyclotron mass associated with the quasiparticle is enhanced by a factor of $(1 + \lambda)$.

As Shoenberg points out in his book, many body effects do not, in general, change the form of LK theory, but only modify its parameters. Testing the modifications of the LK parameters is a subject which this dissertation will address. Namely, the renormalization of the cyclotron mass in the heavy fermion CeB$_6$ is an example of how the interaction of electrons via spin fluctuations affects the functional form of the LK theory. In fact, the observation of the dHvA effect in heavy fermions has revived interest in reformulations of LK theory. I will have more to say about this in Chapter 4. In addition to modification of the LK theory, we shall also see that additional scattering effects must be taken account when working in the mixed state of HTSc. This will be taken up in Chapter 5.
2.3.2 Modifications due to Superconductivity

The experiments reviewed in Chapters 5 and 6 demonstrate that it is possible to observe Landau quantum oscillations (LQO) in the mixed state of extreme type-II superconductors. More important for the high temperature superconductor materials, the experiments demonstrate that it is not necessary to exceed $H_{c2}$ in order to obtain high precision information about the Fermi surface (FS) and the properties of the carriers at the Fermi energy. Thus, valuable information should be obtained about the Fermi liquid state and the electronic structure of HTSc materials. Although there is every indication from the few existing experiments that the measurements of the dHvA effect in these materials are possible, there is very little theory for the normal electrons existing in the mixed superconducting state. Consequently, the importance of the measurements reported in this dissertation lies in the information about the interaction of normal charge carriers with the fluxoid lattice, about how LQO are modified by superconductivity, and about how type-II superconductivity is affected by Landau level quantization—in short, exploration of the new physics of normal electrons in the mixed state—that can be extracted from the data. The study of LQO modifications of super-

\footnote{Reviews of the fermiology of high temperature superconductors (HTSc) focusing on theory and experiment have been written by Abrahams [1991] and Peter [1991] respectively. A review of dHvA experiments in the superconducting state has been written by Springford and Wasserman [1996].}
conductivity is not confined to HTSc materials; *extreme* type-II materials (where the penetration depth is much greater than the coherence length, $\lambda \gg \xi$) are sufficient for profitable investigation.

The Abrikosov-Gorkov (AG) vortex theory of type-II superconductors employs a semiclassical approximation that ignores the Landau level structure of the electron system. Including the Landau level structure into a theory of type II superconductivity leads to some interesting phenomena: (1) the $T_c(H)$ curve develops dHvA-like oscillations in the normal state, (2) reentrant superconductivity at high fields, and (3) the superconducting transition temperature is enhanced by an applied field due to the absence of diamagnetic pair breaking. The fields at which these effects might be observed in type-II superconductors (such as Al, Nb or Pb alloys) would require applied fields of thousands of teslas. However, in low-carrier-density semiconductors and semimetals (such as Ge, GeTe, SnTe, GaAs, Bi, SrTiO$_3$, etc), these effects might be observed using fields of a magnitude routinely achieved [Tesanovic et al., 1991]. Even though the study reported in this dissertation does not aim at verifying this theory, it is an important illustration of how Landau level quantization can effect the properties of metals at high magnetic fields.

The behavior of superconductivity in high magnetic fields is of considerable interest. The theoretical aspects of this subject have been reviewed by Rasolt and Tesanovic [1992]. Several authors have considered the modi-
fications of LQO due to the simultaneous presence of superconductivity and normal electrons in the mixed state [Markiewicz et al., 1988; Maniv et al., 1988; Stephen, 1991; Maniv et al., 1991; Maniv et al., 1992a; Maniv et al., 1992b; Maniv et al., 1993b; Maniv et al., 1993a]. For a quasi-two dimensional superconductor with H perpendicular to the layers, Markiewicz et al. [1988] found that the standard expression for the dHvA amplitude is modulated by an additional factor of

\[
\frac{\sin(2\pi \Theta/\hbar \omega_c)}{(2\pi \Theta/\hbar \omega_c)} \approx \frac{\sin x}{x},
\]

(2.20)

where \( \Theta \) is the effective Debye temperature for the (still unknown) bosons that provide the superconducting pairing. This additional factor raises the possibility that accurate dHvA measurements in the mixed state can provide information similar to that given by tunneling studies in ordinary superconductors [Markiewicz et al., 1988]. Maniv et al. [1993b] have carried this argument further to contend that observations of LQO in the mixed state may provide a way to determine the nature of the pairing mechanism of HTSc materials. They find that the superconducting order parameter exhibits strong LQO at low temperatures and (with some dependence on the value of the in-plane cyclotron mass) that the dHvA-like peaks are split into doublets. The peak-doubling is attributed to enhanced pair-pair repulsion.
at the peaks of the density states, which reduces the superconducting order. Thus, this new structure would appear at least as new dHvA frequencies and perhaps as resolved peaks, and is directly related to the pairing correlation. However, Miyake [1993] strongly disagrees with the conclusions of Markiewicz et al. [1988]. Miyake shows that the oscillatory part of the superconducting order parameter is negligible and does not contribute significantly to the dHvA effect. Miyake goes on to show that the dHvA effect should still be observable in both the normal and mixed states given a sufficiently small gap $\Delta$. He predicts that in hard superconductors where the gap goes to zero at some points along the cyclotron orbit, a measurable amplitude difference of the dHvA effect between the normal and mixed states should be observed. This conclusion seems to call into question the validity of Markiewicz et al.'s calculations, but the prevailing current opinion is that oscillations in the superconducting order parameter are significant in any complete treatment of dHvA in the mixed state [Norman et al., 1995].

In a recent paper, Maniv et al. [1997] have shown that the dHvA amplitude will change sign at a given field $H_{\text{inv}}$ below $H_{\text{c2}}$ in sufficiently pure superconducting materials. This change in sign results from out of phase oscillations in the "superconducting condensation energy with respect to the normal electrons." They describe this effect as "related to the opening of a deep hole in the quasi particle density of states at the highest occupied Lan-
dau band by the increasing [superconducting] order parameter below $H_{c2}$.

They base this conclusion on a mean field theory treatment of a pure type-II superconductor. The highest occupied Landau band is split by the superconducting order parameter. The magnetic subbands cross the FS. Even if a great number of bands are present at the FS this splitting should take place, so in principle this effect is observable in three dimensional materials as well. This effect is very sensitive to phase smearing from imperfections in the lattice, including disorder in the vortex lattice. Maniv et al. cite this disorder as explanation for why no observation of this 180° phase shift has been made in the mixed state dHvA experiments carried out thus far.

Stephen [1991] has calculated the quasi-particle excitations above the gap in the region outside the vortex cores in the mixed state. A Landau level-like structure is found, again leading to dHvA oscillations. The amplitude of the oscillations is found to decrease with increasing value of the order parameter $\Delta$, an effect that is maximized for low Landau quantum level number, i.e. for low carrier density and high applied field. Again, information about the superconductive pairing mechanism is expected to appear in the dHvA oscillations.

Norman et al. [1995] present an exact mean field treatment of the mixed state. They focus on the quasiparticle electronic structure and magnetization in the 2D limit. Landau levels near the Fermi level become vortex core
bound states as the applied field is lowered. Three interactions complicate this calculation: the field dependence of the Landau level broadening, the oscillations of order parameter, the vortex-vortex interaction, and by the fact that translational symmetry in the mixed state is broken by the vortex lattice. They find that when the average of the superconducting gap becomes of the order of the cyclotron energy the amplitude of the dHvA oscillations goes to zero. The results of Norman et al. are in agreement with those of Maki [1991] and Stephen aside from the fact that they find the Landau level broadening varies as a function of $\Delta_0 n_\mu^{-1/4}$ rather than $\Delta_0^2 n_\mu^{-1/2}$, where $\Delta_0$ is the order parameter and $n_\mu$ is the Landau level number.

Markiewicz et al. [1988] suggested that the presence of Landau level quantization must alter the way in which states can be paired to give superconductivity. In their calculations of LQO in the mixed state, they assumed that pairs must be formed within individual Landau levels. In an appendix they show that there are several alternative pairing schemes to the time reversed Cooper pairing that will preserve the Cooper instability and superconductivity, albeit with a lower $T_c$. The calculation by Stephen [1991] of a Landau level-like structure in the quasiparticle spectrum outside the vortex cores also results in a self-consistently calculated superconducting order parameter that has a more complicated structure due to contributions from the Landau levels.
A number of authors have suggested that Landau level quantization should modify the properties of a superconductor [Frohlich and Terreaux, 1965; Rajagopal and Vasudevan, 1966a; Rajagopal and Vasudevan, 1966b; Gunther and Gruenberg, 1966; Brandt et al., 1967; Gruenberg and Gunther, 1968]. Frohlich and Terreaux [1965] predicted that at high enough fields where only one Landau level was occupied, the material would experience a transition into a reentrant superconducting phase. Rajagopal and Vasudevan [1966a] and Gruenberg and Gunther [1968] showed, in addition to reentrant superconductivity, that Landau level quantization would cause $T_c$ to oscillate with increasing magnetic field at low temperatures and that the gap function would experience oscillations with the same period as the dHvA effect. Gruenberg and Gunther also showed that the effect of non-zero temperatures, impurity scattering, or of a charge carrier g-factor differing even slightly from an even integer, would suppress the reentrant superconducting behavior.

Several groups [Rasolt, 1987; Tesanovic and Rasolt, 1989; Tesanovic et al., 1989; Maniv et al., 1993b], have predicted that the presence of Landau level quantization, together with small cyclotron effective mass values, should dramatically smear out and change the shape of the superconducting-normal phase transition boundary (i.e. the $H_d(T)$ curve) from the conventional Abrikosov-Gorkov curve, and the question of reentrant, field-induced superconductivity has been revisited. Maniv and Markiewicz et al. find that the
low-field and high field edges of the phase boundary separate, so that the concept of a critical field $H_{c2}(T)$ becomes less well defined, and the transition to or form the mixed state may appear “anomalously” broadened. They suggest there may be evidence for broadening in $2H$-NbSe$_2$ [Graebner and Robbins, 1976; Markiewicz et al., 1988]. Despite the fact that BKBO is a three dimensional system, we note an apparent broadening of $H_{c2}$ in this system. This explanation might account for broadening of the upper critical field transition in BKBO (see Chapter 6).

In a series of papers by Rasolt, Tesanovic et al., and Norman et al. [Rasolt, 1987; Tesanovic and Rasolt, 1989; Tesanovic et al., 1989; Rasolt, 1992; Tesanovic, 1992; Norman et al., 1992] they predict, as a result of Landau level quantization, a critical temperature below which a new magnetic field-induced superconducting phase must appear, at least when the carrier system is near the quantum limit (very low Landau level number, approaching $\sim 1$). This new superconducting state is re-entrant, i.e. would appear for applied fields above $H_{c2}$, for sufficiently low temperature and for a system with sufficiently low carrier density that all of the carriers could be condensed onto the first Landau level. Rasolt and Tesanovic et al. also find that $T_c$ would increase with increasing field, even exceeding its zero-field value. Maniv and Markiewicz et al. in an extension of their calculation of the broadening of the $H_{c2}(T)$ phase boundary due to Landau quantization, also found a reappear-
ance of the superconducting state at still higher applied field, at low temperature. An interesting difference, though, is that the Maniv and Markiewicz et al. calculation was carried out in the high density limit in which many Landau levels are occupied; which is the case of practical interest for the HTS materials.

The Rasolt-Tesanovic calculations have been carefully re-examined by Rieck et al. [1990] and by Norman [1990]. Rieck et al. agree with Rasolt and Tesanovic et al. that the transition temperature into the field-induced superconducting state $T_{c2}(H)$ remains finite in arbitrarily strong applied fields; and, $T_{c2}(H)$ is an increasing function of $H$ in the extreme quantum limit (where only one Landau level is occupied). However, they find that this behavior is removed either by deviations of the charge carriers’ g-factor from even-integer values, or by the presence of scattering processes (Landau level broadening). Rieck et al. also point out that finding a superconducting material that has the low carrier density ($\approx 10^{17}/cm^3$) required by Rasolt-Tesanovic is not very likely, due to the rapid drop of the zero-field $T_c$ with decreasing carrier density. To address this same question, Norman [1990] numerically solved the Gorkov equations in the limit of only a few Landau levels being occupied, including the effects of impurity scattering and arbitrary g-factor value. Norman finds that when the g-factor differs even slightly (e.g., 0.1) from zero or an even integer value, the degeneracy of the up-spin
and down-spin Landau parabolas is lifted, the peaks in the density or states are attenuated, and $T_c$ is rapidly suppressed. Level broadening due to scattering also was found to suppress $T_c$ somewhat. For low, but still reasonable, values of carrier density ($n \approx 10^{19} \text{ cm}^{-3}$), Norman finds that g-factor value deviations from even integer values will drive $T_c$ down to below the millikelvin range. Reentrant superconductivity, according to Norman, occurs in the special case when the Landau level splitting equals the Zeeman splitting, or a multiple of it. Thus, it appears that a new field-induced superconducting phase may be possible, but certainly remains highly controversial at this time. The restriction to even-integer g-factor values, very little scattering and low carrier density (using accessible magnetic fields) does not suggest any known superconductor as an appropriate material for experiments.

Markiewicz [1991] calculates the magneto-oscillation of the magnetization in the normal state for copper-oxide type HTSc. He suggests that short range charge density wave order [Markiewicz, 1989; Markiewicz, 1990] modifies the LK formulation of the dHvA effect. Markiewicz's calculations are based on the magnetic breakdown formalism of Falicov and Stachowiak [1966] and are corrected for the effects of two-dimensionality [Markiewicz et al., 1987]. He finds that the oscillatory part of the magnetization for Cu-O superconductors in the normal state is
\[ M_{osc} = \frac{2k_BT}{I_c} \sum_i \frac{(-1)^i eF_i}{\hbar c} q^{i_{11}}(ip)^{i_{22}}(ik)^{i_{33}} \ldots 

\ldots C_i \frac{\exp(-\pi m_i/\omega_0 \tau)}{\sinh(2\pi^2 m_i k_BT/\hbar \omega_0)} \cos \left( \frac{2\pi F_i}{B} \right), \quad (2.21) \]

where \( I_c \) is the superconducting layer thickness, the sum is over all allowed closed orbitals, the cyclotron frequency \( \omega_0 = eB/m_0c \), \( m_i = m^*/m_0 \) is the normalized cyclotron mass of the \( i \)th orbit, the dHvA frequency \( F_i = \hbar c A_i/2\pi c \) with \( A_i \) as the k-space area of the \( i \)th orbit, \( C_i \) is a factor proportional to the inverse rotational degeneracy of the orbit, the terms \( q, p, \) and \( k \) are breakdown amplitudes, and the factor \( l_{xi} \) with \( x=1, 2, \) or 3 represents the number of times an electron orbit follows a particular path.

Markiewicz states that careful measurement of the dHvA frequency in the normal state of the two dimensional copper-oxide HTSc, like YBCO, would help to place restrictions on his charge density wave model. Markiewicz has not extended his calculations into the mixed state, but presumably this could be done so that the model could be compared with experimental measurements at fields below \( H_{c2} \).

Despite the lack of a clearly defined FS in their model, Dukan et al. [1991] find that when the amplitude of the superconducting order parameter is very much greater than \( \hbar \omega_c \), dHvA oscillations should be observable. Their calcu-
lations employ a mean field approximation where a large number of Landau levels are occupied. It should be noted that the mean field approximation is of questionable value when applied to two dimensional systems given that strong fluctuations can lead to the melting of the vortex lattice. However, the mean field approximation is more appropriate for three dimensional systems and therefore Dukan et al.'s calculations may be of some interest in the context of our measurements in the 3D superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$. They show that the oscillatory part of the magnetization should take the form of

$$M_{osc}(T, H) \propto \frac{e\hbar}{mc} \frac{E_F}{E_{F}} \left( \frac{\tilde{\Delta}}{\hbar \omega_c} \right)^2 \left( 1 + \left( \frac{T}{\tilde{\Delta}} \right)^4 \right) \cdots$$

$$\cdots \sum_k \sqrt{k} \sin \left( \frac{2\pi k \mu}{\hbar \omega_c} - \frac{\pi}{4} \right),$$

(2.22)

where $l_H$ is the magnetic "length" ($= \sqrt{\hbar c/eH}$), $\tilde{\Delta}$ is the non-oscillatory part of the order parameter amplitude at zero temperature, $E_F$ is the Fermi energy, and $k$ are the Fourier components of the harmonic content. From this it is shown that the amplitude of the dHvA oscillations will be damped as $T^4$, implying that low temperatures will be need to observe the dHvA effect.

Stephen [1992] finds that the condition for the observation of effects due to the Landau quantization of electron orbits in superconductors is $Rl/\xi^2 < 1$, where $R$ is the cyclotron-resonance radius of an electron in the magnetic field, $l = (c/eH)^{1/2}$ is the magnetic "length", and $\xi = \nu_F/\Delta$ is the coherence

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length in the field. Thus close to $H_{c2}$ the dHvA effect might be observed, given the depression of the order parameter $\Delta$ and the augmentation of the coherence length $\xi$ at this critical point. Stephen’s calculations show that the oscillatory part of the free energy is

$$\Omega_{osc} = \sum_{p=1}^{\infty} C_{pd} e^{-\pi p/\omega_c \tau_{\nu}} \cos \left( \frac{2\pi p \mu}{\omega_c} (1 + \delta) - \alpha_d \right),$$

(2.23)

where $C_{pd}$ and $\alpha_d$ are coefficients, $\delta = \pi \Delta^4/8 \omega_c \mu^3$ is a small modulation of the frequency, and $\tau_{\nu}$ is given by

$$\frac{1}{\tau_{\nu}} = \frac{\Delta^2}{\omega_c} \sqrt{\pi/n} \approx \Delta^2 \left[ \frac{\pi}{\mu \omega_c} \right]^{1/2}. \quad (2.24)$$

Stephen attributes the scattering of the excitations to interaction with the vortices. The above equation assumes a dirty superconductor as reflected in the $e^{-\pi p/\omega_c \tau_{\nu}}$ term. Additionally, it is evident that $kT < \omega_c$ is a necessary condition for the observation of dHvA oscillations, since higher temperatures would lead to phase smearing. The requirement that $\omega_c \tau > 1$ leads Stephen to conclude that dHvA oscillations are not likely to persist far below $H_{c2}$. More recent work by Tesanovic and Sacramento [1997] shows that dHvA should be observable in a “pocket” between $H^*$ and $T^*$, where $H^* \sim 50\%$ $H_{c2}(T=0)$ and $T^* \sim 30\% T_c(T=0)$.
As we will see in the discussion in Chapter 5, Harrison et al. [1994] have measured dHvA oscillations as low as $H_{c2}/2$ in the type-II superconductor Nb$_3$Sn. Reported measurements on YBa$_2$Cu$_3$O$_y$ by Haanappel et al. [1993] indicate that dHvA oscillations can be observed well below $H_{c2}/2$. Haanappel's dHvA data begins around 30 tesla; the value of $H_{c2}$ for YBCO is in excess of 100 tesla. Our own dHvA measurements on BKBO show signals down to 15 tesla at 2.2 K. The upper critical field for BKBO at this temperature is at least 27 tesla (see Chapter 6). The indications from experiment are that dHvA in the mixed state and well below $H_{c2}$ is possible.
CHAPTER 3

Experimental Detection Methods and Data Analysis Techniques for Landau Quantum Oscillations

3.1 Detecting Landau Quantum Oscillations

Landau quantum oscillations (LQO) can be measured by a variety of experimental methods. These methods are largely complementary and one cannot be said to be absolutely better than another technique. I will describe the advantages of a few of the most widely used techniques, but the term advantages as used here is tinged with a bias derived from a consideration of the materials I have measured. Each material is different and requires experimental situations carefully selected to accentuate the information required from the measurement.

The historically prime method for the measurement of LQO, used by de Haas and van Alphen for their seminal measurements on bismuth [1930], is the Faraday-Curie method [Shoenberg, 1984, pp. 86 - 87]. This method is also called force magnetometry. A sample is placed in an inhomogeneous field and the mechanical force exerted on it is measured and related to the
magnetization (Force = $\vec{M} \cdot \vec{H}$; thus $M = F/\frac{dH}{dt}$). The disadvantage of this method is that the reduction factor due to the inhomogeneous field is large and the oscillations due to the highest quantum number electrons are quenched. This technique is most useful at high fields where lower quantum number levels are induced to produce signal. Also at low fields the signal tends to die out since the force is proportional to the applied field.

Another method, known as the torque method, does not suffer from the inhomogeneity problem that plagues the Faraday-Curie method. A possible drawback of this method is that the FS must be anisotropic. If the applied field is along a symmetry axis, no signal will result because all torques are balanced (see Equation 2.10). This is not usually a problem as potassium is the only metal with an isotropic FS. A second problem is that the signal tends to drop off rapidly with decreasing field. This technique is best when used at high fields. However, given that fields of up to 20 tesla are routinely generated in many laboratories, the torque method is a viable measurement technique. For example, in single crystals of Au, dHvA can be observed via the torque method at temperatures near 77 K [Vuillemin, 1997, private communication].

Other static methods for measuring LQO are possible, but do not have any relevance to the primary subject of this dissertation. I will therefore proceed to outline the two dynamic measurement techniques employed in the
acquisition of data reported herein: the pulsed field technique and the field modulation technique. Lastly, I will describe the design for a SQUID detection system for the measurement of LQO developed primarily for measuring the dHvA effect in the mixed state of YBa$_2$Cu$_3$O$_7$, but that can be adapted for general use when coupled with the proper sensor coils.

3.2 The Pulsed Field Technique

The basic experimental requirement to observe LQO phenomena is that $\omega_c \tau \geq 1$, where $\omega_c = eH/m_c c$ is the cyclotron angular frequency for an extremal orbit of mass $m_c$, and $\tau$ is the carrier mean free time for large-angle scattering events. This condition implies that, on average, electrons must complete a cyclotron orbit before scattering. Thus, high magnetic fields and single crystal specimens with low carrier scattering rates are needed. Low temperatures are required to produce a sharp, well-defined Fermi edge that yields large amplitude LQO as successive Landau levels are depopulated. Not only must the fields be sufficiently high, but they must also be sufficiently homogeneous to allow for a signal free of phase smearing.

Early in the history of dHvA measurements, before the advent of the superconducting magnet, it was exceedingly difficult to produce high (> 2.5 T) stable fields with the requisite homogeneity. To solve this problem, Shoenberg and J. Vuillemin pioneered the use of pulsed fields for the measurement
of dHvA. By placing a sample in one side of a balanced astatic pair of detection coil solenoids, the magnetization can be measured from the out of balance voltage pickup as the magnet is pulsed. The pickup voltage is

$$v = c \frac{dM}{dH} \frac{dH}{dt},$$  \hspace{1cm} (3.1)

where $c$ is a coupling constant associated with the ratio of sample size and shape to the size and shape of the sensor coil.

The pulsed fields at the NHMFL facility at Los Alamos are produced by resistive coils cooled with liquid nitrogen. Cooling to 77 K reduces the magnet resistance by more than a factor of two and decreases the power dissipation accordingly. A two megajoule capacitor bank is charged to 8 kV and then discharged through the magnet. The resulting magnetic field pulse has a rise time on the order of 10 ms and a slower decay time, such that the entire pulse endures for 40 to 50 ms, producing fields of up to 50 T in a 24 mm diameter bore. One magnet with a 16 mm bore diameter produces pulsed fields up to 60 T.

Designing a pulsed system which allows for the measurement of dHvA is a challenging, but not impossible, task. The major considerations in design pertain to the homogeneous region of the magnetic field from the pulsed magnet and the induction of eddy current heating in the sample. Careful
magnet design and intelligent selection of samples will minimize the adverse
effects of field inhomogeneity. Small samples should be selected (on the order
of 1 - 2 mm) so that they remain confined in the most homogeneous region
of the magnet. Heating of the sample due to eddy currents can be reduced
by slowing the pulse of the magnet, but this limits the available maximum
field. Another solution which does not limit the magnitude of the peak of
the pulse, is to choose the sample geometry such that the radius is much
smaller than the length. In this case, the Joule heating due to eddy current
can be greatly reduced. The mathematical specifics of these considerations
are outlined in Haanappel [1992].

As part of this dissertation, the pulsed field technique was used for mea­
urements of the dHvA effect in YBa2Cu3O7 and Ba0.6K0.4BiO3. The details
will be discussed in Chapter 5 and 6 respectively.

3.3 The Field Modulation Technique

Measurement of the dHvA effect via the field modulation technique was
the primary focus of our investigations. A number of classic descriptions of
this technique are available in the literature [Goldstien et al., 1965; Stark
and Windmiller, 1968]. With the development of superconducting magnets
and stable resistive high field magnets, the advantages of this technique can
Figure 3.1: Example of three different coil configurations used for the measurements discussed in this dissertation.

be exploited in the measurement of a great many interesting systems. I will briefly outline the technique and its advantages.

The field modulation technique requires that a sample be mounted in one half of an astatic pair of pickup coils (see Figure 3.1). This sensor coil is placed in the center of a homogeneous quasi-steady field magnet. A comparatively small ac modulation field is superimposed on the large quasi-static applied field. By using a phase sensitive detection technique (e.g. a lock-in-amplifier), the voltage output from the imbalance in the coil can be measured as a function of field. The voltage output from the astatic pair is

\[ v = c \frac{dM}{dH} (-h_0 \omega \sin \omega t), \quad (3.2) \]

where \( h_0 \) is the magnitude of the modulation field and \( \omega \) is the modulation frequency. In practice, the time dependence of \( dM/dH \) should be included if the magnitude of the modulation field is not vanishingly small. Also, since
M is non-linear in H, the expression for the voltage output contains higher harmonics and takes the form

\[ v = -\alpha \omega \left[ h_0 \frac{dM}{dH} \sin \omega t + \frac{1}{2} h_0^2 \frac{d^2 M}{dH^2} \sin 2\omega t + \cdots \right. \]

\[ \left. \cdots + \frac{h_0^k}{2^{k-1}(k-1)!} \frac{d^k M}{dH^k} \sin k\omega t + \cdots \right] . \tag{3.3} \]

If we take the oscillatory part of the magnetization to be

\[ M = \sum_{r=1}^{\infty} \sum_{j=1}^{n} R_{rj} \sin \left( \frac{2\pi r F_j}{H} + \phi_{rj} \right) , \tag{3.4} \]

then the amplitude of the voltage induced in the detection coil from a modulation field \( h_0 \sin(k\omega t) \) is

\[ v_k = -2\alpha \omega k \sum_{r=1}^{\infty} \sum_{j=1}^{n} R_{rj} J_k(r\lambda_j) \sin \left[ \frac{2\pi r F_j}{H} + \phi_{rj} - \frac{k\pi}{2} \right] , \tag{3.5} \]

where the sum over \( j \) allows for multiple frequencies (see [Shoenberg, 1984, pp. 102 - 107]). The factor \( J_k(r\lambda_j) \) is related to the modulation amplitude, \( h_0 \), and will be discussed below.

This technique is powerful since high field homogeneity can be achieved (usually to within \( 10^{-4} \) over a cubic centimeter for a superconducting magnet and much better over the mm sample sizes used for measurement). Eddy
current heating in large radius samples can be reduced by operating at low modulation frequencies.

The modulation amplitude $h_0$ should be set to maximize the dHvA signal amplitude. The dHvA signal amplitude $|v_\lambda|$ is related to $h_0$ by a Bessel function dependence with the maximum voltage given by

$$|v_\lambda|_{\text{max}} = 2k\omega R(J_k(\lambda))_{\text{max}},$$

(3.6)

where $k$ is the detection harmonic and $R$ is the collected reduction factor. The Bessel function maximums for $k=1, 2, \text{and } 3$ are at 1.8, 3.1, 4.2 respectively. The equation for calculating the appropriate $h_0$ for a known dHvA frequency $F$ is

$$h_0 = \frac{H_0^2 \lambda_{\text{max}}(k)}{F},$$

(3.7)

where $H_0$ is the applied field. From Onsager's relationship (Equations 2.8) the factor $H_0^2/F$ is recognized as the period of the dHvA oscillations $\Delta B$ due to a sheet of FS corresponding to the frequency $F$. It should be noted that to achieve the maximum signal at all applied field, the modulation amplitude should be increased in proportion to $H_0^2$.

In many cases $F$ will not be known. In the case of our original measurements on Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO), we began our search for dHvA signals at a value of $F$ derived from band structure calculations. Thus theoretical cal-
Calculations offer some guide to the experimenter on where to begin the search for dHvA oscillations in previously unmeasured materials.

In general, it is best to try to maximize $h_0$ for the target frequency $F$. However, in a few cases this is either not desirable or possible. When you are trying to measure magnetic interaction (MI) effects, it is best to work at low modulation fields. When the target frequency is low or equivalently from a small piece of FS, the modulation amplitude $h_0$ to maximize the signal might be inaccessible. For example, to maximize a 1 kT orbit at 15 T, $h_0$ must be approximately 650 gauss. Working with modulation fields of this size is difficult when the modulation coil is situated in the bore of a superconducting magnet since it can produce heating that might precipitate a quench. The major disadvantage of these large values of $h_0$ is that it will place a heat load on the refrigeration system. We have found that using modulation fields much over 100 gauss at 40 Hz modulation frequency begins to heat metallic components, including wires and the sample, in a dilution refrigerator. Thus in the case of heavy fermions where temperatures less than 0.5 K are necessary to measure the massive charge carriers, a balance between modulation frequency, amplitude, and temperature must be obtained to optimize the signal. It should be noted that the SQUID technique has been adapted for use in dilution refrigerators to allow very low temperature dHvA to be carried.
out (see Section 3.5). Also the torque and force magnetometry methods are more suited to very low temperature work.

Higher modulation fields were achieved at the NHMFL when we designed a water cooled resistive modulation coil that was wound on the exterior of the dewar tail. The upper limit of this modulation coil is 250 gauss peak at 5 amps of input current. The design and construction of more powerful modulation coils is a technical problem that is being addressed as new resistive magnets are built. As is clear from Equation 3.7, \( h_0 \) must increase as the square of the applied field. The modulation field requirement to maximize the example 1 kT orbit at 30 T is approximately 2610 gauss. This value is for \( k = 1 \), the first harmonic. The requirements for \( h_0 \) are actually almost a factor of two larger (4410 gauss) since under most measurement conditions it is beneficial to detect the second harmonic.

Second harmonic detection is useful because pickup coils produce a linear signal while the sample magnetization is non-linear in its response to the applied modulation field. By detecting at twice the modulation frequency, the fundamental direct pickup due to residual imbalance of the astatic pair can be filtered and only the signal due to the sample detected.
3.4 Instrumentation

The instrumentational setup used to measure the dHvA effect is similar to that described by Goldstien et al. [1965]. A diagram of the setup (Figure 3.2) shows the basic connection scheme. The individual components are discussed below.

3.4.1 The Field Modulation Coil

The field modulation coil for the 18 T cryo-magnetic system at LSU was wound with # 25 copper wire onto a 304 stainless form and potted with 2850 FT high thermal conductivity black epoxy. The windings were embedded with epoxy to ensure that after curing the wires of the coil were immobile. Approximately 1728 turns of wire were wound on the form. The inner diameter of the coil was 1.615 inches and the total length of the coil is 4.725 inches. This length was selected to ensure that the modulation field was homogeneous over a vertical distance large compared to the sample dimensions. The total resistance of the coil at room temperature was approximately 15 ohms. At liquid nitrogen temperature (nominally 77 K) the resistance dropped to 2.2 ohms. At 4.2 K the total resistance of the coil with leads fell below 1 ohm.

The modulation coil was calibrated by running a dc current through the coil and reading the resulting field with an axial Hall probe mounted at the center of the coil. It was found that the coil produced a 146.3 gauss field per
Figure 3.2: The astatic pair is placed at field center. A lock-in-amplifier (LIA) provides the reference modulation signal which is amplified to drive the modulation coil. A data acquisition computer controls the sweep of the main applied field, records the output of the LIA, and records the resistances of the thermometers.
dc amp. The inductance of the coil was measured by incorporating it into a LR circuit and measuring the corner frequency $\omega_c = R/L$. In this way the inductance was found to be 19.2 mH. The impedance of the coil peaked at 3.7 k$\Omega$ at 0.3 MHz at room temperature. However, this coil was used only at low modulation frequencies (17 - 40 Hz) where the impedance is small.

The magnetoresistance of the copper modulation coil was measured at 4.2 K in a 9 tesla superconducting magnet system (also at LSU). The resistance of the coil was measured with a four wire technique to eliminate lead resistance. It was found that at zero field the resistance of the coil was 0.14 ohms. At 9 tesla the resistance was found to be 0.56 ohms, and the dependence of the magneto-resistance on field was linear in this range.

The magnetoresistance of the modulation coil creates an experimental difficulty when measuring the dHvA effect because constant voltage modulation drive sources are used. This means that for a given voltage setting of the power amplifier driving the modulation coil, if the coil resistance changes due to magnetoresistance, the current in the coil will change, altering the modulation field amplitude. Measurements are taken by setting a voltage to give a modulation field $h_0$ and then slowly sweeping the applied field over some range. As described in Section 3.3, the Bessel function dependence of the amplitude $h_0$ must be taken into account if the correct dHvA signal amplitudes are to be extracted from the measured data. In cases where the
$h_0$ required to maximize the dHvA signal amplitude is within range of the instrumental limitations, ideally a new $h_0$ should be set for each field value, thus increasing $h_0$ as a function of $H^2$.* In reality, it is not always possible to increase the modulation field in this way. Therefore, during the analysis procedure (described below), the dHvA signal data should have their amplitudes adjusted so that the Fourier analysis yields the correct amplitudes. This is easily accomplished if the modulation amplitude is constant. The entire data set can be multiplied by the proper Bessel function factor calculated from Equation 3.7. However, if the modulation coil is wound from copper wire, a net modulation amplitude decrease with increasing applied field results from the increase in the magnetoresistance of the wire. Thus multiplying by a constant factor is not an accurate amplitude correction. In practice, the modulation amplitude should be recorded in the data set along with the other data so that the modulation field correction can be calculated at each field.

Another possible solution, for work at high fields, is to wind a coil out of a wire whose magnetoresistance saturates at some field lower than the measurement field range. To this end, we designed and built a modulation coil

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*This capability has been implemented for measurements at LSU; version 1.6 of our dHvA Data Acquisition software programmed in LabView can adjust $h_0$ on the fly when the proper parameters concerning the target frequency are entered. The software calculates the drive voltage signal to be sent to the modulation coil power supply at each field value and updates it. This version of the software assumes that the SR850 LIA is to be used as the drive signal source.
wound with aluminum wire. The magnetoresistance of aluminum saturates in fields of a few tesla. The difficulty of working with Al might outweigh its benefits, since Al wire is soft and cannot be drawn into sufficient lengths to wind an entire coil. This requires the splicing of several lengths of Al wire together with copper joints. Because of the oxide layer that forms on the surface of Al, soldering to it is nearly impossible. Copper joints can be machined and crimp connections made to the Al wire.

The design and operation of modulation coils at high field requires careful calculation of the coil's specifications. For our steady field measurements at the NHMFL in Tallahassee, we constructed a modulation coil designed to supply 500 gauss-peak as described in the proposal supplied in Appendix A. Despite our hopes to achieve these levels of modulation we found that we could not supply sufficient cooling (~ 250 watts) to the coil to prevent the wires from overheating and melting. We were, thus, limited to 5 amps rms as a maximum current from the modulation power supply—roughly 250 gauss-rms.

A modulation coil that maximizes the output field while minimizing the power necessary to generate that field has a mean diameter equal to the coil length. This follows from the relation:

$$B = \mu_0 \frac{I}{d} \left[ \frac{\beta}{(1 + \beta^2)^{1/2}} \right], \tag{3.8}$$
where \( \mu_0 = 4\pi \times 10^{-7} \, \text{N/A}^2 \), \( d \) is the wire diameter, \( I \) is the current, and \( \beta \) is the length (or height) of the coil divided by its diameter. This is not the optimum design for dHvA measurement given that a coil with these dimensions the modulation field lacks sufficient homogeneity to prevent phase smearing. For the coils constructed for use at the NHMFL, we set the length of the modulation coil to be twice that of the diameter to increase the homogeneous region.

### 3.4.2 Detection Coils

We have used a number of designs for our detection coils. The simplest design, the astatic pair, is shown in Figure 3.1. The coil form is machined out of epoxy rod and wound with approximately 2000 turns per coil of 50 gauge (0.001 inch diameter) copper wire with a polyvinyl-butyral coating. The pair is balanced by measuring the unbalanced voltage output when a modulating field is applied. Turns are added to or subtracted from the balance coil until the total output is zeroed. This process yields detection coil pairs which are balanced to one part in \( 10^4 \). Once the pair is balanced, a small dc current is run through the wires to melt the heat activated epoxy wire coating, thus potting the coil. An additional protective coat of suitable epoxy is applied to the exterior of the pair to prevent injury to the fine wires.

A better balance is achieved by adding a small third coil to the astatic pair. By trimming the imbalance of the pair with this third coil, a balance
of one part in $10^5$ is attained. However, once the sample is installed in the astatic pair, cooled down, and balance achieved with the aid of this third coil, one finds that the balance is rapidly tipped as the applied field is ramped. The magnetoresistance of the copper wires and the gross magnetic properties of the sample are enough to change the balance significantly over the field range swept out by the applied field. When detecting at first harmonic, this imbalance in the detection coils leads to a slope in the data which must be removed before analysis can be performed. If this slope is constant, it can be eliminated by detecting at the second harmonic.

The detection coils are placed such that the sample is located at the center of the applied field. The dilution unit we use at LSU has a glass tail mixing chamber with an epoxy rod on which the detection coils can be mounted. The superconducting magnet was mounted on an adjustable support system such that we were able to set the field center to correspond to our sample position at room temperature. In the resistive magnets at the NHMFL, the detection coils were placed at the end of a sample probe which is, nominally, a stainless tube through which twisted pairs of copper wire were run down to the coils. The center of field, in this arrangement can be found, by modulating the modulation coil which has been centered around field center. The output from one of the detector coils can be plotted as a function of position. The maximum output signal is taken as field center. Once the field center is
found, the probe is fixed to the dewar so that the detection coil does not slip from the center during the course of the measurement.

### 3.4.3 The Coil Balancing Techniques

Prior to actual measurements, a Coil Cancellation Amplifier (CCA) is used to balance the output of a detection coil pair (see Section 3.4.2). The sample and balance coil output is fed into the CCA. By adjusting the amplitude and phase of the balance coil, the output of the astatic pair can be tuned to near-zero output. A schematic diagram of the CCA is shown in Figure 3.3.
3.4.4 Sample Rotation

The aim of any Fermiological study on a new material is the determination of the FS geometry. To gain a complete picture of the FS, dHvA measurements must be made at a variety of sample orientations with respect to the applied field. One way to rotate the sample conveniently requires the construction of a gear system which allows the user to modify the sample orientation from a room temperature control on the sample probe. Thus the sample orientation can be changed without pulling the probe from the cryogenic system.

The sample is initially oriented with respect to the detection coil axis by making Laue backscattering diffraction images of the crystal structure. A goniometer is used to orient the sample while in the diffraction apparatus so that the desired axis will lie parallel to axis of the detection coil once the sample mounting rod has been inserted into the coil. Once the oriented sample is installed in the detection coil, the coil is placed in the rotator which can be set so that the axis of interest will be parallel to the applied field once the rotator is inserted into the cryo-magnetic system. The rotator mechanism constructed for the measurements reported here allows for rotation in one plane. Careful mounting of the sample and alignment with respect to the rotation plane should be observed so that one knows what rotation plane one is in.
To facilitate *in situ* rotation of samples in the magnetic field, a rotating mechanism was designed and constructed (see Appendix D for design details and diagrams). Two sizes of rotators were constructed: one with an approximate diameter of 0.75 inches and another with an approximate diameter of 0.50 inches. The maximum diameters are determined by the diameter of the cryogenic dewars available. Each were machined out of 1266 clear epoxy that we cast into rods under vacuum. The spiral gear was designed such that one rotation of the drive rod would produce an eight degree rotation in sample orientation.

Sample coils were placed in the gear ball with their twisted leads threaded through holes drilled in the axles. Special care was taken to glue down all leads so that they would not vibrate when the modulation field was turned on, or in the case of pulsed field, when the field was pulsed.

### 3.4.5 Cooling the Sample

For measurements at temperatures below 300 mK, we used an Oxford built dilution refrigerator (DF) with a glass tail mixing chamber. Readers in need of detailed information on the operation of DFs should consult Lounasmaa’s book [Lounasmaa, 1974] with supplemental information supplied by the “Cornell book,” edited by Richardson and Smith [1988]. The DF (see Figure 3.4) operates with an 80 to 20 percent mixture of $^4$He to $^3$He commonly called the mash. This mash will separate (phase separation) in the
mixing chamber with the lighter $^3$He rising above the heavier $^4$He. The phase separation is not complete, the $^4$He contains at least a six percent $^3$He impurity; this phase is therefore called the dilute phase. By pumping on the dilute phase at temperatures below 0.7 K, $^3$He will be preferentially removed. To maintain the equilibrium between the $^3$He rich phase and the dilute phase, some of the $^3$He in the $^3$He rich phase crosses the phase boundary. This evaporation of $^3$He from the dilute phase to the rich phase removes heat from the system similar to the heat removal obtained by lowering the pressure on any liquid by creating a vacuum over its surface. Essentially, the dilute phase acts as a very good vacuum which pumps on the $^3$He rich phase, because it consists mainly of superfluid $^4$He with an extremely low ($< 10^{-5}$ torr) vapor pressure below 0.5 K. While in operation, $^3$He is continuously fed back into the $^3$He rich mixture.

In principle, DF operation is a complicated affair with the possibility that many things could go wrong. Leaks in the gas handling system and in the DF itself are the major problem. Leaks in the gas handling system (depending on where they are) will allow air into the DF and thus plug the $^3$He flow impedance capillary on the feedback condenser side. Leaks of this type on the dilute phase pumping still side are less lethal to operation, but they invariably cause the cold traps installed in the system to remove all gases except He to work less efficiently by constantly plugging them up. A
Figure 3.4: Mash is cooled in the 1 K Pot and liquified in the Condenser. The liquid passes through an impedance line and is cooled further via a heat exchanger anchored to the Still. Further stages of heat exchangers cool the liquid until it reaches the Mixing Chamber (MC). The phase separation line in the MC is the coldest part of the refrigerator. The dilute phase runs back up to the Still which is constantly pumped with a diffusion pump (or a Roots Blower).
leak in the DF itself will prevent the refrigerator from working at all, since the mash will escape into the inner vacuum can and cause a thermal short between the DF and the 4 K liquid helium bath in which it is immersed. Leak checking is the ritual duty of anyone who would successfully operate a DF.

For the work done at the NHMFL and the pulsed field facility at Los Alamos, two simpler cooling methods were used. For work below 1.5 K, a $^3$He refrigerator was used. A $^3$He fridge is nothing but a long stainless tube with a vacuum jacket on the end which goes into the field center. This stainless tube is inserted into a bath of liquid $^4$He and $^3$He gas is put inside of the $^3$He fridge. The $^4$He bath is pumped to below 2.1 K, the condensation temperature of $^3$He at 1 torr, and the $^3$He is allowed to condense. When a column of liquid $^3$He of sufficient height to cover the sample is condensed into the stainless vacuum jacketed tube, then the $^3$He is pumped and can be cooled down to temperatures as low as 300 mK. In practice, at the NHMFL in Tallahassee, temperatures below 0.5 K were never achieved. Temperature control is accomplished by placing a small heater made of a twisted length of manganin wire at the end of the sample probe. A PID temperature controller can be used together with a low temperature thermometer (like a thick chip resistor, see below) to adjust the current level passed through the heater.
The temperature controller dynamically adjusts the heater level to maintain
the desired temperature.

To make measurements between 1.5 and 4.2 K, the sample probe can be
placed directly into the 4He dewar. By adjusting the pumping speed, tem­
peratures between 1.5 and 4.2 K can be maintained. Overall the temperature
range described here is not large, \( \sim 4 \) K. However, the absolute temperature
is changed by a factor of \( \sim 100 \) (0.04 to 4 K). This temperature range, then,
is equivalent to changing from room temperature to about the temperature
of the sun.

3.5 The SQUID Technique

The field modulation technique described above suffers from a technical
limitation associated with the production of modulation fields of sufficient
size to maximize dHvA signal (see Appendix A). Even if modulation fields of
the size necessary to observe a 1 kT orbit could be achieved, they would never
be of practical use in a dilution refrigerator where a modulation field of that
size would rapidly heat any metallic elements, i.e. samples, wires, pumping
lines, etc., in the mixing chamber leading to a loss of base temperature.
Clearly, there is some need in this context for a sensitive detection method
which does not cause heating. Such a method was developed and tested by a
Japanese group [Sato et al., 1993] and more recently by Springford’s group in

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Bristol, England [Hill et al., 1997]. They used a Superconducting Quantum Interference Device (SQUID) to detect the voltage output from a balanced pair of detection coils.

We have developed a similar system for use in the 33 tesla Bitter magnet at the NHMFL (see Figure 3.5). The SQUID itself is about ten inches above the field center where the field is ~ 0.2 T at 33 T and is enclosed in a Nb metal can centered in a low field region created by a system of four superconducting coils that cancel the fringing field of the main magnet over a length of 10 cm.

The SQUID probe is a model "DP" dc SQUID available from Biomagnetic Technologies, Inc.* The probe is attached to a model 400 feedback/bias unit which allows for the adjustment of skew and modulation of the SQUID. The output of the feedback unit is sent to a model 40 dc SQUID Control Unit. The control unit puts out a signal proportional to the voltage pickup detected by the SQUID. This can be read directly or used together with field modulation and a LIA to detect dHvA signals.

To detect dHvA oscillations a pair of detection coils are wound. These coils must have only a few turns (approximately 40 turns per coil) to minimize the resistive load on the SQUID input and to lower the total inductance of sensor coils (to less than 2 μH). For our SQUID, best results are achieved if the total load is less than 3 ohms. Sato et al. [1993] found that detection coils

*4174 Sorrento Valley Blvd., San Diego, CA, 92121.
Figure 3.5: The SQUID operates in a Nb shield at 4 K in a low field region (< $H_{c1}$ for Nb) created by a superconducting cancellation coil system. Sensor coils are mounted in field center. A modulation field is optional.
wound out of superconducting Nb-Ti wire yield stronger dHvA amplitudes than coils wound with copper wire, but above 20 tesla normal wire coils must be used.

Measuring the dHvA effect with this system is, in principle, simple. Once the SQUID amplifier is locked, the main field can be ramped. The automatic zeroing function of the SQUID electronics filters out all but the oscillatory voltage signal from the balanced pair. The amplitude of the resulting dHvA signal is proportional to the sweep rate. That is the output voltage is proportional to dM/dt which in turn is proportional to dH/dt. I say that the operation of the SQUID is simple in principle, because at the time of writing this dissertation, we have yet to overcome the elimination of noise sources intrinsic to the measurement environment which prevent the SQUID electronics from unlocking while the main field is ramping. The probable cause of this noise is mechanical vibration in the sensor coil leads. Once this problem is fixed, this measurement system will be tested again in the early Fall of 1997. This SQUID system was designed primarily for the measurements to be made on the YBa$_2$Cu$_3$O$_7$ epitaxial films (see Chapter 5) to match the low impedance of the detection coils in this case.

The SQUID technique can be coupled with the field modulation technique. By modulating the field as the main field is ramped, a lock-in-amplifier can be used to detect the SQUID output signal with increased sensitivity.
3.6 Thermometry at Low Temperatures

Temperatures were determined with the aid of several calibrated resistance thermometers. The following resistance thermometers were used: ruthenium oxide chip resistors packaged in cans and calibrated by Scientific Instruments, * one calibrated germanium thermometer from Lakeshore Cryotronics, † and several Cernox chip resistors manufactured and calibrated by Lakeshore Cryotronics.

At zero field, temperatures below 100 mK were determined in the DF by the nuclear orientation method [Marshak, 1983]. A small single crystal of $^{60}$Co was mounted on the tail of the mixing chamber so that it was immersed in the mash. The crystal was attached to a copper plate with a low temperature solder to increase its thermal contact with the mash. $^{60}$Co decays and emits a gamma rays in a dipole pattern with respect to the direction of its moments. Above 100 mK, the moments associated with the Co atoms are randomly oriented such that the total gamma ray emission is isotropic. As the Co gamma source is cooled below 100 mK the moments overcome their thermal disorder and begin to align anti-ferromagnetically. Since the Co single crystal is anti-ferromagnetic; therefore, the nuclear alignment is ± the internal field of the crystal along the [100]. As the temperature decreases,

*Scientific Instruments, Inc., 4400 W. Tiffany Drive, West Palm Beach, FL 33407.
†Lakeshore Cryotronics, Inc., 64 East Walnut Street, Westerville, Ohio, 43081.
the moments become increasingly more aligned and a macroscopic dipole emission pattern emerges. A photo-multiplier tube placed along the dipole axis measures the number of gamma rays emitted along the moment’s axis. By comparing the number of gamma events above 100 mK (the warm count) with the number of events below 100 mK (the cold count), an extremely accurate determination of the temperature can be made.

We used nuclear orientation thermometry to calibrate a number of ruthenium oxide thick chip resistors below 100 mK for use as thermometers during dHvA measurements (see below).

3.7 Thermometry in Magnetic Fields

Extracting physical parameters from dHvA signals requires knowledge of the temperature at which the measurements were made. Given that most resistive thermometers have magnetoresistive properties, temperature determination and control is difficult when working at high fields. To solve the problem of temperature control in a magnetic field we made an extensive study of ruthenium oxide - bismuth ruthenate chip resistors. In this section, I report the results of a study of the magnetoresistance below 1 K and the temperature cycling of these chip resistors used as cryogenic thermometers. These measurements and results have been accepted for publication in Cryogenics and will appear in a forthcoming issue of that journal.
3.7.1 Introduction

Since the first publications reporting the properties of RuO₂ and Ru₂Bi₂O₇ thick film chip resistors for use as cryogenic thermometers [Koppetski, 1983; Doi et al., 1984; Li et al., 1986], these types of resistors have been employed for the measurement of low temperatures in many laboratories. Thermometers having a room temperature resistance of 1000 Ω are most useful below 1 K and have a large temperature coefficient of resistance in this range. A typical calibration curve for one such thermometer, labeled R2 below, is shown in Figure 3.6 and its sensitivity function, d(lnR)/d(lnT), is shown in Figure 3.7. Thermometers made from chip resistors are useful because of their small size, low cost, and a magnetoresistance comparable to carbon glass. They are ideal for use in the temperature range 0.025 to 4 K [Li et al., 1986; Bosch et al., 1986; Meisel et al., 1989; Uhlig, 1995]. In general, the 1 kΩ resistors can be used to measure temperatures up to about 40 K with reasonable sensitivity. Above 100 K, the resistance versus temperature curve is not monotonic. No systematic results for several resistors concerning the magnetoresistance below 1 K and stability upon temperature cycling have been published to date.
Figure 3.6: Resistance as a function of temperature from 25 to 100 mK for R2.
3.7.2 Measurements

3.7.2.1 Magnetoresistance

We have made measurements below 1 K of the magnetic field dependence of the resistance of five thick film chip resistors having a nominal resistance at room temperature of 1000 Ω. One calibrated thermometer mounted in a can was obtained from Scientific Instruments (SI) (labeled R1). Four resistors (R2, R3, R4, and R5) were purchased directly from Dale Electronics of Norfolk, Nebraska, USA (Model RCWP-575) and measured without packaging. The measurements on the packaged SI thermometer were performed at LSU with R1 emersed in the mash of a bottom loading non-metallic dilution refrigerator in fields between zero and 16 T. Measurements on the unpackaged

Figure 3.7: Temperature dependence of the sensitivity function, \( \frac{d(\ln R)}{d(\ln T)} \) of R2.
R3 - R5 were performed at the National High Magnetic Field Laboratory (NHMFL) emersed in the mash of a top loading dilution refrigerator in fields between zero and 18 T. One of the resistors, R2, was measured to 32 T in a $^3$He refrigerator using a NHMFL resistive magnet. The resistors R3 - R5 had been temperature cycled at least 60 times to 77 K, and the SI calibrated thermometer had been cycled to stability before the field dependent measurements (see below).

The four measured temperatures at which measurements on R1 were made were obtained from the zero field sensitivity curves provided by SI for this thermometer and agree with other thermometers (calibrated Ge above 0.075 K and nuclear orientation below 0.1 K) at zero applied magnetic field. Below 0.05 K, this thermometer started to lose thermal contact with the bath and extremely long (> 0.5 hr) times to reach equilibrium were required. The data on R1 were recorded between zero and 16 T during field sweeps at a rate of 0.05 T/min and include data for both increasing and decreasing field sweeps. During all of the measurements, another thermometer mounted on the top of the mixing chamber and in a region where the field never exceeded 100 gauss was monitored and found not to change. The resistances measured from the field sweeps were checked at constant field intervals of 1.0 T for both increasing and decreasing fields and were found to give the same values ob-
tained during the field sweeps. The R1 resistance measurements were made with a low power AC resistance bridge (RV-Elektroniikka, Model AVS-46).

At the NHMFL, R3 - R5 were measured in a top loading dilution refrigerator at 0.028 K from zero to 18 T in a superconducting magnetic system and one of them, R2, was measured at 0.62 K from zero to 32 T in a resistive magnet. These resistors were mounted either emersed in the $^3$He-$^4$He mixture of a dilution refrigerator, or in the $^3$He liquid of a single shot $^3$He refrigerator. For the dilution refrigerator measurements, the magnetic field was swept both up and down at a rate of 0.33 T/min, and in the resistive magnet the sweep rate was 0.533 T/min. In both cases, these sweep rates were sufficiently low for the magnetoresistance to be reproduced between up and down sweeps and no changes occurred when the sweeps were stopped. In the NHMFL dilution refrigerator, four-wire measurements were done with an excitation current of $10^{-8}$ A at 13 Hz with the voltage across each resistor measured with a lock-in amplifier. It might be noted that another chip resistor was measured during the low temperature measurements of R3 - R5, but the data shows evidence of bad electrical contact: the measured resistance values jumped up and down during all of the field sweeps. At the higher temperature used in the resistive magnet, a Conductus Model LTC-20 Resistance bridge was used with a 1 mV excitation and the $^3$He vapor pressure monitored during the field sweeps.
3.7.2.2 Temperature Cycling

In measurements on a separate set of five resistors, we have measured the stability of the resistance of chip resistor thermometers upon repeated cycling from room temperature to 77 and 4.2 K of four (labeled R6 -R9) nominally 1000 Ω thick film chip resistors from the same batch purchased directly from Dale Electronics and one uncycled and uncalibrated packaged thermometer from SI (R10). For all of the cycling measurements, the resistors were embedded in thermally conducting epoxy on a copper cylinder mounted on the end of a long stainless steel tube that could be immersed in either liquid nitrogen or liquid helium. The measurements at liquid nitrogen temperature were done in an open container filled to the same depth for each cycle with the copper cylinder immersed to the bottom of the cryostat. More care was taken in the nominally 4.2 K measurements. Prior to each cycle, the liquid helium depth in a storage dewar was measured so that the copper was six inches below the surface for each cycle. Resistance values were recorded only after the system came to equilibrium and the readings ceased to change. Atmospheric pressure was measured with a mercury manometer and recorded at the time of each cycle, and calculations of the temperature of the liquid helium were made. On each cycle, the temperature at which the reported resistance values are listed as 4.2 was the same to within 0.001 K. All of these DC resistance measurements were made with a four-wire con-
nection to each resistor using a Hewlett Packard Model 3457A multimeter ($10^{-4}$ A excitation current, corresponding to the $30k\Omega$ scale). The excitation level used is higher than that recommended for use in situations where the user wishes to avoid heating, but using high excitation currents yields more stable readings. It should be noted that we did not observe any evidence of heating in this measurement configuration; this was checked by changing to lower excitation currents and monitoring the resistance of the chip.

3.7.3 Results

3.7.3.1 Magnetoresistance

For the chip resistors at the lowest temperature of measurement, 0.028 K, the magnetoresistance becomes large and negative at low fields, then reverses direction, heading back to zero at higher fields, but not crossing the zero resistance change line below 18 T. The results for R3 - R5 are shown in Figure 3.8 for data from a 0.33 T/min down sweep. As is clearly seen, the magnitude of the negative magnetoresistance change increases with the magnitude of the zero field resistance.

For the measurements on R3 - R5 at the NHMFL, near zero field for increasing field sweeps a large positive spike in the resistance is seen as the sweep is started before the magnetoresistance becomes negative. This effect is enhanced when the sweep rate is increased to 0.66 T/min and is decreased in the down sweeps. Thus, the magnitude of this spike is sweep rate and sweep
Figure 3.8: Percentage resistance change as a function of applied magnetic field for R3, R4, and R5 at 0.028 K between zero and 18 T. The zero field resistances for each resistor are listed on the graph.
direction dependent. We do not know the origin of this spike or whether it is intrinsic to the resistors. An attempt was made to reduce the flux jumping near zero field in the Nb$_3$Sn magnet that could cause voltage spikes in the leads, but this did not remove the spikes.

The same negative magneto-resistive behavior is seen in R1 at higher temperatures of 0.084 K (3 times the temperature at which R3 - R5 were measured) and 0.117 K, but the magnetoresistance becomes positive at less than 5 T at these higher temperatures. At temperatures of 0.142 K and above, the magnetoresistance is entirely positive with the total change becoming much smaller as the temperature is raised. No zero field positive resistance jumps were observed in the R1 data where very slow sweep rates were used. The R1 results are displayed in Figure 3.9.

Taking the most extreme example, we have calculated the apparent temperature change at 0.028 K by fitting the zero field calibration data and calculating $\Delta T$ as the difference between the zero field field temperature value and the temperature calculated using the curve fit from the resistance measured in fields between zero and 18 T for R4 as shown in Figure 3.10. This is the temperature range where the largest resistance change for a small change in temperature occurs and corresponds to a change of about twenty-five percent in temperature at the maximum negative magnetoresistance.
Figure 3.9: Resistance change for R1 (0.27, 0.14, 0.12, and 0.08 K) as a function of applied magnetic field.
Figure 3.10: Apparent temperature of R2 obtained from the zero field calibration between zero and 18 T at 0.028 K.

At 0.62 K, the total resistance change of R2 is about 20 percent at 32 T. In the higher temperature measurements, which used the resistive magnet, no initial sharp resistance increase is observed even though a much higher sweep rate was used. For the 0.62 K measurements, the vapor pressure of the $^3$He bath was monitored during the field sweep and found to change less than 0.01 mbar, corresponding to a temperature change of < 5 mK. However, the overall resistance change of 20 percent is an apparent temperature change of 0.175 K.
3.7.3.2 Temperature Cycling

Measurements were made over a period of three months on five chip resistors with a total of 98 complete temperature cycles. For each cycle, the following procedure was performed on each of the five resistors: 1) an ambient room temperature measurement; 2) a 77 K measurement; 3) another room temperature measurement; a 4.2 K measurement; and 5) a final room temperature measurement. Thus, each resistor was cycled from room temperature to 77 K or below 196 times. These chip resistors have been designed to be nearly temperature independent at room temperature. They are stable to within $\pm 100 - 200$ ppm/K for $\pm 50$ K around 300 K, and therefore show no significant change in resistance with small variations in room temperature. Because of this, it was not necessary to employ a controlled room temperature bath.

These 1000 $\Omega$ resistors are most useful for temperature measurements below 4.2 K, and we show in Figure 3.11 the results for each resistor of the 4.2 K resistance measurements as a function of cycle number. All of the resistors showed an initial increase in resistance with temperature cycling. The change in resistance in the first 60 cycles (120 to 77 K and below) is significant. From calibrations on other resistors of this type, the average observed 30 $\Omega$ change corresponds to approximately 0.2 kelvin at 4.2 K. After 40 to 50 cycles they began to become more stable, but two (R7 and
Figure 3.11: Resistance for five resistors at 4.2 K during temperature cycling. R8) showed a definite jump after 50 cycles and one (R7) lost contact during some cycles after 77 cycles. The temperature cycling of the epoxy causes it to crack and probably led to the intermittent open circuit in R7 at low temperatures. In each case, the resistance changes upon cycling between 300 and 4.2 K became stable to within approximately ±1Ω(±0.03K) out of 1200 Ω for each successive cycle. The initial increase in resistance with cycling is evident in both the initially uncycled commercial resistor that is mounted in a gas filled can and in the resistors embedded directly in epoxy. Therefore, it would appear that the temperature cycling effect is due to the resistance element, substrate, and glass enclosure, rather than to the mounting or lead connection method.
The 77 K and 300 K results are shown in Figures 3.12 and 3.13. The resistance changes at 77 K are more erratic, but also tend to stabilize after approximately 60 cycles (note that 120 cycles to 77 K or below are made for the sixty 77 K readings). Part of the scatter in the 77 K data is due to the fact that no attempt to control the temperature of the liquid nitrogen in the open container was made. Depending on the amount of absorbed oxygen in the nitrogen bath, the temperature could have changed by several degrees. Both the nominal 77 and 300 K results mirror the 4.2 K changes in that both become more stable after 60 cycles. The 300 K results are actually a better indicator than the 77 K results to predict stability of the 4.2 K resistances. This partially is due to the fact, mentioned above, that these resistors have been specifically designed to have a low temperature coefficient of resistance around 300 K and variations in room temperature have little effect. This result also indicates that the cycling resistance changes are intrinsic to the chip resistors resistive element.

3.7.4 Discussion

Below 0.150 K, the magnetoresistance of chip resistors is negative at low fields, crosses the zero field value, and becomes positive at higher fields. This type of behavior generally agrees with that found in Reference [Li et al., 1986] and is presumably due to weak localization [Anderson, 1958]. Above 0.2 K, the magnetoresistance is entirely positive and overall decreases as
Figure 3.12: Resistance for five resistors at 77 K during temperature cycling.

Figure 3.13: Resistance for five resistors at 300 K during temperature cycling.
the temperature is increased. At all measured temperatures, the resistance measured above 4 T is a monotonically increasing function of applied field, and is directly proportional to $B^{1/2}$ for all temperatures and resistors. In Figure 3.14 we show the magnetoresistance of R1 and R2 plotted against $B^{1/2}$ for five of the measurement temperatures. It can be seen that this behavior covers a wide temperature and field range. Resistor R2 exhibits the $B^{1/2}$ field dependence at 0.62 K from about 3 to 32 T as shown in Figure 3.15. This square root dependence on the field is what might be expected from the conduction mechanism experiencing weak localization with correlations [Alshuler et al., 1980], i.e. electron-electron scattering. While the field dependent resistance curves vary from resistor to resistor depending on the individual zero-field resistances, and perhaps the production batch, at the same temperature, the same general field dependent properties are observed in all resistors. From this data on a limited number of samples it can be seen that thermometers of this type can be calibrated for use in high magnetic fields, but for accurate measurements of temperature, the calibration should be done on an individual basis.

The major conclusion to be drawn from the temperature cycling results is that, if chip resistors are to be used as calibrated thermometers, the calibration should not be done until at least 120 cycles to below 77 K have been done. However, one only needs to record room temperature resistance val-
Figure 3.14: Square root dependence of resistance change on applied magnetic field between 2.5 tesla and the maximum measurement field for two resistors, R1 and R2, at five temperatures.
Figure 3.15: Square root dependence on applied magnetic field of resistance change between 3 T and 32 T for R2 at 0.62 K.
ues to determine when the resistance values have become stable. Given that it is probable that microcracking is responsible for the resistance changes observed during repeated cycling, it is reasonable to take precautions to prevent excessive heating above room temperature of a calibrated chip resistor to ensure that annealing of the microcracking does not undo the calibration.

3.8 Data Analysis

3.8.1 Determination of dHvA Frequencies and Amplitudes

Values of applied field, dHvA signal voltages (X, Y, R, and Θ) from the lock-in-amplifier, four-wire resistance measurements of the thermometers, and the time at which each data point is taken, are recorded as columns in a file on the data acquisition computer. A series of macros were written for our data analysis package * to allow quick processing of all data files immediately after any given field sweep. The field values were converted to inverse field so that any dHvA signals would be seen as periodic. The dHvA data was interpolated to produce a new data set of equally spaced voltage readings in 1/B. The interpolation was accomplished by fitting between adjacent data points in the original data with a polynomial fit. New, evenly spaced data points were selected so that each new point would lie at the appropriate inverse field value and by selecting a corresponding new voltage

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*Igor Pro v. 3 by WaveMetrics, Inc., P. O. Box 2088, Lake Oswego, OR, 97035.*

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reading from the local fit of original data points. Also, at this time any adjustments needing to be made in the data were carried out: e.g. field calibration adjustments, corrections to compensate for the magnetization field of the sample, rescaling of the dHvA amplitudes due to improper modulation amplitudes, etc. We also tested whether it made any difference if these adjustments were carried out on the DFT spectrum peaks; the results were the same regardless of when in the data analysis process such adjustments were made. The interpolated data sets were inspected visually to ensure that they matched the wave shape of the original data set. This interpolated data set was then subjected to a Fast Fourier Transform (FFT) to determine the frequency values of any peaks. A special algorithm was written in C to allow for a more versatile Fourier analysis of the dHvA data. A listing of the C code is provided in Appendix C. This algorithm performed the Fourier integrals for specified frequencies. It did this by multiplying the data set by a cosine at the test frequency to get the real part and by a sine to get the imaginary part. The integration is done with a trapezoidal routine. Since the algorithm analyzed a discrete set of specified frequencies, we called it a Discrete Fourier Transform (DFT). The advantage of the DFT is that an analysis can be carried out over a small range of dHvA frequencies not dependent on the total number of data points. In all cases, the frequency values yielded by FFT and DFT were the same. The amplitude of the peaks
in the DFT spectrum yield the amplitude of the dHvA oscillations associated with a particular frequency.

Additionally, to decrease the bin spacing when using the FFT routine, the interpolated data sets could be padded with any number of zeros so long as the total number of points was a multiple of $2^n$. This zero padding method or “super” FFT yielded the same accuracy in frequency determination as the DFT routine, but had the advantage of a short run time.

A number of time saving features were built into the data analysis package. Macros for finding all the peaks in a given Fourier spectrum together with their amplitudes and half widths assisted in the processing of the large number of data sets taken during any given data taking period.

By using our custom set of Igor macros and the DFT algorithm, we were able to determine the frequencies and relative amplitudes of the dHvA oscillations of our samples at various fields and temperatures.

### 3.8.2 Determination of the Cyclotron Mass

The cyclotron effective mass is an average of the inverse Fermi velocity corresponding to an extremal orbit on the Fermi surface,

$$m^* = \frac{\hbar}{2\pi} \int \frac{dk}{\nu_\perp}. \tag{3.9}$$
The mass of each orbit is determined from the temperature dependence of
the dHvA oscillation amplitude (see Section 2.2).

Relative amplitudes $A$ are determined from the peak heights in the DFT
spectrum. The procedure is to plot first $\ln \left( \frac{A}{A_0} \right)$ against $T$. The resulting slope
(calculated by linear regression), $\frac{am^*_H}{H}$, yields a first estimate of $m^*$. Then,

$$\ln A \left[ 1 - \exp \left( \frac{-2(a m^*_H T)}{T} \right) \right]$$

is plotted against $T$. The resulting slope gives a new value for $\frac{am^*_H}{H}$ which can
be put back into Equation 3.10 and refit by linear regression. This iteration
is continued until the value of the slope converges to some stable value (i.e.
a value that does not change in the least significant digit upon successive
iteration).

3.8.3 Determination of the Dingle temperature

As seen in Equations 2.12 and 2.13, an amplitude reduction factor that
is dependent on field enters into the dHvA equations. The amplitude of the
dHvA oscillations at a given field value is given by

$$A_r \approx \frac{T H^{-n} R_D}{\sinh (\alpha r \frac{T}{H})},$$

(3.11)
where \( n = \frac{1}{2} \) for modulation varied as \( H^2 \) or \( n = \frac{5}{2} \) for weak modulation [Shoenberg, 1984, pp. 371-373].

To determine the Dingle temperature, one must first accurately gauge the amplitude of the dHvA peaks at a given field value. The best method for doing this is to select a region which contains roughly ten oscillations and then perform a DFT on that region. The amplitude of the transform peak will yield a value which is good at the mean field value of the region. Several amplitudes can be gauged in this fashion. When enough points are available, a Dingle plot can be made. This is a plot of

\[
\ln \left[ A_p H^n \sinh \left( \alpha \frac{T}{H} \right) \right] \text{ vs. } \frac{1}{H}.
\]  

(3.12)

The slope of the resulting straight line is \( \alpha p z \), where \( \alpha = 14.69 \frac{m}{m_0} \frac{T}{K} \).

The drawback of this method of determining the Dingle temperature is that one must first know the value of \( m^* \) accurately. As we will see later in the case of CeB\(_6\), \( m^* \) is a dramatically changing function of applied field. Thus \( \alpha \) in equation 3.12 is constantly changing. To get around this problem an approximation can be made. If \( \alpha p T / H \) is large enough, the sinh can be replaced with \( \frac{1}{2} \exp \). Now, \( \ln \left( A_p H^n \right) \) can be plotted against \( 1/H \). The resulting slope is \( \alpha p (x + T) \). To get an accurate estimate of the Dingle temperature,
Table 3.1: dHvA frequencies for pure Au[111]. Values reported here are taken from Halse [1969], a report of the Jan and Templeton [1967] measurements and Coleridge and Templeton [1972].

<table>
<thead>
<tr>
<th></th>
<th>Jan &amp; Templeton (1967)</th>
<th>Coleridge &amp; Templeton (1972)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bellies</td>
<td>44.9273 ± 0.001</td>
<td>44.9279 ± 0.006</td>
</tr>
<tr>
<td>necks</td>
<td>1.53199 ± 0.001</td>
<td>1.53119 ± 0.0004</td>
</tr>
<tr>
<td>ratio</td>
<td>29.3261 ± 0.0001</td>
<td>29.3418 ± 1.2 ×10^-5</td>
</tr>
</tbody>
</table>

one must still determine $\alpha$, but the advantage of this approximation is that the linearity of the Dingle plot itself is independent of $\alpha$.

3.9 Evaluation of the Measurement System

For accurate determination of dHvA frequencies in new materials, it is necessary to have very precise knowledge of the field and to know also how well the measurement system reproduces known results. To accomplish both of these tasks, dHvA measurements have been carried out on a single crystal of Au oriented in the [111] direction. The dHvA frequencies of Au oriented in this direction are known with a high degree of accuracy. The values of the belly and neck orbits are reported in Table 3.1.

To check the field calibration of the magnets used in this study, a series of dHvA measurements on Au were run. We find that our measurements are in good agreement with the values given in Table 3.1.

A DFT of eleven oscillations above 20 tesla for the Au[111] sample is shown in Figure 3.16. The peak due to the fundamental and one harmonic are
Figure 3.16: This is a DFT of ten oscillations between 25 T and 29 T in a Au[111] single crystal sample. The fundamental frequency is 1.529 kT and one harmonic is present at 3.058 kT.

The width of the peaks corresponds to the low number of oscillations in the data set. The peak frequencies are determined by finding the maximum of the peak. The accuracy of the frequency determination is limited to the resolution of the DFT. Typical frequency accuracies are on the order of a few tesla.

Both the belly and neck orbits were measured. In Figure 3.17, an FFT of the fundamental and first harmonic of the Au belly orbit is shown. This FFT was done on more than one hundred oscillations. No frequency shift
Figure 3.17: This is an FFT of the neck oscillations above 20 T in a Au[111] single crystal sample. The fundamental frequency is 44.934 kT and one harmonic is present at 89.9 kT.

is observable over the range of the data. Because the modulation amplitude was set near the Bessel function maximum for the first harmonic of the belly orbit, the dHvA harmonic frequencies are attenuated. In reality, due to the Shoenberg effect the belly signals are nearly triangular and contain high harmonic content that is not observed because they are over modulated.

One feature of the data taken of the belly orbit that is resolved with the DFT routine is the presence of side bands on the fundamental belly peak. These side bands arise from magnetic interaction between the belly and neck
Figure 3.18: This is an DFT of fundamental peak (44.934 kT) due to the [111] bellies in a single crystal of Au. Notice the side bands. They are due to the neck orbits. The peak to peak spacing between the main peak and each of the sidebands is 1.53 kT.

orbits (see p. 24). Careful measurement of difference in the frequency of the peak and the two sideband peaks is 1.53 kT, or the frequency of the neck orbits.

In the 18 T superconducting magnet system at LSU, the field calibration was checked with an oriented single crystal of Pd. These measurements confirmed the accuracy of a determination of the field calibration by NMR.

The measurements on Au and Pd demonstrate that the dHvA measurement system constructed for the measurements reported in this dissertation

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is capable of highly accurate and reliable determinations of the information that can be extracted from the dHvA effect.
CHAPTER 4

The Fermi Surface of Cerium Hexaboride

4.1 Introduction

4.1.1 Heavy Fermions

Heavy fermions (HFs) are materials whose conduction electrons have a large effective mass. These materials usually contain rare-earth (e.g. Ce) or actinide (e.g. U) ions with unfilled 4f or 5f shells respectively. The interesting physical properties of HFs are governed by the interactions of nearly localized f electron states. At high temperatures, HFs act like they contain weakly interacting magnetic moments immersed in a sea of conduction electrons with normal masses [Hess et al., 1991], but at low temperatures the f electrons interact strongly. The temperature at which the f electrons begin to interact with sufficient strength to induce changes in the specific heat coefficients and the susceptibility is called the coherence temperature $T^*$ and varies from material to material.
HF's exhibit many different ground states: antiferromagnetic (CeB$_6$), superconducting (UPt$_3$), paramagnetic, and semiconducting (CeNiSn).* Like $^3$He the specific heat of HF's varies linearly with temperature (at low temperatures), and the magnetic susceptibility is independent of temperature. This suggests that HF physics might be adequately modeled by the Landau Fermi liquid theory. However, the many body effects present in HF's indicate that although the major physical features of HF's at low temperatures might be modeled well with Landau Fermi liquid theory, it is ultimately too simple a theory to account for microscopic effects. Attempts to develop a microscopic theory of HF's begin with Kondo theory [Kondo, 1964] a description of the low temperature effects of a single magnetic impurity in a sea of conduction electrons. The Kondo model is analogous to HF's if the f electron states, each possessing a magnetic moment, are viewed as magnetic impurities. The generalization of Kondo theory to heavy fermions is found in the Anderson Lattice Model or the single impurity model. It is worth noting that a "non-Kondo" theory has been put forward by Sheng and Cooper [1995]. They treat the f electrons as a mixture of two types of liquid, a non-magnetic and a magnetic liquid. Thus the f electrons retain both their itinerant and local

---

*The physics of heavy fermion materials has been review by Stewart [1984] and by Fisk et al. [1986].
nature. All local degrees of freedom are retained; whereas, in the Kondo picture, these local degrees of freedom are destroyed.

4.1.2 The Rare-earth Hexaborides

The class of materials known as rare-earth hexaborides contains a single heavy fermion material, CeB$_6$.$^\dagger$ The related material LaB$_6$ has no 4 f electron and is an ordinary metal. PrB$_6$ and NdB$_6$ are marked by the presence of magnetically ordered local moments. SmB$_6$ is a mixed valence material.

Experimental studies of the heavy fermion CeB$_6$ have focused on the strong renormalization of the cyclotron mass of the charge carriers. The persistent mystery of CeB$_6$ has been the field dependence of its cyclotron mass. Low temperature specific heat (LTSH) and dHvA studies have established that the cyclotron mass of the quasiparticles in CeB$_6$ is reduced by an order of magnitude for applied fields from 7 to 50 tesla (see Figure 4.11). The effective mass (as determined from dHvA measurements) ranges from $26 \pm 1$ at 7.1 T down to $3.06 \pm 0.13$ at 46.9 T. Many dHvA studies have been made of CeB$_6$ [van Deursen et al., 1982; Deursen et al., 1985; Joss et al., 1987; Onuki et al., 1989; Matsui et al., 1993; Haanappel et al., 1992; Harrison et al., 1993]. Despite this attention, CeB$_6$ still presents interesting problems for the researcher.

$^\dagger$Some of the earliest experimental work done on the physical properties of CeB$_6$ was carried out by Fisk [1969].
In this chapter, I will discuss the problem of the determination of the cyclotron effective mass of the conduction electrons in CeB$_6$, the dependence of the effective mass on field, and present the first detailed study of the magnetic field dependence of the dHvA frequency. I present results from a new dHvA study of CeB$_6$ designed to yield a determination of the dHvA frequency as a function of field and to extend previous dHvA mass measurements to lower temperatures and lower fields. I will provide an assessment of current research on CeB$_6$ and place the findings of this study in that context. I will conclude with recommendations for future experimental and theoretical research.

4.2 Cerium Hexaboride

CeB$_6$ is structurally similar to LaB$_6$ but differs in that the Ce has an f electron whereas the La does not. CeB$_6$ like all rare-earth hexaborides crystallizes in the cubic CsCl structure; the Ce ion is centrally located in a cube surrounded by octahedra of B ions located at the corners of the cube (see Figure 4.1).

CeB$_6$ is grown in a molten Al flux crystallizing at about 1400° C. All measured crystals are close to stoichiometry. Since these crystals were grown in an Al flux it might be possible for dHvA signals to arise from the Al contaminant. This is a concern, but as the measurements reported below...
Figure 4.1: The structure of CeB$_6$. 
will demonstrate, neither the frequency or the effective mass characteristics of CeB₆ correspond to known properties of the Al Fermi surface.*

The first dHvA measurements of CeB₆ were made by van Deursen et al. [1982] in a 40 tesla slow pulse magnet (the highest useful field value was ≈ 33 T). Data was taken at temperatures below 1.8 K. For the belly orbit, corresponding to a sample orientation of [100], they found a dHvA frequency of 8.66 kT and an effective mass of $6 \pm 1 m_e$ at 30 T for the conduction electrons. A value of $8 \pm 2$ was found for the scattering parameter $m^* T_D$. The dHvA frequency was measured as a function of angle. Despite a difference in the size of the Fermi surface of CeB₆ as compared to LaB₆ (CeB₆ is 10 percent larger), a qualitative similarity was evident. Thus, the FS of CeB₆ might be similar to the proposed FS for LaB₆ [Arko et al., 1976; Ishizawa et al., 1977] (see Figure 4.2). Subsequent measurements have all supported this conclusion. Detailed band structure calculations by Suvasini et al. [1996] extrapolate a more detailed FS.

A summary of the angular dependence of dHvA frequencies is given in Figure 4.3. Measured dHvA frequencies are given for CeB₆ in Table 4.1.

The magnetic phase diagram was mapped out by Komatsubara et al. [1980]. Later, Effantin et al. [1985] refined the measurements and published

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*The $a_3$ orbit of CeB₆ does correspond to the $\eta$ orbit in Al; however, the $\eta$ orbit disappears within 2.5 degrees of the [100], whereas the 8.6 kT orbit observed for CeB₆ persists for more than 10 degrees of rotation [van Deursen et al., 1982].

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Figure 4.2: The Fermi surface of LaB$_6$.

Table 4.1: Summary of reported dHvA frequencies in CeB$_6$.

<table>
<thead>
<tr>
<th>F (kT)</th>
<th>Field Range (T)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.67</td>
<td>8 - 14</td>
<td>Onuki et al.</td>
</tr>
<tr>
<td>8.66</td>
<td>12 - 22</td>
<td>Joss et al.</td>
</tr>
<tr>
<td>8.68</td>
<td>30 - 40</td>
<td>Haanappel</td>
</tr>
<tr>
<td>11.0</td>
<td>30 - 50</td>
<td>Haanappel</td>
</tr>
</tbody>
</table>
Figure 4.3: The angular dependence of the dHvA frequencies for CeB$_6$ as reported by Onuki et al. [1989] is shown here.
a revised phase diagram shown in Figure 4.4. From measurements of the splitting of the $^{11}B$ NMR line Takigawa et al. [1983] inferred antiferromagnetic order in Phase II. The log T resistivity and negative magnetoresistance in Phase I indicates a strong Kondo effect [Jaccard and Flouquet, 1985]. All dHvA measurements have been made in phase II, the anti-ferro quadrupolar (AFQ) moment phase. However, according to the theoretical description of Uimin et al. [1996] and Uimin [1997], the AFQ phase should give way to a paramagnetic phase at fields above 25 T for temperatures below 0.5 K. The absence of a phase transition is in keeping with the fact that the AFQ state is induced by the applied magnetic field and thus sufficiently high fields should quench the anti-ferromagnetic ordering.

The ground state is a four fold degenerate $\Gamma_8$ level; the $\Gamma_7$ is 545 K higher in energy [Zirngiebl et al., 1984]. Horn et al. [1981] had deduced from their magnetization measurements that the ground state of CeB$_6$ is the $\Gamma_7$ doublet. However, subsequent experiments showed the $\Gamma_8$ quartet to be the ground state [Sato et al., 1984]. Neutron scattering and specific heat data are consistent with a $\Gamma_8$ crystal field ground state.

4.3 Resistivity Measurements

Resistance measurements were made on one single crystal from a batch made by Z. Fisk. We confirmed the existence of the two critical points $T_N$ and
Figure 4.4: The magnetic phase diagram of $\text{CeB}_6$ exhibits three main phases at zero field separated by two magnetic ordering temperatures: the quadrupolar ordering temperature $T_Q = 3.2$ K and the Néel temperature $T_N = 2.4$ K. Below $T_N$, phase III is characterized by a complex magnetic ordering which is destroyed at fields larger than 1 - 2 T; the exact field is orientation dependent.
Figure 4.5: The quadrupolar ordering temperature $T_Q = 3.2$ K and the Néel temperature $T_N = 2.4$ K are shown in this resistance versus temperature curve for CeB$_6$.

$T_Q$ and noted that the resistivity of this sample was in good agreement with the values measured by other groups. The zero field resistance measurements made at LSU are shown in Figure 4.5.

Several previous studies of the resistivity of CeB$_6$ have been conducted [Takase et al., 1980; Marcenat et al., 1990a; Marcenat et al., 1990b]. Takase et al. measured the electrical resistivity and the magnetoresistance of single crystals of CeB$_6$ at temperatures between 1.3 and 300 K and at fields up to 8.5 tesla. Marcenat et al. made measurements between 80 mK and 4 K at fields
up to 7 tesla. At zero field the resistivity of CeB$_6$ is strongly temperature dependent. Due to its negative magnetoresistance, the resistivity of CeB$_6$ decreases with increasing field. It is possible that this change in resistivity is significant enough to force us to consider the Dingle temperature to be a temperature dependent quantity.

### 4.4 Low Temperature Specific Heat Measurements

The first low temperature specific heat (LTSH) measurements on CeB$_6$ were made by Lee and Bell [1972]. They made measurements below 25 K in zero field and found an peak at 2.31 K corresponding to a magnetic phase transition $T_N$. A smaller peak appears in their data around 3.4 K that was later interpreted to be $T_Q$. Fujita et al. [1980] made measurements up to 77 K and in fields up to 1.8 T to map the field dependence of the two peaks in the specific heat, thus constructing the first rudimentary magnetic phase diagram for CeB$_6$ (see also [Komatsubara et al., 1980]). The paramagnetic susceptibility of CeB$_6$ was measured by Aoki and Kasuya [1980] and interpreted with the anisotropic exchange interaction. Peysson et al. [1986] extended the specific heat measurement in applied fields to determine the critical peaks up to 8 tesla. Two subsequent studies by Bredl [1987] and Müller et al. [1988] focused on measurement of the LTSH below 1 K to
determine the electronic specific heat coefficient $\gamma$. Müller et al. compared their values with cyclotron masses determined by the dHvA effect.

New low temperature specific heat measurements were made on one sample of CeB$_6$ at the University of Florida. These measurements were made at temperatures from 0.4 K to 1.3 K in fields of 0, 2, 7, 8.5, 10, 12, and 14 tesla. The data is shown in Figures 4.6 and 4.7.

Bredl [1987] reported similar measurements on 1 g polycrystals of CeB$_6$ at temperatures between 0.04 K and 1 K and in fields up to 8 tesla. Bredl's study intended to yield values of the electronic specific heat coefficient, $\gamma$.

---

*Many thanks to Jungsoo Kim and Greg Stewart for performing these measurements.*
as a function of field. Bredl notes that a nuclear contribution to the low temperature specific heat arises from the Zeeman splitting on nuclei with nonzero spin. (In the case of CeB₆ these contributions are derived from the ¹⁰B and ¹¹B.) This nuclear Schottky specific heat $C_{\text{nuc}}(T)$ has a maximum at millikelvin temperatures in a few tesla of applied field. The magnitude of $C_{\text{nuc}}(T)$ can be calculated from nuclear data and assuming a uniform 'effective field' $B_{\text{eff}}$. The Schottky specific heat anomaly has the form

$$C_S = Nk_B \left( \frac{\mu_BB_{\text{eff}}}{k_BT} \right)^2 \left[ \frac{e^{\mu_BB_{\text{eff}}/k_BT}}{1 + e^{\mu_BB_{\text{eff}}/k_BT}} \right]^{-2}. \quad (4.1)$$
Bredl goes on to note that the high temperature tail of a Schottky anomaly approaches an $A B_{eff}^2 T^{-2}$ law, where $A$ is $4N\mu_B^2/k_B$. This $A B_{eff}^2 T^{-2}$ term should be subtracted from the specific heat data before extracting cyclotron mass values. Müller et al. [1988] calculate $A$ to be 22.36 $\mu$JK/T$^2$. With this nuclear term added, and no other contribution from phonons, magnons, etc., a plot of $C T^2$ versus $T^3$ curve should yield a straight line: $C_{LT}(T) = A B_{eff}^2 T^{-2} + \gamma T$. $B_{eff}$ is obtained from the intercept of the $C T^2$ versus $T^3$ plot. Bredl finds that $B_{eff}$ exceeds the applied field by about 0.2 tesla for fields up to 8 tesla.

However, the data from Florida does not yield the same results. In Figure 4.8 we show the Florida data plotted as $C T^2$ versus $T^3$. We note that at all of the higher fields we do not get straight lines when the experimental data is plotted as $C T^2$ versus $T^3$. Since Bredl's data did not go above 1 K, we restricted our comparative analysis to points in our data below 1 K. Even below 1 K, a straight line fit did not represent the data very well and in all cases the quantity $A B_{eff}^2$ was a negative quantity. As the applied field increases, the shape of the $C T^2$ versus $T^3$ curves become more linear. The 14 tesla curve is only approximately linear; however, it suffers from the negative intercept problem. We conclude from our measurements that the nuclear contribution to the low temperature specific heat is not the only contribution other than electronic.
Figure 4.8: Low temperature specific heat data of a CeB$_6$ single crystal plotted as a function of CT$^2$ versus T$^3$ for comparison with Bredl [1987].

After subtracting off the contribution due to the nuclear Schottky anomaly, Bredl was able to fit his zero field data by adding two magnon contributions to the specific heat:

$$C(T) = \gamma_0 T + \beta_1 T^3 + \beta_2 T^3 \exp\left(\frac{-\delta E}{k_B T}\right), \quad (4.2)$$

where $\gamma_0 = 0.26$ J/K$^2$ mol, $\beta_1 \approx 0.4$ J/K$^4$, $\beta_2 \approx 0.9$ J/K$^4$, $\delta E/k_B \approx 0.45$ K. We fit our zero field data to Equation 4.2 and find that it yields a negative value for $\gamma$ signifying that it is not a good fit to our data. Bredl admits the failure of this description in finite magnetic fields. Bredl goes on to postulate...
that the specific heat data might be explained by a normal anti-ferromagnetic spin wave term and an anomalous electronic term.

Müller et al. [1988] extended the low temperature specific heat measurements presented by Bredl up to 22 T. They found a value of $\approx 250 \text{ mJ/mole K}^2$ for the electronic specific heat coefficient, $\gamma$, at zero field in good agreement with Bredl [1987]. As shown in Figure 4.9, our zero field measurement yield a much lower value, $\approx 100 \text{ mJ/mole K}^2$. Also our 2 tesla value is 14% lower than that reported by Bredl. For fields above 7 tesla our measurements are in excellent agreement with Müller et al. [1988].

Much work remains to be done concerning the low temperature specific heat measurements on CeB$_6$. To understand properly the shape of the specific heat as a function of temperature, an adequate model which accounts for the various phenomena contributing to the specific heat must be constructed. Bredl [1987] suggests a number of possible models, but we find that the models fail when applied to our data. Accurate determination of $\gamma$ as a function of field is important since it can be compared with the cyclotron mass values derived from dHvA measurements.

4.5 Calculation of Fermi Surface Geometry

As stated above, the CeB$_6$ FS is similar to that of LaB$_6$, having ellipsoids centered on X points connected by necks oriented along the $\Gamma - M$ direction.
Figure 4.9: Our measurement of the magnetic field dependence of the electronic specific heat coefficient $\gamma$ is compared with those reported by Bredl [1987] and Müller et al. [1988]. For the purposes of comparison, we determined $\gamma$ the same way Müller et al. did—by extrapolating the $C/T$ vs $T^2$ curve to the zero field crossing. The curvature at the higher temperatures are ignored.
One remarkable difference is that the $X$ centered ellipsoids are 10 percent larger in CeB$_6$ than in LaB$_6$. Using the notation of Onuki et al. [1989], shown in Figure 4.3, the $\alpha_3$ orbit is the main observed frequency at 8.6 kT. The $\gamma$ orbit encloses the $M$ point, the $\epsilon$ orbit encloses the $\Gamma$ point, and the $\rho$ orbits enclose the $\Gamma - M$ pockets.

To explain the larger size of the CeB$_6$ belly orbit as compared to LaB$_6$, band structure calculations have been performed by a number of groups [Langford et al., 1990; Norman and Min, 1987; Suvasini et al., 1996]. In these calculations, $f$ electrons are treated in many ways, as core or band states either with or without spin polarization. Results from the polarized $f$ band calculations yield small belly orbits. It seems that the paramagnetic $f$ core calculation fits best with the data, but it does not account for the 10 percent increase in size. Norman and Koelling [Norman and Koelling, 1992] speculate that the size discrepancy reflects too simplified a model for the $X$ ellipsoids; the shape of the ellipsoids is slightly more complex, containing anisotropies, in CeB$_6$. The $f$ band calculations of Suvasini et al. [1996] yield enlarged $\alpha$ orbits. This does not agree with Norman's calculations. I will have more to say of Suvasini et al.'s calculations below.

Onuki et al. [1989] attribute the increased size of the Fermi surface and the mass enhancement as compared to LaB$_6$ and PrB$_6$ to the weak hybridization of the $4f$ electrons with the conduction band. Magnetic ordering at low
temperatures is brought about through an exchange coupling between the \( f \) moments and the conduction elections.

The modeling of the CeB\(_6\) is far from complete. The findings of Joss \textit{et al.} [1987] do not rule out a single spin FS. The Norman and Koelling calculations yield two Fermi surface sheets, a spin up and a spin down sheet. The calculations of Suvasini \textit{et al.} show that the \( \alpha \) orbit is at least partially polarized. Norman and Koelling offer several suggestions for how band structure calculations could be modified: (1) "incorporating Hund's second rule effects in an \( f \) band calculation," (2) "properly include the spatial anisotropy of the \( f \) electron in an \( f \) core calculation," and (3) employ a Kondo renormalized band calculation (see [Zwicknagl, 1988]).

4.6 The Cyclotron Mass Problem

The incongruity of the dHvA cyclotron masses and those gained through LTSH measurements was noted in two papers by Joss \textit{et al.} [1987] and Joss \textit{et al.} [1988]. They measured dHvA with field modulation at fields between 12 and 22 tesla at temperatures down to 60 mK in a home-made plastic dilution refrigerator. For the [100] belly orbit they found a frequency of 8.68 kT with cyclotron mass approaching \( 18 \ m_e \) at 12 tesla. Values of the cyclotron mass obtained by LTSH ranged from 25 to 30 \( m_e \) in the same field region.
Joss et al. concluded that the f electron of the Ce ion is weakly hybridized. They appealed to unpublished band structure calculation by Norman and Min [1987]. Additionally, the discrepancy between the dHvA and LTSH effective mass, they asserted, is accounted for in the dramatic field dependence of the electron mass. Noting that dHvA is only sensitive to itinerant electrons occupying the extremal piece of the Fermi surface, they pointed out that general agreement between dHvA and LTSH results could be reached if the inverse Fermi velocity was integrated over the entire Fermi surface. Any remaining difference in the dHvA and LTSH cyclotron masses could be accounted for by appealing to the insensitivity of dHvA to localized electrons—a factor to which LTSH is sensitive. The electronic density of states at the Fermi level is given by

\[ N_F = \frac{1}{4\pi^3} \int_{FS} \frac{ds}{\hbar \nu}, \]

an integration of the inverse Fermi velocity over the entire Fermi surface. \( N_F \) is proportional to the \( \gamma \) factor derived from LTSH. Joss et al. [1988] propose that the Ce f electron hybridizes weakly with the conduction bands. This weak hybridization enhances the mass of the conduction electrons, but does not destroy the local moment associated with the Ce. dHvA is not sensitive to localized effects and thus dHvA measurements will systematically underestimate the cyclotron mass.
Another interesting observation put forward by Joss et al. concerned the absence of exchange splitting of the Fermi surface. They conclude that the "exchange interaction between the conduction electrons and the local magnetic moments of the f-electrons must be very small." [Joss et al., 1988]

According to Onuki et al. [1990], the local moment on the Ce and its anti-ferromagnetic ordering should lead to electron spin splitting (exchange splitting) at the Fermi surface. This spin splitting would manifest itself as two frequency peaks in the dHvA spectrum. The cyclotron mass of the up spin orbit might be considerably lighter than the down spin orbit. The heavier mass of the down spin orbit would make it more difficult to observe. Thus Onuki et al. [1990] suggest that if the cyclotron effective mass of the unobserved down spin orbit was factored in, this would account for the discrepancy between dHvA and LTSH measurements. The problem with this explanation is that this alternative spin sheet has yet to be observed. It is possible that the proposed sheet lies above the Fermi level, in which case it would not serve as an explanation of the mass enhancement. However, interpreting the observed dHvA frequency as arising from a single spin sheet provides an explanation of the field dependence of the dHvA frequency of the $\alpha$ orbit in CeB$_6$.

At least two alternative hypotheses as to why dHvA cyclotron masses are lower than LTSH effective masses can be put forward. First, magnetic
breakdown might play some role in the field dependence of the mass. If conduction electrons are tunneling into open orbits, they would go unaccounted for in a dHvA measurement. If the rate of tunneling is sufficiently high, this could lead to an artificially low value for the cyclotron mass as determined from dHvA. However, if the general shape of the mass versus field curve as determined by dHvA and LTSH remains the same, then Joss et al.'s conjecture is supported and magnetic breakdown would act as a small correction rather than the source of the difference. Second, we have investigated the applicability of the L-K equations to the analysis of this material. The L-K equations apply well to weakly interacting electronic systems; it is less clear that the L-K equations can be used to garner information about heavy fermion systems where the electron interactions cannot be characterized as weak. Proper modification of the theory of dHvA in these systems might adequately account for the difference in cyclotron masses as measured by dHvA and LTSH. Below I will discuss the effects of allowing for strong correlations in the derivation of the L-K equations. We shall see that the main effect of introducing correlations or other many body effects is a renormalization of parameters rather than a fundamental reformulation of the L-K equations. Additionally, cyclotron masses are derived from a measurement of the temperature dependence of the amplitude. When this amplitude dependence is measured other reduction factors are held constant. For example, the Dingle
temperature, $T_D$, is assumed to be constant as a function of temperature. Thus, the difficulty of disentangling and isolating various many body effects may be high.

Various theoretical attempts have been made to account for the renormalization of the cyclotron effective mass in CeB$_6$. It has been proposed by Norman and Min [1987] that the cyclotron mass versus field data can be fit using the Kondo resonance model proposed by Schotte and Schotte [1975]. The fit applied by Norman and Min is of the following form:

$$\frac{m^*}{m_b} = \frac{A\Delta^2}{(\Delta^2 + (gH^2))^2} \quad \text{(4.4)}$$

where $A$ is the zero field value (extrapolated to be $47 \frac{m^*}{m_b}$), $\Delta$ is the resonance width (9.3 K was the value used by Norman and Min), $g$ is the $g$-factor ($6/7$), $m_B = 0.56$, and $H$ is the applied magnetic field.$^4$ In a separate paper, Norman and Koelling cite the large value for the cyclotron mass as a reason for why the $f$ core model is an inadequate description of the CeB$_6$ band structure.

An alternative model due to Wasserman et al. [1989] (discussed below) provides another possible fit to the cyclotron mass data.

$^4$It should be noted that the parameters for this fit were derived in a system where $k_B$ and $\mu_B$ are equal to one. Converting from this unitless system, one finds that Norman and Min used $g = 2$. 

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Figure 4.10: $m^*$ as generated by Wasserman et al. (Equation 4.11), by Norman and Min (Equation 4.4), and by an empirical function.
No calculation of the cyclotron mass as a function of field has been made based on the non-Kondo model of Sheng and Cooper [1995].

4.7 Magnetic Field Dependence of the Cyclotron Mass of CeB$_6$

The following section was submitted in a condensed form to Physical Review B for publication.

4.7.1 Introduction

During the last fifteen years the Fermi surface of the heavy fermion compound cerium hexaboride (CeB$_6$) has been the focus of several de Haas-van Alphen (dHvA) studies [van Deursen et al., 1982; Joss et al., 1987; Onuki et al., 1989; Matsui et al., 1993; Haanappel et al., 1992; Harrison et al., 1993; Hill et al., 1996; Hill et al., 1997]. This work has shown that the cyclotron mass of the conduction electrons in CeB$_6$ varies by nearly an order of magnitude when seen in fields ranging from 8 to 50 tesla. A persistent question has marked these experimental investigations: why has the spin splitting of the $\alpha_3$ orbit not been observed at high fields?

In a 1991 review paper, Springford [1991] noted that the dHvA frequency of the $\alpha_3$ orbit varied slightly over a limited field range. Previous measurements by Joss et al. [1987] showed no change in the dHvA frequency to within 0.5 percent over the range of fields they investigated (12 T to 22 T).

*An experimental review of work on CeB$_6$ has been given by Joss [1990].

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Additionally, Onuki et al. [1989] searched for evidence of a frequency change over the field range of 8 T to 14 T and found a change less than 1 percent; they concluded that to within their reported experimental error the frequency did not change.

We report here new measurements of the frequency and mass of the $\alpha_3$ orbit that extend the field range of measurement from 7 T to 50 T. From these measurements we are able to see a more complete picture of the field dependence of the dHvA frequency and effective mass.

4.7.2 Experiment

The present measurements were carried out on two different samples and at three different laboratories. The low field data (7 T - 14 T) were obtained at LSU using a low-frequency magnetic field modulation technique with modulation frequencies of 17 Hz and 40 Hz. We used a bottom loading $^3$He-$^4$He dilution refrigerator to reach temperatures between 25 mK and 200 mK. The intermediate field data (20 T - 30 T) were taken at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL. These measurements were carried out in a $^3$He refrigerator at temperatures between 0.5 K and 1 K and in a resistive magnet using field modulation at 17 Hz and 40 Hz. The measurements above 30 T were done in pulsed fields at the Service National des Champs Magnétiques Pulsés at Toulouse in the temperature range from 1.7 K to 2.5 K.
The results of the mass measurements reported in several experiments including the present results are shown in Figure 4.11 along with a fit to the data that will be discussed below. The mass is calculated from measurements of the amplitude in constant field intervals at four to six different temperatures. Our results show that the measured mass continues to rise as the measurement field decreases to a value of \((26 \pm 1) m_e\) at 7.1 T. In addition it is seen that the mass variation flattens out at high fields where it has a value of around 3.5. Thus, a change in mass of about a factor of 7 is observed over the 40 T field range.

For each frequency measurement, a Fourier transform was done on twenty-five to fifty oscillations to determine the frequency. An example of the raw data taken at LSU is given in Figure 4.12. Data sets of this sort were analyzed using the Fourier analysis techniques described above. An example FFT is shown in Figure 4.13.

For accurate determination of dHvA frequencies, the precise value of the applied magnetic field must be known. Field values are generally estimated from a measurement of the current flowing in the magnet or from the voltage drop across some known load. This estimate is fairly accurate since such values are calibrated against NMR measurements. Thus, all the experimentalist needs to worry about is getting his sample precisely in the field center (or to within 5 mm of field center). Centering the sample is accomplished by
Figure 4.11: The $m^*/m_0$ data is taken from Joss et al. [1987]; Onuki et al. [1989]; Haanappel [1992]. The lowest field point, 7.1 T, is from measurements made at LSU ($m^* = 26.4 \pm 1$). Wasserman et al.'s theoretical fit to the cyclotron mass data is shown.
modulating the magnet and extrapolating the field by making a plot of the amplitude of the pickup voltage versus the z direction.

The above method is sufficient if only one magnet will be used to make all the measurements on any given sample. Since the effective mass of the electrons in CeB$_6$ increases so dramatically as the applied field is lowered, it is necessary, at low fields, to make measurements at extremely low temperatures—hence a dilution refrigerator and a superconducting magnet was used to make low field measurements. As an objective standard by which to check the field calibration of each magnet, the dHvA effect in a single crystal of Au was measured in each system. The resulting dHvA oscil-
Figure 4.13: FFT of the dHvA peaks. Temperature is 100 mK. The main peak (experimental value F = 8.8 kT) is the $\alpha_3$ orbit at an applied field of 13 T. Note: this figure is not included in the published paper.

In pulsed field measurements, frequency changes are easily measured, but the absolute value of the frequency is not accurate due to phase shifts in the signal caused by varying field penetration into the sample and phase shifts associated with the data acquisition electronics. Frequencies measured by the low frequency field modulation technique do not have this problem. Therefore we have scaled the lowest field pulsed field frequency to the 30 T dHvA frequency measured with low frequency field modulation.
The measured frequencies for the $\alpha_3$ orbit are shown in Figure 4.14, again with a fit to the data to be discussed below. The overall frequency change over the 40 T range is approximately 4 percent and is clearly visible. We believe that this is the first reported observation of a field dependent dHvA frequency in fields far below the quantum limit. Previous studies by Joss et al. [1987] and Onuki et al. [1989] were not able to resolve this frequency change because they carried out their measurements over a narrower range of fields. In the field range investigated by Joss et al. (12 to 22 T), the frequency change is approximately 1 percent. The range investigated by Onuki et al. was narrower (8 to 14 T), corresponding to a frequency change of a little more than 0.5 percent.

4.7.3 Discussion

For readers not familiar with the details of the dHvA effect, we give a short introduction to the analysis used for these results. Because of the large and field-dependent effective masses, it is reasonable to expect evidence of spin splitting in the dHvA measurements Shoenberg [1984] and, therefore, we describe how electron spin enters into the dHvA effect.

The semi-classical theory of the dHvA effect is given by the Lifshitz-Kosevich (L-K) formula [Shoenberg, 1984]. The oscillatory magnetization
Figure 4.14: Measured values of the $\alpha_3$ orbit dHvA frequency. The data are compared with the frequencies derived from Wasserman et al.'s modified L-K equation.

$M_{\text{osc}}$ can be written schematically as

$$M_{\text{osc}} = C \sin \left( \frac{2\pi F}{B} + \phi \right),$$

(4.5)

where $C$ is an amplitude prefactor including the temperature and field dependence of the amplitude of the dHvA effect [Shoenberg, 1984], $F$ is the dHvA frequency, $B$ the magnetic field and $\phi$ a phase factor. Note that it is from the temperature dependence of $C$ at constant field that the effective mass values are determined.
The dHvA frequency depends on the extremal area enclosed by the cyclotron orbits (Onsager relation):

\[ F = \frac{\hbar}{2\pi e} A. \]  \hspace{1cm} (4.6)

A magnetic field splits the energy bands into two subbands separated by the Zeeman energy, \( \Delta E = g\mu_B B \), where \( g \) is the electronic \( g \)-factor and \( \mu_B \) is the Bohr magneton. Accordingly, the area enclosed by an electron orbit is different for spin up and spin down subbands, and to first order equals

\[ A^\pm = A_0 \pm \left( \frac{\partial A}{\partial E} \right) \frac{\Delta E}{2}, \]  \hspace{1cm} (4.7)

where \( \left( \frac{\partial A}{\partial E} \right) = (2\pi m/\hbar^2) \) is proportional to the effective mass \( m \) of the electron and \( A_0 \) is the area enclosed by the orbit in the absence of spin splitting.

Each subband contributes to the dHvA signal according to the L-K formula. Using the Onsager relation with the two different extremal areas, one obtains, to within a constant phase \( \phi \),

\[ M_{\text{osc}} = \frac{C}{2} \left[ \sin \left( \frac{2\pi F}{B} - \psi \right) + \sin \left( \frac{2\pi F}{B} + \psi \right) \right], \]  \hspace{1cm} (4.8)
where the phase factor $\psi$ depends on the $g$-factor and the effective mass of the electrons:

$$\psi = \frac{\pi}{2} g \frac{m}{m_e}.$$ 

The first sine term represents the magnetization due to the up spin band and the second sine term is from the down spin band. Thus, there are two sets of oscillations, both periodic in $\frac{1}{B}$, having exactly the same frequency, but shifted in phase. Both orbits give the same frequency at all fields because the phase is normally field independent.

However, in CeB$_6$ the effective mass changes dramatically, by a factor of 7, as a function of field in the range 7 T to 47 T as shown in Figure 4.11 [Joss et al., 1987; Onuki et al., 1989; Haanappel, 1992]. Since the $\text{dHvA}$ phase is directly proportional to $m^* = \frac{m}{m_e}$, the phase would thus be field dependent, and the periodicity of the two sets of oscillations would change with field. With the mass decreasing with field by a factor of 7, the phase should go through several revolutions of $2\pi$ over a field range of 40 T. The resulting measured $\text{dHvA}$ signal should thus exhibit beating with several zero amplitude fields and peak splitting. This can be seen more easily if Equation 4.8 is rewritten as

$$M_{osc} = C \cos \left( \frac{\pi}{2} g \frac{m}{m_e} \right) \sin \left( \frac{2\pi F}{B} + \phi \right). \quad (4.9)$$
From this equation, we can see that the field dependent mass leads to an amplitude modulation. The peak splitting is a more subtle feature to resolve, requiring a low Dingle temperature and a signal rich in harmonics. However, measurements of the $\alpha_3$ orbit in CeB$_6$ do not exhibit the amplitude variation the above equation implies. (This is consistent with the observations of Joss et al. [1987].) From Equation 4.8 one can see that if only one spin direction is present in the observed dHvA signal, then the frequency would be field dependent for a field dependent effective mass because only one of the two sine terms would be involved. The resulting equation for the oscillatory magnetization is

$$M_{osc} = \frac{C}{2} \sin \left( \frac{2\pi F}{B} + \left( \frac{\pi}{2} g \frac{m}{m_e} \right) + \phi \right). \quad (4.10)$$

One can collect terms involving the field dependence and factor out the periodicity in $\frac{1}{B}$ to see the field dependent frequency. For example, if $\frac{m}{m_e}$ were proportional to $\frac{1}{B^2}$, then the frequency should decrease as $\frac{1}{B}$.

From the current observation that the dHvA frequency is indeed field dependent, we hypothesize that the $\alpha_3$ orbit of CeB$_6$ is due to a segment of the band structure that has only a single spin direction because field dependent dHvA frequency is most easily explained by a spin polarized Fermi surface. If the Fermi surface is not spin polarized, then the measured dHvA
frequency is always seen to be field independent. Our conclusion does not agree with that of Harrison et al. [1993] who deduce that the \( \alpha_3 \) orbit is unpolarized based on extrapolation of their Dingle plot to infinite field. A band structure calculation by Suvasini et al. [1996] suggests the polarization of the \( \alpha_3 \) orbit is 21 percent of the total polarization at the Fermi energy. An added conclusion of these calculations is that the \( \alpha_3 \) orbit is non-degenerate and therefore not subject to further spin-splitting in a magnetic field.

To compare the measured values of frequency against what we expect from the discussion above, we inserted the measured dHvA masses into Equation (4.10) and solved for the resulting frequency. As shown in Figure 4.15, these field dependent values of \( m^* \) impart a field dependence to the frequency. The linear fit to these data is merely to aid the eye and was adjusted to pass through the data points by allowing the \( g \) factor to vary. To give a reasonable fit in this manner, we found that the \( g \) factor for the conduction electron must be increased to values larger than 8.

Magnetization measurements have shown that there is a magnetic moment associated with the Ce ion. In the temperature range pertinent to our dHvA experiment and at fields of around 7 T, the magnetization per Ce ion is approximately 0.8 \( \mu_B \) and saturates at a value of 1 \( \mu_B \) at fields above 15 T [Horn et al., 1981]. This magnetization contributes to the total \( \vec{B} \) field seen by the electrons. The magnitude of the \( \vec{B} \) field in the sample

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Figure 4.15: Frequencies calculated from uncorrelated L-K theory for a single spin using measured dHvA masses for CeB₆.

depends on sample shape [Crabtree, 1977]. The sample used for the present low field measurements was roughly cubic, about 1.5 mm on a side. We have made corrections to the magnetic field to account for this magnetization and note that this causes the observed dHvA frequency changes to become more pronounced with the largest changes at low fields. Since \( \mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \), we can write the magnetic field \( \mathbf{B} \) in terms of the applied field \( \mathbf{H} \) and the magnetization \( \mathbf{M} \). The magnetization per unit volume can be calculated from the values for the moment quoted above and the lattice constant \( a = 4.14 \times 10^{-10} \) m. An example calculation yields: assuming 0.8 \( \mu_B/\text{Ce ion} \) shifts the
frequency at the lowest field, 8.2 T, from 8.8 kT to 9.0 kT, representing a 2.3 percent change. The corresponding shift in frequency at 28.75 T using 1 \( \mu_B/Ce \) ion is only 1 percent.

The L-K equation was derived on the premise that the conduction electrons interact weakly with other lattice phenomena, but several theoretical studies [Luttinger, 1961; Fowler and Prange, 1965; Engelsberg and Simpson, 1970; Stamp, 1987; Rasul, 1989; Wasserman et al., 1989] of the dHvA effect have taken couplings into account.

The theory developed by Wasserman et al. [1989] starts from the Anderson lattice model and takes into account strong correlations. This theory yields an expression that models the field dependence of \( m^* \) in the dHvA effect in the following manner:

\[
\frac{m^*}{m_b} = 1 + \frac{2Dn_f}{Nk_BT_K} \left[ 1 + \frac{g\mu_B J B}{k_BT_K} \right]^{-2},
\]

where \( m_b \) is the unrenormalized band mass of the electrons, \( T_K \) is the Kondo temperature, \( D \) is the density of conduction band states, \( n_f \) is the mean occupation number of the \( f \) level.

Wasserman et al. were able to fit the observed mass with the parameters \( m_b = 0.56 \, m_e, \, T_K = 15 \, K, \, 2Dn_f = 1.5 \, eV, \, J = \frac{5}{2}, \, g = 1.1, \) and \( N = 6 \). The
fit of the effective mass data to Equation 4.11 is shown in Figure 4.11 along with the mass values from dHvA measurements.

The modified L-K expression for the oscillatory part of free energy, $\Omega_{osc}$, derived by Wasserman et al., is

$$\Omega_{osc} = C' \cos \left[ \frac{2\pi}{B} \left( F_0 - \frac{2Dn_f g_m B \pi J \mu_B B}{N(k_BT_K + g\mu_B J B)^2} \right) \right], \quad (4.12)$$

where $C'$ is the modified phase smearing factor that includes the mass variation. This expression can be differentiated to obtain the magnetization. We have used Equation (4.12) to calculate the frequency as a function of field. Using the same parameter values that Wasserman et al. used to fit the field dependence of the mass, we find that this yields a reasonable fit to the measured frequency data.

However, the validity of the parameters employed by Wasserman et al. should be questioned [Haanappel, 1992]. The parameters $N$, $J$, and $g$ were derived from the free Ce$^{3+}$ ion. Hund's rules were used to calculate $N$ and $J$ while $g$ was calculated using the Landé formula. Crystal field effects modify these parameters. The cerium atoms are in an octahedral cite in the cubic structure, and the spin orbit coupling ground state for a single 4f electron is $^2F_{5/2}$ which is split into a higher energy $\Gamma_7$ doublet and a ground state $\Gamma_8$ quartet by the crystal field, [Goodrich and Everett, 1966]. The $g$ factor for
the 4f electrons in the $\Gamma_8$ quartet is 10/7. Finally, the Kondo temperature used, 15 K, is slightly higher than the 5 K to 10 K derived from resistivity measurements [Takase et al., 1980], and five times larger than the $\approx 3$ K derived from neutron scattering [Horn et al., 1981]. Sato et al. [1984] estimated $T_K$ by fitting the temperature dependence of the susceptibility to the DeGennaro-Borchi equation [DeGennaro and Borchi, 1973] and find that it is approximately 1-2 K.

We have refit Equation (4.11) using $N = 4$ and $J = \frac{3}{2}$ to reflect the $\Gamma_8$ quartet. This narrows the bandwidth from 1.5 eV to 0.8 eV and raises the Kondo temperature and the $g$ factor to 20.7 K and 2.17, respectively. This change improves the fit to the dHvA frequency data, as is seen in Figure 4.14. To reduce $T_K$ to between 5 K and 10 K, to correspond with electrical resistivity measurements [Takase et al., 1980], requires narrowing the bandwidth even further, but doing so results in a field dependence of the frequency less than is observed.

We find that a modified L-K formulation that allows for strong correlations provides a reasonable model for the field dependence of the frequency in addition to being an excellent fit to the measured dHvA mass values. The one problem with this model is the high Kondo temperature required to fit the data. This may be due to the fact that here we focus on electrons involving the $\alpha_3$ orbit, whereas transport measurements sample all electrons.
It is important to note that the dHvA frequency change in CeB₆ does not imply that the area of the ω₃ orbit changes as a function of field. The area remains constant while the observed frequency changes. The area calculated from the constant frequency using the modified L-K fit is larger than the previously reported area. We find that the ω₃ orbit gives an area that is 40 percent of the Brillouin zone area, corresponding to a zero field frequency of 9525 T. This frequency is closer to the value given by Suvasini et al. of 10870 T for the ω₃ orbit derived from a band structure calculation which treats the f electron as a valence electron.

One outstanding feature that is not resolved from these measurements is the difference (about a factor of 2 at low fields) between the overall average of effective mass measured by specific heat and that seen in the dHvA effect [Joss et al., 1987; Onuki et al., 1989; Harrison et al., 1993; Bredl, 1987; Müller et al., 1988; Onuki et al., 1990]. At high fields (> 20 T), the specific heat mass and the dHvA mass approach the same values. If, as Onuki et al. conjecture, the difference is due to unobserved Fermi surface sheets with heavy masses, then their masses must also decrease with increasing field to the observed field dependence of the specific heat and one would expect signals from other Fermi surface sheets to emerge at high fields. Haanappel's pulsed field measurements reveal an 11 kT frequency at high fields. This frequency has an associated effective mass of 6.5 ± 2.2 at 43.4 T, which is a
higher mass than the $\alpha_3$ orbit [Haanappel et al., 1992]. This frequency was also observed by Harrison et al. [1993] who measured a lower value of the mass: $1.4 \pm 0.4$ at 44.4 T. It is unlikely, in the light of our measurement of a field dependent frequency for the $\alpha_3$ orbit, that this is the missing down spin sheet to which Onuki et al. allude. This frequency could be due to magnetic interaction (the Shoenberg effect) with the $\gamma$ hole orbit ($F = 2.19$ kT [Onuki et al., 1989]) which would be much more likely to occur with spin polarized Fermi surface sheets. According to Sollie and Schlottmann [1990] at high fields the Shoenberg effect could be observed. The absence of a difference frequency in the data is not surprising since the amplitudes of the sum and difference frequencies need not be the same. In this case the amplitude of the difference frequency could easily be reduced so that it is not unambiguously resolved in the Fourier spectrum. The case has been made that this frequency is due to magnetic breakdown [Harrison et al., 1993; Haanappel, 1992] similar to that conjectured for the $\alpha$ orbit in LaB$_6$ [Arko et al., 1976]. However, the neck region where this is supposed to occur is much larger in CeB$_6$ than in LaB$_6$ [Suvasini et al., 1996].

All dHvA measurements in CeB$_6$ have been carried out in a magnetic field-induced ordered state that has been described as an antiferro-quadrupolar moment phase (phase II) [Effantin et al., 1985]. At zero field, no magnetic ordering is present as is shown by neutron diffraction measurements [Effantin
et al., 1982], but NMR measurements give evidence of a field induced ordering in phase II [Takigawa et al., 1983]. Subsequent neutron diffraction experiments in a field of 7.6 T showed antiferromagnetic ordering consistent with the splitting of the four fold degenerate $\Gamma_8$ ground state into two doublets having quadrupolar moments of $\pm Q$ [Effantin et al., 1985]. The results presented in this paper, evidence for a polarized Fermi surface, have implications for the interpretation of the magnetic structure of phase II when these spin polarized itinerant electrons are taken into account.

From our measurements and analysis, we reach two conclusions: (1) The Fermi surface sheet giving rise to the $\alpha_3$ orbit is a polarized single spin sheet. One calculation of the electronic structure of CeB$_6$ has produced a partial polarization of this Fermi surface sheet [Suvasini et al., 1996]. (2) A modified form of the L-K equation that includes correlations can be used to account for both the field dependent effective mass and frequency measured by the dHvA effect in CeB$_6$. Finally, we note that even after twenty years of effort and a multiplicity of experiments, we believe CeB$_6$ is an unsolved problem in heavy fermion physics and deserves more experimental and theoretical attention.
4.8 Suggestions for Further Study

dHvA measurements of CeB₆ must be extended to lower fields. This can be done with more sensitive measurements techniques (e.g. the SQUID detection technique introduced in Chapter 3) and by working at temperatures below 25 mK. Also evidence of the neck orbits should be sought at fields as low as 2 T. At these fields the specific heat coefficient $\gamma$ changes most dramatically. The masses of all the CeB₆ orbits should be measured as a function of field.

A series of measurements should be made on alloys of (La, Ce)B₆. Presumably, the polarization of the FS should turn on at some concentration of Ce in the alloy. dHvA measurements on this series of alloys would give us a chance to see the transition of the FS from a 3d metal to a 4f heavy fermion with strong interactions. Because of the high resistivity at low fields of (La, Ce)B₆ alloys, these measurements would have to made at high fields where the resistivity is low (see Figure 4.16). The samples for these measurements have grown by Z. Fisk at the NHMFL. Pulsed field measurements have already been carried out on these samples, but have yet to be fully analyzed. Excellent signals were seen in all samples at a variety of temperatures. Determination of the cyclotron mass as a function of field and cerium concentration can be extracted from this data. The dHvA effect in these
Figure 4.16: Resistivity is plotted as a function of field for various concentrations of $\text{La}_{1-x}\text{Ce}_x\text{B}_6$. The plot is taken from a paper by Sato et al. [1985].

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samples will be measured in the resistive magnets at the NHMFL within the next year to accurately determine frequencies.

Finally, high field resistivity measurements should be made to test the predictions of Uimin et al. [1996] concerning the quenching of anti-ferromagnetism in CeB$_6$ at high fields. This transition could also be measured via LTSH above 25 tesla.
CHAPTER 5

Landau Quantum Oscillations in Superconductors

5.1 Introduction

The study of superconductivity is quickly approaching its century mark, but the field has not failed to continue to produce interesting and exciting problems. Actually, superconductivity presently enjoys a second childhood born out of discoveries by Bednorz and Müller [1986] of a superconducting transition temperature, $T_c$, of 30 K in the La-Ba-Cu-O system and by Wu et al. [1987] of a $T_c$ in the Y-Ba-Cu-O system above 90 K. Before these discoveries, it was generally accepted that the reigning microscopic theory of superconductivity, BCS theory [Bardeen et al., 1957; Scalapino et al., 1966], did not allow for transition temperatures higher than about 21 K. Bednorz and Müller and Wu et al. blew the top off of this supposed limit. There ensued an experimental and theoretical frenzy to find higher $T_c$ materials and to devise theories that could account for superconductivity at such (relatively) high temperatures. A decade after these sensational discoveries the excitement has cooled somewhat, but high $T_c$ superconductivity commands
the attention of a large part of the research efforts of condensed matter physicists. Periodically, a press conference will be called to announce yet another high $T_c$ material that goes superconducting at a slightly higher temperature than the previous spotlight material [Laguës et al., 1993]. Technological applications are the primary impetus for the development of higher $T_c$ materials. But for the physicist, even high temperature superconductors with modest $T_c$'s around 30 K present exciting challenges.

Many different theories attempt to explain high temperature superconductivity. A number of reviews are available; see [Schrieffer, 1990; Anderson and Schrieffer, 1991; Ford and Saunders, 1997] The central question for any theoretical mechanism of high temperature superconductivity concerns the nature of the normal quasi-particle states. It is from the normal quasi-particles that pairs are formed resulting in the superconducting state below some critical temperature. The central question can be formulated like this: Is the normal state a Fermi liquid, i.e. exhibit metallic properties, or is it exotic [Anderson and Ren, 1990b; Varma, 1990; Anderson and Ren, 1990a; Levin et al., 1991; Lee, 1991; Yu and Freeman, 1991; Pickett et al., 1992]? One conclusive signature of a Fermi liquid-like normal state is the existence of a Fermi surface (FS), although other quasi-particle ground states also might exhibit marginal Fermi surfaces [Anderson and Ren, 1990b; Anderson and Ren, 1990a; Varma et al., 1989; Varma, 1991; Anderson, 1991]. Experimen-
tal evidence from positron annihilation [Smedskjaer et al., 1988; Peter et al., 1988; Tanigawa, 1989; Haghhighi et al., 1990; Berko et al., 1991; Jarlborg, 1991], photoemission [Arko et al., 1989; Imer et al., 1989; Olson et al., 1990; Campuzano et al., 1990], and rudimentary dHvA measurements [Mueller, 1990; Mueller, 1991; Smith et al., 1990; Kido et al., 1990; Kido et al., 1992a; Kido et al., 1992b; Fowler et al., 1992; Haanappel, 1992; Bykov et al., 1995] suggests that a FS indeed exists in YBa$_2$Cu$_3$O$_7$ (YBCO) and Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212). However, no definitive picture of either the FS topology or the effective mass anisotropy has been determined experimentally.

If the normal state of high temperature superconductors (HTSc) is a Fermi liquid, as the above referenced experiments suggest, then any theory explaining the cause of superconductivity in these materials will involve charge carriers on the FS. Regardless of whether the ground state is a strong Fermi liquid, marginal Fermi liquid, holon liquid, etc., Landau quantum oscillations (LQO) in the free energy should exist. It is fundamentally important and interesting to know the topology of the Fermi surface and the additional information that can be obtained from LQO.

Details of the FS topology are needed in order to understand—and to calculate—the strength of the pairing interaction, to distinguish between various models of the ground state, as well as to calculate many anisotropic superconducting and normal-state properties that involve FS integrations.
(e.g., the thermoelectric power) [Cohn et al., 1991; Cohn et al., 1992]. In particular, experiments are needed that can test the validity of the single-electron approximation that is inherent in band structure calculations [Massigna et al., 1987; Yu et al., 1991; Massida et al., 1991; Pickett, 1989] and, indirectly, calculations of properties based on these band structures [Li and Callaway, 1991]. Truly rigorous experimental tests require sensitivity to the relatively low Fermi energies (E_F) and carrier concentrations (in comparison with "normal" superconductors) that are found in high temperature superconducting materials. Experiments capable of detecting shifts in E_F due to a change in carrier concentration are especially valuable. Detailed measurements of LQO are ideal for these purposes. Measurements of LQO can yield momentum values at E_F as well as cyclotron effective masses for the orbits observed, to which predictions can be compared [Cochran and Haering, 1968; Shoenberg, 1984]. Mass enhancement factors (due to electron-phonon coupling) that relate to the superconducting pairing mechanism are a direct result of comparisons between single particle calculations of the effective mass and measured values.

Over and above the basic FS properties that can be obtained from LQO measurements in the normal state there is now strong experimental evidence, and theoretical support, that LQO phenomena exist and can be observed directly in the mixed state of type-II superconductors. Graebner and Robbins

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[1976] were the first to observe LQO below $H_{c2}$ in a type-II superconductor, in the layered (quasi-two dimensional) dichalcogenide $2\text{H-NbSe}_2$. Further dHvA measurements on this material have been made by Corcoran et al. [1994b] and Rettenberger et al. [1995]. D. H. Lowndes et al. observed strong dHvA oscillations in the mixed state of the A-15 superconductor $V_3Si$ [Lowndes et al., 1990a; Mueller et al., 1992]. Further studies on $V_3Si$ have been carried out by Corcoran et al. [1994a]. Kido et al. [1990] reported dHvA oscillations in the susceptibility of c-axis-aligned, epoxy-embedded single crystal powders ($\approx 20 \, \mu m$ grain size) of $\text{YBa}_2\text{Cu}_3\text{O}_7$, using steady magnetic fields up to 27 T, far below $H_{c2}$ for YBCO. The FS cross section and effective mass found by Kido et al. are in good agreement with the smaller of the two cross sections found by Mueller, Smith et al. at Los Alamos [Mueller, 1990; Smith et al., 1990; Fowler et al., 1992] (using flux compression and magnetic fields $> 100$ T). Haanappel et al. have measured similar epoxy embedded single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [Haanappel, 1992; Haanappel et al., 1993]. A Russian group has reported dHvA signals in YBCO samples given to them by the LANL group in fields of up to 230 T using the magnetocumulative generator MC-1 [Bykov et al., 1995]. We have observed LQO in $\text{Ba}_{0.8}\text{K}_{0.4}\text{BiO}_3$ [Goodrich et al., 1993] (see the next chapter). Additional observations have been made on the organic superconductor $(\text{ET})_2\text{Cu(\text{NCS})}_2$ [van der Wel, 1994] and the borocarbide superconductor $\text{YNi}_2\text{B}_2\text{C}$ [Goll et al., 1996a].
Several theoretical papers [Markiewicz et al., 1988; Maniv et al., 1988; Stephen, 1991; Stephen, 1992; Takane, 1993; Maniv et al., 1992a; Maniv et al., 1992b; Maniv et al., 1993b; Maki, 1993; Wasserman and Springford, 1994] also predict Landau level quantization and strong quantum oscillations in the mixed state of extreme type-II superconductors (e.g., the HTSc materials), but with the important conclusions that the LQO should be modified from the standard Lifshitz-Kosevich form, in such a way as to provide information about the strength of the pairing correlation and the superconducting state itself [Markiewicz et al., 1988; Stephen, 1991; Maniv et al., 1993b].

From a quick glance at the Lifshitz-Kosevich (LK) theory, one might conclude that to observe LQO phenomena the material must be driven into its normal state (i.e. above $H_{c2}$) given that LK theory assumes a normal metal. Assuming this were true, measurement of the dHvA effect in YBCO might prove nearly impossible given that $H_{c2}$ is higher than most magnetic field generation systems can deliver. Driving YBCO into its normal state using non-destructive pulsed field magnets would require the measurement to be carried out at liquid nitrogen temperatures. Recalling that low scattering rates are a necessary requirement for the observation of dHvA, we might conclude that making measurements in the normal state of YBCO would be difficult given that it has a higher resistivity in its normal state than normal metals. This increased resistivity is presumably due to short relaxation
times. Short relaxation times can be due to scattering by crystal imperfection, electron-electron (e-e), and/or electron-phonon (e-p) interactions. As single crystal samples become more perfect, one sees that e-p or e-e scattering become dominant scattering mechanisms. Another possibility for high resistivity in HTSc materials ($\rho = m^*/n e^2 \tau$) is that the carriers have a large effective mass, but the two preliminary dHvA measurements [Mueller, 1990; Smith et al., 1990; Fowler et al., 1992; Kido et al., 1990] for YBCO both obtain values of $m^* \approx 2 - 7 m_e$. If the current carriers have a small charge, e.g. holons, the resistance also could be high. However, models based on holons would not show field-induced diamagnetism, which also was observed in the preliminary dHvA measurements [Mueller, 1990; Smith et al., 1990; Fowler et al., 1992; Kido et al., 1990]. Thus, in high quality HTSc crystals, one expects to be able to observe the dHvA effect at low temperatures, if the problems associated with high critical fields can be overcome.

In one approach to overcoming this problem, a group at Los Alamos National Laboratory [Fowler et al., 1992] used pulsed magnetic fields in excess of 100 tesla (implosive flux intensifier) and reported observing dHvA oscillations, corresponding to three different FS cross-sections, in samples of single crystal YBa$_2$Cu$_3$O$_7$ powders ($\approx 10 \mu$m grain size) that had been cast and oriented (c-axis || to H) in an epoxy matrix. This technique may allow one to exceed $H_{c2}$, but it is very insensitive compared to steady-field dHvA
spectrometer capabilities using the field modulation technique described in Goldstien et al. [1965]; Stark and Windmiller [1968] and [Shoenberg, 1984, pp. 102 - 124]. The implosive flux intensifier technique destroys the sample and part of the measurement apparatus each time a data set is taken, and, therefore, is limited with respect to studies aiming at a full characterization of the sample FS. Non-destructive pulsed fields up to 50 tesla were used by Haanappel [1992]; Haanappel et al. [1993] to measure dHvA oscillations in similar powders of YBa$_2$Cu$_3$O$_7$ at Grenoble. Haanappel's measurements show dHvA oscillations starting at about 20 T.

5.2 Observation of the dHvA Effect in Superconductors

In this section, I will discuss the experimental conditions necessary for the observation of the dHvA effect in the normal state ($H > H_{c2}$) and in the mixed state ($H_{c1} < H < H_{c2}$) of HTSc materials.

5.2.1 Measurements in the Normal State

The zero-field superconducting transition temperature $T_c$ of the layered HTSc materials is controlled by the number of holes in the copper-oxygen planes. The zero-temperature upper critical field $H_{c2}$ is expected to scale approximately linearly with $T_c$, since $H_{c2} \approx 0.72 T_c (dH_{c2}/dT)$ in the clean limit [Helfand and Werthamer, 1966; Werthamer et al., 1966; Tinkham, 1980; Welp et al., 1989]. Empirical evidence shows that $H_{c2}(T)$ increases below $T_c$,
and is approximately $-1.5 \, \text{T/K} < \frac{dH_{c2}}{dT} < -1.9 \, \text{T/K}$ (with H parallel to the c-axis) for typical Cu-O based HTScs [Welp et al., 1989]. If we take $-1.9 \, \text{T/K}$ as a worst case (from the standpoint of achieving fields greater than $H_{c2}$), and if we operate at $T \approx 1 \, \text{K}$, then $H_{c2}(\text{tesla}) \approx 1.37 \, T_c(\text{kelvin})$. Consequently, if we wish to use magnetic fields in the range between 12 and 18 T for normal-state dHvA measurements, then we need specimens with $T_c$'s ranging from 8 K to 13 K. YBCO with its $T_c$ approaching 100 K is not a possible candidate material for normal state measurements in steady fields.

Using epoxy embedded, field aligned samples of YBCO made at LANL, Bykov et al. [1995] reported measuring dHvA in the normal state of YBCO using an ultra-high field pulse, flux compression generator. They achieved fields of up to 230 tesla for their measurements. Fourier analysis of their data revealed frequencies of 3.8 kT, 10 kT, 13 kT, and 20 kT. Only their lowest orbit agrees with previous measurements (see Section 5.2.3). They speculate that their 10 kT orbit might correspond to the 12 kT orbit predicted by band structure calculations. Since the 13 kT and 20 kT orbits are barely above the noise level, they make no strong claims concerning the origin of these peaks.

dHvA measurements in the normal state of Nb$_3$Sn using the pulsed field method have been carried out by Arko et al. [1978] and Wolfrat et al. [1985]. The latter study measured twelve frequencies (all below 1 kT) in three different symmetry directions having masses ranging from 0.6 to 1.8 $m_e$. Below,
I will present the results of our own measurements on Nb$_3$Sn and compare them with findings by Harrison *et al.* [1994].

### 5.2.2 Scattering Effects

The $r^{th}$ harmonic of the dHvA signal is exponentially attenuated as the carrier scattering rate increases, according to the factor [Cochran and Haering, 1968]

$$K_r = \exp\left[-\alpha r \left(\frac{m_e T_D}{H}\right)\right],$$

where $\alpha = (2 \pi^2 k_B/e\hbar)$, $r$ is the harmonic index, and $T_D$ is the Dingle temperature. $T_D$ is related to the Lorentzian half-width $\Gamma$ of the Landau levels and to the orbitally averaged large-angle scattering rate, $\langle \frac{1}{\tau} \rangle$, by

$$T_D = \left(\frac{\hbar}{2\pi k_B}\right) \langle \frac{1}{\tau} \rangle = \frac{\Gamma}{\pi k_B},$$

Thus, the ratio $(m_e \langle \frac{1}{\tau} \rangle / H)$ controls the dHvA signal amplitude. The value of this quantity that is needed to observe dHvA oscillations from a particular extremal orbit is given by the cyclotron resonance condition,

$$\frac{\omega_c}{\langle \frac{1}{\tau} \rangle} = \frac{e}{c m_e \langle \frac{1}{\tau} \rangle} > 1,$$

For HTSc materials, the important scattering events are charged-impurity scattering and diffuse scattering at grain and/or twin boundaries. However,
the epitaxial YBCO films grown at ORNL have mean free paths inferred from resistance measurements on the order of 200 to 500 Å at \( T = 1 \) K.

The oscillatory component of the magnetic susceptibility was calculated using the standard Lifshitz-Kosevich expression (see Section 2.2), modified to include the effects of a quadratic FS (non-zero contribution in the \( k_z \) direction of the Landau levels) [Khan et al., 1970]. The parameters used in the calculations are: the average orbital Fermi momentum \( k_F = 0.1 \) Å\(^{-1}\), the effective mass \( m^* = 4 m_e \), the temperature \( T = 25 \) mK, and the oscillation phase \( \phi = \pi/4 \). These are typical values expected from energy band calculations for YBCO, and are comparable to observations of Mueller [1990]; Smith et al. [1990]; Fowler et al. [1992] and Kido et al. [1990]. In Figure 5.1, the results of calculations for three different values of the mean free path, over the field range accessible in the LSU 18 tesla magnet system are shown. The signal amplitude for carriers with \( l_o = 1000 \) Å is large even in the 8 to 12 tesla range, but orbits with \( l_o = 250 \) Å do not produce an appreciable dHvA amplitude until the 12 to 18 tesla range is reached. These results are calculated for experiments in the normal state, but also may be valid for experiments in the mixed state (\( H < H_{c2} \)) if the L-K amplitude expression (or equivalently, the condition \( \omega_c/(\sqrt{\tau}) > 1 \)) is not significantly modified.
Figure 5.1: The oscillatory component of the susceptibility as calculated from L-K theory (Equation 2.9) is shown for various scattering parameters calculated from estimates of the mean free path $l_0$.

5.2.3 Measurements in the Mixed State

LQO were first observed in the mixed state of a type-II superconductor by Graebner and Robbins [1976] in the layered dichalcogenide 2H-NbSe$_2$. They observed a slightly ($\approx 3 \pm 1\%$) increased dHvA frequency for $H < H_{c2}$, and an increased Dingle temperature $T_D$, which they attributed to scattering of the orbiting normal carriers by the fluxoid lattice. They also speculated on the possibility of observing LQO in the mixed state of A-15 superconductors.

Both Graebner and Robbins and Markiewicz et al. [1988] have pointed out that the magnetic field inhomogeneity associated with the fluxoid lattice in a type-II superconductor is not a barrier to observing the dHvA effect, espe-
cially in an extreme type-II material (like the HTSc materials). Markiewicz et al. find that "dHvA oscillations should persist not only near $H_{c2}$ but at much lower fields as well - as long as the field inhomogeneity is weak." They also suggest that direct information can be gained about the pairing energy and that pairs in strong magnetic fields do not involve time-reversed states. For large values of the Ginzburg-Landau parameter $\kappa$, the field penetration depth $\lambda$ is so much larger than the superconducting coherence length $\xi$ that the internal fields are essentially uniform because the fluxons overlap considerably [Eilenberger, 1967]. For HTSc materials, $\kappa$ is on the order of 100 whereas for regular type-II materials values of $\kappa$ range around 5. Aoki et al. [1992] failed to observe dHvA oscillations in metallic Nb because field inhomogeneity within the sample damped out the effect. For HTSc materials, the average field variation at high applied field strengths is of order $4\pi M \ll H_{c1}$ ($\approx$ several hundred gauss for YBCO). Consequently, at applied fields of 15 tesla, phase smearing reduction of a dHvA signal with period $H^2/F$ becomes noticeable only for dHvA frequencies greater than 1000 tesla (at higher applied fields, higher frequencies could be observed). Our measurements are sensitive to carriers that are not inside the coherence-length-diameter core of the vortices, but are in the more extended region of the mixed state between vortex cores in the much longer penetration depth accompanying the cores.
Figure 5.2: dHvA amplitude vs. reciprocal applied field for V$_3$Si with H parallel to [100]. The amplitude of the oscillations above $H_{c2}$ (the left side of the figure) has been reduced by a factor of 2. The measured value of $H_{c2}$ is also indicated.

Lowndes et al. [1990a] and Mueller et al. [1992] observed dHvA oscillations both above and below $H_{c2}$ in the A-15 superconductor V$_3$Si. Using the field modulation method in a resistive magnet at the Francis Bitter National Magnet Laboratory, at least two branches of oscillations were observed between 15 and 19 tesla at a temperature $\approx$ 1.5 K, over angular range of 35 degrees away from [100] in a [100] plane, as shown in Figure 5.2. The amplitude of the oscillations below $H_{c2}$ was about 1/4 as that above $H_{c2}$. At
[100], a careful analysis [Mueller et al., 1992] reveals that there are two FS extremal cross sections, corresponding to dHvA frequencies of 1.986 kT and 1.496 kT, and cyclotron effective masses of \( \approx 1.15 \pm 0.1 \) m\(_e\) and \( \approx 0.4 \pm 0.2 \) m\(_e\), respectively. In contrast to the results of Graebner and Robbins for 2H-NbSe\(_2\), the dHvA frequencies for V\(_3\)Si were found to be invariant above and below H\(_{c2}\), to within \( \leq 0.5 \) %.

Mueller [1990]; Mueller [1992]; Smith et al. [1990]; Kido et al. [1990]; Haanappel [1992]; Haanappel et al. [1993] and Bykov et al. [1995] have reported observing dHvA oscillations in the susceptibility of oriented YBa\(_2\)Cu\(_3\)O\(_7\) powders that have been cast in epoxy and field-oriented during the hardening process. Mueller et al. and Smith et al. carried out experiments in a 105 tesla pulsed field generated by implosive flux compression. However the dHvA oscillations are believed to have been observed in the mixed state [F. M. Mueller (private communication)]. In these experiments, the peak field is reached in about 69 microseconds after the pulse is initiated; the sample, its cryogenic container, and the hollowed-out brass block in which the current flows are destroyed at about 93 microseconds when the explosive shock front catches up with the trapped flux [Mueller, 1990]. Three distinct dHvA frequencies (and some harmonics) were reported from experiments carried out at temperatures between 2.3 K and 3.9 K: \( F_1 \approx 3.5 \) kT (with a mass \( \approx 7.4 \)
In contrast, the experiments of Kido et al. [1990] were carried out in steady magnetic fields ranging from 10 to 27 tesla by the field modulation method, using the hybrid magnets of the High Field Laboratory at Tohoku University in Japan. Using temperatures between 1.8 K and 3.1 K, they found a single dHvA frequency of \( \approx 0.54 \) kT (with a mass \( \approx 2.1 m_e \)), in fair agreement with the lower of the two frequencies found in the Los Alamos experiments.

Haanappel [1992], using pulsed fields up to 40 tesla and a similar epoxy embedded field aligned powder of YBa\(_2\)Cu\(_3\)O\(_7\), found frequencies of 0.52 kT and 0.74 kT. He also reported smaller amplitude frequencies at 0.37 kT, 0.65 kT, and 0.88 kT. The slight differences in frequency were explained as possible differences in sample stoichiometry. Haanappel also noted that the dHvA frequencies of YBCO seemed to be field dependent. Analysis on the low field portion of his data gave frequencies of 0.53 kT, 0.68 kT, 0.86 kT, and 1.2 kT. He speculates that the reduction of the internal field due to the Meissner effect contributes to the apparent frequency change although the degree of the frequency shift is also dependent on eddy current heating in the sample.
dHvA measurements in the normal and mixed states of Nb$_3$Sn were reported by Harrison et al. [1994]. They made their measurements in pulsed fields up to 40 tesla in a temperature range from 1.3 K to 2.2 K. They found five frequencies in the mixed state and two additional frequencies in the normal state heretofore unobserved. Their principle conclusions were that both the frequencies and effective masses remain unchanged upon going from the normal to the mixed state. However, they did observe a marked attenuation of the amplitude of the oscillations upon entering the mixed state. They proposed an additional scattering term which damps the dHvA amplitude in the mixed state. The reduction factor can be expressed as

$$R_{\nu} = e^{\frac{-\pi}{\nu \tau_{\nu}}},$$ (5.4)

where

$$\frac{1}{\tau_{\nu}} = \frac{\Delta_{\text{orbit}}^2 2\pi^{1/2}\Lambda}{\hbar \nu_F};$$ (5.5)

$\Delta_{\text{orbit}}^2$ is a spatially averaged order parameter, $\nu_F$ is the Fermi velocity, and $\Lambda = \sqrt{2\hbar e H_0}$. Harrison et al. state that the reduction factor is due to increased scattering events experienced by the quasiparticles in the mixed state. This field dependent scattering is due to the superconductivity. (Additional measurements by Springford’s group provided confirming results in the mixed state measurements of V$_3$Si, see [Corcoran et al., 1994a]. Equation 5.5 pro-
duced a reasonable fit to their mixed state dHvA measurements.) What is interesting about this reduction factor is its dependence on the order parameter $\Delta_{\text{orbit}}^2$. By measuring the reduction of the dHvA amplitude in the mixed state for a particular orbit as a function of angle of the applied field, the order parameter can be mapped out; thereby, the gap anisotropy can be measured sensitively by the dHvA effect. Of course, the gap in Nb$_3$Sn is isotropic, but it is of special interest to have a way of measuring the gap in the HTSc materials if Harrison et al. should be proved correct. The theoretical details of quantum oscillations in the mean square order parameter in the mixed state for two dimensional HTSc materials are given in papers by Maniv et al. [1992a]; Maniv et al. [1992b] and Maniv et al. [1993a]. Maniv et al.'s results provide additional support for the prediction by Tešanović et al. [Tesanovic and Rasolt, 1989; Tešanovic et al., 1989; Tešanovic et al., 1991] and Maniv et al. [1990] of reentrant superconductivity due to resonant pairing at high fields as discussed in Chapter 2. The search for this new kind of superconductivity will be an experimental challenge for those of us working with high magnetic fields.

To show that our dHvA system was capable of measuring signals in the mixed state we made our own measurements on Nb$_3$Sn at the NHMFL in Tallahassee, FL. Our measurements were made on a single crystal of Nb$_3$Sn oriented in the [100]. In the mixed state between 15 tesla and $H_{c2}$ ($\approx 19.7$
we measured the dHvA signal at temperatures around 1.5 K. We compare our frequencies with those measured by Harrison et al. [1994] in Table 5.1. Aside from the 729 kT frequency our measurements are in fair agreement with those of Harrison et al. [1994]. A DFT of a data set taken in the mixed state is shown in Figure 5.3. The broadness of the peaks is due to the fact that the Fourier transform was performed on a limited number of available oscillations. Our measurements in the normal state proved inconclusive since these measurements were carried out in a 20 T superconducting magnet, such that few normal state oscillations could be measured. We found a possible frequency around 1890 tesla as compared with Harrison et al.'s at 1618 tesla in the normal state. Earlier measurements by Arko et al. [1978] and Wolfrat et al. [1985] did not observe any frequency higher than 810 tesla in the normal state.

Table 5.1: Comparison of measured dHvA frequencies in the mixed state of Nb$_3$Sn. Values of $m^*$ are taken from Harrison et al. [1994].

<table>
<thead>
<tr>
<th>LSU F(T)</th>
<th>Harrison et al. F(T)</th>
<th>$m^*$ ($m_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>228±5</td>
<td>238±6</td>
<td>0.9±0.3</td>
</tr>
<tr>
<td>333±5</td>
<td>338±6</td>
<td>1.0±0.3</td>
</tr>
<tr>
<td>506±10</td>
<td>573±10</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>-</td>
<td>670±12</td>
<td>1.7±0.4</td>
</tr>
<tr>
<td>729±11</td>
<td>798±11</td>
<td>2.1±0.3</td>
</tr>
</tbody>
</table>
Figure 5.3: An example DFT of a data set taken around 1.5 K in the field range 15 T to just below the onset of $H_c2$ at 19.7 T.

In Chapter 6 we will present dHvA measurements on $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ carried out in quasi-steady and pulsed fields. But briefly, we find that oscillations are observed in mixed state.

Incidentally, coupling low temperatures with high fields has led to additional mixed state results in the heavy fermion compounds with a superconducting ground state. For example, Hedo et al. [1995] have reported normal and mixed state measurements in CeRu$_2$. Most recently dHvA oscillations in the superconducting mixed state of URu$_2$Si$_2$ were reported by Ohkuni et al. [1997].

5.3 Experiment and Results

We have carried out measurements on epitaxial films of YBCO in the mixed state. (A discussion of the experimental details and results for mea-
urements on BKBO is reserved for Chapter 6.) The measurements have been carried out in the resistive magnets (fields up to 33 T) at the NHMFL in Tallahassee, FL and in the pulsed field magnets (fields up to 50 T) at the NHMFL at Los Alamos National Laboratory. Measurements were made at temperatures ranging from 0.5 K to 4.2 K.

The importance of defect-free, single crystal samples as a necessary condition for successful measurement of the dHvA effect has led us to develop and fabricate epitaxial films of YBCO. The samples were grown at Oak Ridge National Laboratory by D. H. Lowndes and co-workers. Epitaxial films, typically with a thickness of 0.4-2 microns, have several significant advantages for the measurements carried out: (1) High quality, well-oriented crystalline specimens can be grown with spatially uniform properties; see Lowndes et al. [1990a]; Norton et al. [1990]; Christen et al. [1990]; Budai et al. [1991]; Norton et al. [1991]; Lowndes et al. [1990b]; Lowndes et al. [1990c] and Lowndes et al. [1990d]. (2) For at least some HTSc, epitaxial films can be grown in different orientations simply by changing the growth conditions. For example, both a⊥ and c⊥ films of the rare-earth (RE) 123 family have been grown by the pulsed laser ablation method at ORNL. (3) Carrier concentration is easily controlled in films, either via changes of oxygen content [Lowndes et al., 1990e] or by RE doping [Sales and Chakoumakos, 1991] (hole filling [López-Morales et al., 1990; Seaman et al., 1990]), both in the 123 family materials.
and in the low-$T_c$ Bi-2201 phase. (4) In some cases, high quality epitaxial film specimens can be grown of crystalline phases or compositions that are impossible to stabilize in bulk crystals. An example is the new hole-doped pseudo-123 compound $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [Norton et al., 1991]. This capability is a direct consequence of having an epitaxial template for crystal growth.

This dissertation focuses on only one of these compounds, YBCO. It should be pointed out that this work has been carried out in a context including work on a number of HTSc epitaxial films. Future experimental efforts will focus on other HTSc systems such as $\text{Bi}_2\text{Sr}_{2-\delta}\text{RE}_{\delta}\text{Cu}_1\text{O}_{6+\delta}$ ($\text{RE} = \text{La or Sm}$), Bi-2201, Bi-2212, and YBCO/PBCO superlattices.

In order to achieve maximum sensitivity to dHvA oscillations in the magnetic susceptibility of thin film specimens, we used the low frequency field modulation technique described in Section 3.3. Recently, we constructed and tested a SQUID system for detecting dHvA oscillations (see Section 3.5). The optimum orientation of epitaxial film samples with respect to the field is perpendicular to the surface of the sample. Thus arranged, the demagnetizing factor for the superconducting film specimen is such that maximum field penetration occurs. However, due to the fact that the normal component of the $\vec{B}$ field is continuous through the sample, the only parts of the sample that will give rise to an oscillatory effect are the edges [Shoenberg,
Figure 5.4: Conceptual diagram of the comb sample geometry. YBCO epitaxial films were deposited on SrTi$_2$O$_3$ substrates by laser ablation and lithographically patterned. Each sample had twenty-five “teeth.”

1984. Therefore we have made a sample and pickup coil to optimize the edge effects.

The general concept of the dHvA sample and detection coil system is shown in Figure 5.4. The sample is an epitaxial film single crystal deposited on a SrTi$_2$O$_3$ substrate and lithographically patterned into the shape of a comb. For c axis-perpendicular HTSc films, the a-b orientation, with the field parallel to c, is unimportant for the dHvA effect. Each tooth and the base of the comb is 50 microns wide. This pattern is produced by lithographically processing a single crystal epitaxial film deposited by laser ablation.

The detection or pickup coil for this sample geometry is also produced by optical lithography. The coil consists of 20 micron strips (wires), spaced so as to run along the edge of the sample. Care was taken to prevent the wires from overlapping the edges of the samples. A conceptual diagram of
the pickup coil is shown in Figure 5.5. The pickup coil is deposited onto MgO substrate since optical transparency facilitates alignment with the patterned YBCO film. Additionally, MgO has nearly the same thermal contraction as SrTi$_2$O$_3$ at low temperatures. Leads were initially attached to the contact pads with a low temperature solder, but later, to avoid heating, the leads were pressed to the pad with indium metal. A second single loop balance coil installed on the rotating part of the sample probe was connected astatically with the sample coil. Balance was achieved by fine tuning the angle of the balance coil.

Many data sets were taken on the YBCO epitaxial films. The results of the analysis are still inconclusive since the signal to noise ratio in both the
Tallahassee (steady field) and the Los Alamos (pulsed field) measurements is 
too low to resolve dHvA signal unambiguously. A number of frequencies have 
been observed around those reported in previous published measurements, 
but since these peaks do not appear in all data sets we cannot conclude that 
this coincidence indicates a successful measurement. Some signal averaging 
has been tried on data sets taken at the same temperatures and field ranges, 
but this has not provided any clear resolution of dHvA frequencies.

The failure to resolve clearly the dHvA effect in early measurements of 
YBCO epitaxial films might have been due to a combination of factors: (1) 
improper pickup coil design and (2) improper sample handling. Originally, 
the wires in the pickup coils were placed such that they overlapped the edge 
of the sample. It was realized after our initial measurements that this con­
figuration led to a significant reduction in signal pickup since an induced 
current in the coil would tend to cancel itself out; i.e. the current in the part 
of the wire over the sample would run counter to the current in the part of 
the wire not over the sample. This problem was fixed, but sample handling 
could have compromised the later measurements. Several glues were tested 
for their utility in attaching the pickup coil’s MgO substrate to the sample 
substrate. It was found after some time that Duco Cement had an adverse 
reaction with the YBCO crystals. Later, GE varnish was used. Although 
GE varnish did not seem to harm the sample, upon repeated cycling from
room temperature to liquid helium temperature the GE varnish would eventually become ineffective and the sample would detach from the pickup coil. The other possible mistake that was made concerned the attachment of the twisted pair leads to the Au contact pads. Initially, a low temperature solder was used together with an organic flux. Attaching of the leads therefore required the repeated low level heating of the sample and prolonged contact with the flux. It is unknown to what extent these practices might have harmed the sample. To rule out the possibility that such soldering placed an undue strain on the sample, we have adopted a pressed indium metal contact procedure. The contact is placed on a hard flat surface; a small piece of indium is placed on the pad; the wire is place on the indium; a second piece of indium is placed on top of the wire; firm, constant pressure is evenly applied to the indium/wire sandwich until the indium alloys with the Au contact.

5.4 Future Measurement on YBCO

As mentioned in Section 3.5, a SQUID dHvA detection system has been developed for the 33 T resistive magnet at the NHMFL. This system will be used in the near future to attempt measurements of epitaxial films of YBCO.
CHAPTER 6

Magnetization Measurements on \( \text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3 \)

6.1 Introduction

The discovery of high \( T_c \) superconductivity in \((\text{La, Ba})_2\text{CuO}_4\) Bednorz and Müller [1986] was partly inspired by the bismuthate superconductor, \( \text{Ba(Pb, Bi)O}_3 \). Subsequent cuprate superconductors commanded the attention of a great many researchers because of their high \( T_c \)'s (on the order of 100 K). The discovery of high \( T_c \) superconductivity (HTSc) in the bismuthate system \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) (BKBO) ten years ago began an equally significant, complementary course of research into the nature of HTSc [Mattheiss et al., 1988; Schneemeyer et al., 1988]. BKBO is interesting for a number of reasons: (1) it contains no copper, (2) it is an isotropic conductor, (3) it has no evident magnetic ordering, implying that its conduction mechanism is different than that of the cuprate superconductors, (4) its superconductivity occurs at the boundary of a metal-insulator transition (a commonality with the cuprates) [Hinks et al., 1988a; Dabrowski et al., 1988; Sato et al., 1989], (5) normal state resistivity measurements demonstrate a non-metallic behavior
[Dabrowski et al., 1988], (6) it has two related compounds: Ba$_{1-x}$Rb$_x$BiO$_3$, that has a $T_c$ of $\approx 29$ K for $0.28 \leq x \leq 0.44$ [Itti et al., 1991], and Ba(Pb, Bi)O$_3$, a more conventional superconductor with a $T_c$ of $\approx 12$ K [Batlogg, 1984], and (7) both BKBO and Ba(Pb, Bi)O$_3$ (BPBO) have a comparatively low density of states (low carrier densities), given their high values of $T_c$. BKBO is a cubic perovskite. It has a superconducting transition temperature $T_c$ approaching 32 K for $x = 0.40$. Based on measurements of the oxygen isotope effect, it appears that superconductivity in BKBO has a BCS character, and it has a gap of $2\Delta/kT_c = 3.5$. An initial report of a possible nonphonon mediated conduction mechanism in BKBO was presented by Batlogg et al. [1988]; however, measurements of the large oxygen isotope effect indicate phonon-mediated pairing [Hinks et al., 1988b; Loong et al., 1989; Loong et al., 1991; Loong et al., 1992]. Inelastic neutron scattering results reported by Braden et al. [1995] confirm this conclusion by showing a strong electron phonon coupling. Additionally, electron-phonon coupling was observed by Raman scattering [McCarty et al., 1989]. A review of bismuthate superconductivity has been given by Batlogg et al. [1989]. Reviews of the physical properties of Ba$_{1-x}$K$_x$BiO$_3$ has been give by Weller et al. [1988]; Lee et al. [1990]; Jin et al. [1992] and Baumert [1995].

*The superconducting properties of BKBO and BPBO are discussed in Grumann et al. [1994].*
Figure 6.1: The electronic band structure of Ba$_{0.6}$K$_{0.4}$BiO$_3$. 

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Figure 6.2: Intersections of the Fermi surface of BKBO with high symmetry planes.
Superconductivity in BKBO occurs at a metal-insulator transition similar to the cuprates. For $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x \geq 0.37$ it is a superconductor, but as the potassium concentration is decreased it enters abruptly a semiconducting phase (see the phase diagram in Figure 6.3). A calculation of the multicritical phase diagram allowing for random field effects was done by Aharony and Auerbach [1993].

Figure 6.3: The phase diagram for BKBO taken from Pei et al. [1990].

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6.2 Magnetization Measurements on BKBO

The results and discussion presented in this section comprised the body of a paper soon to be submitted for publication.

6.2.1 Introduction

There have been many previous measurements of the magnetic properties of superconducting Ba$_{1-x}$K$_x$BiO$_3$ reported in the literature [Batlogg et al., 1988; Welp et al., 1988; McHenry et al., 1989; Grader et al., 1990; Huang et al., 1991]. For $x = 0.4$, single crystal measurements of $H_{c1}$ were made by Grader, Hebard, and Schneemeyer [Grader et al., 1990] using an electrodynamic force balance technique on micron-sized single crystal samples. It was found that lower critical field values measured on their near perfect single crystals were much higher (250 gauss at 10 K) than the $H_{c1}$ values reported by Batlogg et al. [1988] on powdered samples of similar composition (90 gauss at 10 K). Further measurements of $H_{c1}$ on large single crystals have been done by Huang et al. [1991] who also reported low values of 95 gauss at 5 K. All of these measurements were done on samples of imprecisely known demagnetization factors. For single crystals, in Grader et al. [1990], $H_{c1}$ is found to vary linearly with temperature over the range of temperatures measured (7 - 22 K) whereas in Huang et al. [1991] the $H_{c1}$ versus temperature curve shows a downward curvature as $T = 0$ is approached.
The upper critical field $H_{c2}$ was reported also in Batlogg et al. [1988], and extensive $H_{c2}$ studies of powdered samples of varying composition were done by Welp et al. [1988]. Constant field temperature dependent magnetic measurements were done by Batlogg et al. [1988] with the result that a linear negative slope of $dH_{c2}/dT = -0.5 \, \text{T/K}$ between 20 and 29 K was observed. Constant-field, temperature-dependent resistive measurements were done also by Welp et al. [1988]. Several potassium concentrations were measured. For $x = 0.4$, a slope of -0.6 T/K was found at temperatures well below $T_c$. A slight, positive curvature of $dH_{c2}/dT$ was found near $T_c$ in all of the samples measured in Welp et al. [1988]. Recently, Samuely et al. [1996] have used tunneling measurements on low $T_c$ samples ($T_c = 20$ K) to determine $H_{c2}$ as a function of temperature; they find much lower values of $H_{c2}$ than in other measurements.

Several recent measurements of the magnetic properties of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in Gatalskaya et al. [1996] and Goll et al. [1996b] and in an earlier paper by McHenry et al. [1989] have focused on the reversibility field as a function of temperature. In their study of flux creep in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, McHenry et al. found the reversibility field never to exceed 0.8 T down to 5 K. In samples of nominal composition ($x = 0.34$), Gatalskaya et al. [1996] find good agreement near $T_c$ with a power law form $H_r \approx (1 - T/T_c)^m$ with $m = 1.45$. For samples having a $T_c$ of 20 K, force magnetometer measurements over a temperature
range of 0.4 to 20 K by Goll et al. [1996b] show a continual upward curvature of $H_r$ extending to 25 T at 0.4 K. Thus different groups have measured widely different values for $H_r$ on different samples.

We report extensive studies of the magnetization of single crystal samples of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Bi}_3$. Magnetic field dependent hysteresis curves of the magnetization at constant temperature were recorded at temperatures ranging from 1.3 to 32 K in applied fields from zero to 27 T, and the temperature dependence of the magnetization was measured from above room temperature down to below the superconducting transition temperature. From these measurements, we derive several quantities: (1) the complete temperature dependence of the lower critical field $H_{c1}$, (2) the upper critical field $H_{c2}$, (3) the reversibility field $H_r$, and (4) the thermodynamic critical field $H_0$. All of these critical fields are determined as a function of temperature. In addition, the temperature dependence of the normal state susceptibility is determined.

The crystals used in this study were grown by scaling up the electrosynthetic method described by Norton and Tang [1991]. The high $T_c$ (> 30 K) found for these crystals suggests that they were very close to the optimal superconducting stoichiometry. Subsequent X-ray analysis showed the $1 \text{ mm}^3$ facets used in these experiments were single perovskite crystals with a mosaic spread of less than $2^\circ$. 

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6.2.2 Measurements

The low field (< 5.5 T) measurements near $T_c$ reported here were made using a Quantum Design MPMS SQUID magnetometer. Several precautions must be made in measurements on superconductors near $T_c$ using a measurement system of this type. There are two basic problems. First, the magnetic moment of the sample holder can easily become larger than that of the sample near $T_c$, and the maximum moment of the sample holder combined with the sample shifts along an axis parallel to the applied field. When this occurs, the output voltage from the SQUID pickup coils is not centered and spurious results in the calculation of the magnetic moment can occur. To overcome this problem, we held the samples in long quartz tubes having an inner diameter slightly smaller than the largest dimension of the sample to be measured. The empty quartz tube extends through all three pickup coils of the magnetometer during a complete vertical scan of the magnetometer; it was verified that the tubes produced a negligible signal over the scan length used. For most of the low field measurements, the samples were inserted into the tubes with the maximum dimension parallel to the axis of the tube, then turned slightly to hold them in place. Care was taken to center the sample in the pickup coils at each temperature because of the displacement due to thermal contraction of the quartz tube. When the measurements on the spherical sample were done, the above procedure was not possible and
it was secured to the inside of the quartz tube with a small piece of Kapton tape. This mounting limited the measurements to a minimum field of about 0.5 mT. The second problem with low field SQUID magnetometry is that the superconducting magnet retains trapped flux at low fields. The trapped flux can be removed partially by cycling between positive and negative fields with decreasing final fields. This was done at each temperature at which a measurement for $H_{cl}$ was performed.

One of the problems in determining $H_{cl}$ has been the fact that the sample demagnetizing factor is of importance for this measurement. Without a controlled demagnetizing geometry, flux begins to penetrate the sample at different fields depending on position in the sample. For this reason we produced a single crystal sphere for the $H_{cl}$ measurements. Starting with a crystal of approximately $1.5 \times 1.5 \times 1.5 \text{ mm}^3$ and a $T_c$ of 30 K we ground it into a sphere in an air driven racetrack using a diamond sandpaper abrasive. The resulting sphere had a diameter of 1 mm. After grinding the sphere, it was annealed in $O_2$ for 24 hours at 400 °C. Laue pictures showed no signs of strain.* After this processing the sample used for the $H_{cl}$ measurements had a $T_c$ of approximately 29 K.

For temperatures between 2 and 32 K both constant temperature magnetic field hysteresis curves and constant field temperature hysteresis curves

*We are indebted to Larry Hults and J. L. Smith for annealing and x-raying this sample.
were recorded on two different crystals. For the constant temperature (T = 22.5 K) measurements, we found after measurements at a few temperatures from 0 to \( +H_{ext} > H_{c2} \) back through 0 to \(-H_{ext} > H_{c2} \) and then to \(+H_{ext} > H_{c1} \), the symmetry of the complete hysteresis curves could be used to reduce the number of field points taken at a given temperature. An example of a complete constant temperature hysteresis curve is shown in Figure 6.4, and an example of the reduced set of data giving all the information contained in Figure 6.4 is shown in Figure 6.5. Also shown in Figures 6.4 and 6.5 are the points chosen to be the reversibility fields and \( H_{c2} \). For each measurement, the temperature was first raised to \( \approx 50 \) K (\( T > T_c \) at \( H = 0 \)) then lowered to the measurement temperature in zero field. Thus, all constant temperature data reported here are for zero field cooled samples.

The constant field measurements were started at a temperature above \( T_c \). The samples were cooled to 4.5 K in zero field, the field applied, the temperature slowly raised, point by point, to above \( T_c \) while recording magnetization, then again cooled to 4.5 K during the measurement in the applied field. An example of a complete cycle of this type of data is shown in Figure 6.6. Again, near \( T_c \), the magnetization is extremely small and care was taken to avoid the effects of the sample holder. Finally, we measured the magnetization at several temperatures in constant field in the normal state from 32 to 300 K to determine the normal state susceptibility.
Figure 6.4: Constant temperature magnetization at low applied fields of Ba_{0.6}K_{0.4}BiO_3 at 22.5 K. The position of the reversibility field is indicated.

Further measurements of $H_{c2}$ and $H_r$ were done using a cantilever force magnetometer at the National High Magnetic Field Laboratory (NHMFL) in a 27 T resistive magnet at temperatures from 1.4 to 19 K. The sample used for these measurements had a $T_c$ of 30 K. An example of the constant temperature magnetic hysteresis curve taken with the force magnetometer is provided in Figure 6.7.

6.2.3 Results

In addition to the separate $H_{ci}$ measurements, there are several critical fields to be obtained from the hysteresis data: $H_0$, $H_{c2}$, and $H_r$. The thermodynamic critical field $H_0$ is obtained only from the constant temperature data while $H_{c2}$ and $H_r$ were measured both at constant temperature and
Figure 6.5: Hysteresis in the magnetization as a function of applied field of \( \text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3 \) at 20.0 K from zero to \( +H_{c2} \) to zero to \( H_{c1} \). These reduced data sets were used to obtain all critical points.
Figure 6.6: Example of a magnetization hysteresis taken at constant field (H = 50000 G).

constant field. None of the critical fields can be determined in a straightforward manner and we state in detail how we have extracted them from the data. Between approximately 18 and 32 K, the two highest critical fields were determined using the SQUID magnetometer. Below 18 K, $H_{c2}$ was in excess of the maximum field of the SQUID magnetometer (5.5 T). Above 10 K, $H_{c1}$ was sufficiently low that no reliable data could be obtained on the same samples used for higher critical fields.

6.2.3.1 $H_{c1}$

Values of $H_{c1}$ reported here were obtained from the spherical sample from 4.2 to approximately 17 K. Typical low temperature, low field magnetization
Figure 6.7: Hysteresis in the magnetization as a function of applied field of Ba$_{0.6}$K$_{0.4}$BiO$_3$ at 16.0 K from zero to $+H_c$ to zero. This data is the magnetization determined from the force magnetometer. $H_r$ is indicated. The arrows show the direction of the field sweep. Note that as $H$ goes to zero, the force also goes to zero.
Figure 6.8: Magnetization as a function of applied field for the spherical sample of Ba$_{0.6}$K$_{0.4}$BiO$_3$ at a number of temperatures. The temperatures from from 5 K for the highest curve to 17.5 K for the lowest.

curves for several temperatures are shown in Figure 6.8. The initial slope of the curve is given by $M/H = V/4\pi(1-D)$, where $V$ is the volume of the sample and $D$ is the demagnetization factor. Only when the sample geometry is such that $D = 0$ will this constant slope extend to $H_{ci}$, at which point the magnetization would abruptly decrease. When $D \neq 0$, the field penetrates the sample at different points gradually until the entire sample is in the mixed state. We shaped a single crystal sample into a sphere, hence the initial slope is smaller and the transition from the Meissner to the mixed state sharper than for the crystals that have roughly a cubic shape.
To determine the value of $H_{c1}$, the following procedure was used. The low field, linear portion of the curve was fit with a line. The field point at which the measured value of magnetization deviated from the straight line was taken to be $\frac{3}{2}H_{c1}$. Values obtained from this fit for $H_{c1}$ are plotted as a function of temperature in Figure 6.9.

6.2.3.2 $H_0$

The thermodynamic critical field is obtained by integrating the irreversible contribution to the magnetization, $M_R(H) = [M(H_{incr}) + M(H_{decr})]/2$, from zero to $> H_{c2}$. Since SQUID magnetometry measurements require a constant applied field during the measurement, and the data were accumu-
Figure 6.10: Values of the thermodynamic critical field for sample $N$ obtained from integration of the magnetic hysteresis curves as a function of temperature.

lated point by point we have numerically integrated the hysteresis curves to obtain $H_0$ at each temperature. The temperature dependence of $H_0$ is shown in Figure 6.10 for both samples measured at low fields. We have elected not to calculate values for $H_0$ from the high field-low temperature data until the anomalous “fishtail” structure, also noticed by Gatalskaya et al. [1996], is fully understood. The fishtail adds area below the magnetization curve; thus, thwarting any attempt of straightforward analysis.
6.2.3.3 $H_{c2}$

A typical plot of the magnetization of one of the single crystals for increasing field from zero tesla to above $H_{c2}$ is shown in Figure 6.5. There are several points about this curve that make determination of $H_{c2}$ complicated. Between $H_{c1}$ and $H_{c2}$ the curve is never linear in applied field, and an extrapolation to $H_{c2}$ from a linear portion of the curve in the superconducting state near $H_{c2}$ is not possible [Hao et al., 1991]. Above $H_{c2}$ BKBO is diamagnetic (mainly due to the atomic core contribution to the magnetization) and the total magnetization never becomes positive upon passing from the superconducting to the normal state. To obtain a consistent value for $H_{c2}$, we have fit the linear diamagnetism data in the normal state above $H_{c2}$ to a straight line and taken the field at which the magnetization deviates from the extrapolated line to zero field to be $H_{c2}$. From values of $H_{c2}$ obtained in this manner, we show the temperature dependence of $H_{c2}$ for a single crystal sample in Figure 6.11 along with the determination of $H_{c2}$ from the constant field data to be discussed below. The minimum in the magnetization curve in this field region is fairly broad for all of the samples, but this analysis technique gives values of $H_{c2}$ consistent with the ones that are obtained from temperature dependent data at constant field [Batlogg et al., 1988; Huang et al., 1991].
Figure 6.11: Values of $H_{c2}$ measured as a function of temperature for sample N are shown along with the values of $H_r$ and $H_{c2}$ for sample F. $H_{c2}$ values from both constant field and constant temperature measurements for sample N are represented by a □. $H_{c2}$ values for sample F, the sample used in the force magnetometer measurements, are represented by a ◇. The arrow indicates that at temperatures below 10 K $H_{c2}$ exceeded fields of 27 tesla. $H_r$ values from both constant field and constant temperature measurements sample N are represented by a △. $H_r$ values for sample F are represented by a ★. The dotted line fit is from Gantmakher et al. [1996].

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Using the 21 K values of $H_{c1}$ and $H_{c2}$, the Ginzburg-Landau parameter, $\kappa$, was calculated from the relation

$$\frac{\ln \kappa}{2\kappa^2} = \frac{H_{c1}}{H_{c2}}.$$  \hspace{1cm} (6.1)

We find that the value of $\kappa$ is approximately 64. This compares favorably with the value reported by Kwok et al. [1989] of $\kappa = 59$.

6.2.3.4 $H_r$

At temperatures above 15 K for the single crystals, we are able to determine the value of applied field at which the hysteretic behavior becomes reversible $H_r$. We have taken this field to be the value of $H$ at which the increasing and decreasing applied field have the same measured values of $M$. The temperature dependence of $H_r$ for sample F is shown in Figure 6.11.

6.2.3.5 Temperature Dependent Constant Field Data

Measurements of the temperature dependence of the magnetization at constant field give the same information in the T-H plane through measurements of critical temperatures, $T_{c2}$ and $T_r$, as do the constant temperature field dependent measurements. A view of one set of data taken at constant field is shown in Figure 6.6. The temperature at which the measurement deviates from a constant on the high temperature side is taken to be $T_{c2}$. The temperature at which the increasing and decreasing measurements deviate is
Figure 6.12: Measured values of $H_{c2}$ (○), $T_{c2}$ (⊗), $H_r$ (◇), and $T_r$ (□) as a function of temperature for sample N.

$T_r$. One can see from the data presented in Figure 6.12 that the two different measurements give the same result.

6.2.3.6 Normal State Susceptibility

The normal state susceptibility was calculated from the difference of two magnetization curves taken at 0.3 T and 5.0 T at temperatures from 31 K to 350 K (shown in Figure 6.13). The difference of the magnetization measurements, $\Delta M$, was taken as the absolute magnetization at a field of 4.7 T. The quartz tube sample holder contributes a small signal to the magnetization;
Figure 6.13: The inverse of the normal state susceptibility as a function of temperature for two Ba$_{0.6}$K$_{0.4}$BiO$_3$ samples.

this has been measured and subtracted from the difference magnetization. BKBO is a normal state diamagnet. A paramagnetic upturn is visible in the data at temperatures below 150 K.

6.2.4 Discussion

The temperature dependence and the magnitudes of the critical fields measured here are different from that expected from an ordinary type-II superconductor. In general, the critical fields have different dependences from what is expected and some new phenomena are observed. We begin with a discussion of the normal state susceptibility.
In their initial measurements of the normal state susceptibility, Cava et al. [1988] found large extraneous paramagnetic contributions presumably due to the presence of unreacted KO$_2$ in their samples. In a following paper [Batlogg et al., 1988], the same authors corrected their data with an estimate of the core diamagnetism ($\chi_c \approx -7.5 \times 10^{-5}$ emu/mol). From their energy band calculations Mattheiss and Hamann [1988] determined the density of states at $E_F$ in Ba$_{0.6}$K$_{0.4}$BiO$_3$ to be 0.46 states/eV. Using this value, we calculate the contribution to the susceptibility due to Pauli paramagnetism to be $2.7 \times 10^{-5}$ emu/mol. Our measurements show that the normal state susceptibility at $T = 300$ K is $-5.3 \times 10^{-5}$ emu/mol (see Figure 6.13), and this value agrees with that reported by Hundley et al. [1989] and Uwe et al. [1996] for a potassium concentration of $x = 0.40$. When the core diamagnetism is subtracted from the 300 K measured value of $\chi$, the calculated Pauli term is obtained. Our measurements show an increase in the normal state paramagnetism below 150 K. We have attempted to fit the data below 150 K to a Curie-Weiss function and have found that the data does not exhibit this dependence. Thus we conclude that the increased paramagnetism is not due to a localized impurities. The cause of this increase has not yet been explained.

As a result of our upper critical field measurements, we found that a power law fit where $H_{c2}$ and $H_r \sim (1 - T/T_c)^m$ yielded values of $m = 1.58$ and 1.97 for $H_{c2}$ and $H_r$ respectively (see Figure 6.14). Gatalskaya et al. [1996] found
for $H_r$ that $m = 1.45$ for a sample with a potassium concentration of 0.34. Also, Goll et al. [1996b] report a value of $m = 1.5$ for $H_r$ in their below optimum potassium concentration sample. Our samples had a potassium concentration of $\approx 0.40$.

Welp et al. [1988] report a critical slope $dH_{c2}/dT$ of -0.63 T/K for $x = 0.40$ and of -0.86 T/K for $x = 0.37$. Values of $H_{c2}$ were measured by Welp et al. between 10 K and 25 K for the $x = 0.40$ sample and no positive curvature of the $H_{c2}$ versus temperature was reported. Like Affronte et al. [1994] and Gantmakher et al. [1996], we observe a positive curvature in the $H_{c2}$ versus temperature curve; however, we observe an enhanced curvature as
compared to the results of Gantmakher et al. [1996]. This curvature deviates significantly from the universal behavior predicted by Werthamer, Helfand, and Hohenberg (WHH) [Werthamer et al., 1966] for superconductors with weak electron-phonon coupling. Gantmakher et al. [1996] find that their $H_{c2}$ data fits the function

$$H_{c2}(T) = 32.2 - 1.8 T + 0.025 T^2,$$

(6.2)

as shown in Figure 6.11. Our $H_{c2}$ data show a greater curvature than the fit of Gantmakher et al. [1996] and we believe a second order fit greatly underestimates the probable value of $H_{c2}(T=0)$. We have found a best fit to our curve using a fourth order polynomial,

$$H_{c2}(T) = 62.932 - 6.058 T + 0.225 T^2 - 3.54 \times 10^{-3} T^3 + 1.56 \times 10^{-5} T^4. \quad (6.3)$$

No physical significance can be attributed to this fit. The value of $H_{c2}(T=0)$ is very sensitive to the order of fit so it is difficult to determine it precisely, but we believe that Gantmakher et al.'s value of 32.2 T might be too low, the above fit giving about twice this value. Gantmakher et al. [1996] comment that the positive curvature is enhanced by disorder in the sample; therefore,
the enhancement of the curvature and correspondingly in $H_{c2}(T=0)$ may be
ascribed to an intrinsic disorder in BKBO.

From our determination of $H_r$ we observe that the irreversibility line
deviates from WHH theory and displays a positive curvature. Similarly, Goll
et al. [1996b] observe a positive curvature in $H_r$ versus temperature. Again
our values of $H_r$ are enhanced when compared with the values of Goll et al..
A best fit to our $H_r$ curve is again a fourth order polynomial,

$$H_r(T) = 30.2 - 3.77 T + 0.234 T^2 - 7.46 \times 10^{-3} T^3 + 9.19 \times 10^{-5} T^4.$$ (6.4)

Similarly, the thermodynamic critical field, $H_0$, has a positive curvature as is
shown in Figure 6.10.

Samuely et al. [1996] have determined the upper critical field $H_{c2}$ by
Andreev reflection in point-contact junctions, a measurement of the super­
conducting density of states. They find no positive curvature of the the $H_{c2}$
versus temperature curve and claim that their measurements confirm an ad­
herance of BKBO to WHH theory. This contradicts all magneto-transport
measurements that uniformly show $H_{c2}$ and $H_r$ as a function of temperature
in BKBO deviate from WHH theory.

One clear conclusion that can be drawn from the upper critical field mea­
surements on BKBO is that the transition from the superconducting state

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to the normal state as a function of applied field is broad. That is, the $H_{c2}$ value is not a sharply defined function. The cause for this might be related to Landau quantization effects in the material. As shown by a number of theorists [Gunther and Gruenberg, 1966; Markiewicz et al., 1988; Rasolt and Tesanovic, 1992], Landau quantization can play an important role in the superconducting properties of certain materials at high fields and low temperatures. Most calculations have been done for 2D superconductors, but it is not unreasonable that some of the effects predicted for these 2D systems should manifest in 3D superconductors like BKBO. The low-carrier density and high $T_c$ of BKBO make it a respectable candidate for the observation of Landau quantization effects, and the oscillations of $H_{c2}$ as a function of field may be occurring. If an appreciable oscillation of $H_{c2}$ occurs in BKBO, the result would be a blurring of the low-field and high-field phase boundaries of the mixed to normal state. In their 1989 paper, Tesanovic et al. [1989] identified BKBO as a candidate material for observing reentrant superconductivity. Our measurements of $H_{c2}$ do not contradict their suggestion. In fact, our measurements call for further investigation of BKBO to higher fields and lower temperatures to determine if $H_{c2}$ actually diverges as $T$ approaches zero.

The broadening of the transition might be due to a higher order phase transition from the mixed to normal state in BKBO [Kumar, 1994; Kumar,
Kumar [1997] shows that when both the specific heat and the susceptibility are continuous across the transition, then it is possible that the order of the transition is higher than two. This follows from the thermodynamic equation for the superconducting phase boundary,

\[
\left( \frac{dH_c}{dT} \right)^2 = \frac{\Delta C}{T_c \Delta \chi},
\]

where \( \Delta C \) is the discontinuity in the specific heat and \( \Delta \chi \) is the discontinuity in the susceptibility. If both of the discontinuities are zero, then the function is indeterminate; hence, if \( \Delta C \) and \( \Delta \chi \) are zero, the transition cannot be second order. Additionally, Kumar [1997] concludes that higher order transitions are only possible if the normal state of the material is diamagnetic. For BKBO, it seems that all of these conditions are satisfied.

Several studies of the specific heat of BKBO have been done [Hundley et al., 1989; Graebner et al., 1989; Stupp et al., 1989; Alba, 1992]. All but one study [Graebner et al., 1989] conclude that \( \Delta C \) is zero across the transition. Because of the large phonon contribution to the specific heat, it is difficult to extract the comparatively small value of the electronic specific heat across the transition. A calculation by Kwok et al. [1989] that shows the BCS discontinuity in BKBO to be \( \Delta C/T_c \approx 3.75 \text{ mJ/mole K}^2 \) or \( \Delta C = 120 \)
mJ/mole K if $T_c = 32$ K. This value is calculated from the relation

$$
\Delta C/T_c = \left( \frac{1}{8} \pi \kappa^2 \right) \left( \frac{dH_{c2}}{dT} \right)^2,
$$

where $\kappa$ is the Ginzburg-Landau parameter calculated from $\ln\kappa/2\kappa^2 = H_{c1}/H_{c2}$.

At $T_c$, the magnitude of the total specific heat is approximately 15 to 20 J/mole K. The expected discontinuity is approximately 0.1 J/mole K. Previous measurements of the specific heat performed at LSU by Chun Xu and Goodrich [1989] using a sensitive ac technique by Chun Xu et al. [1990] did not detect a jump in $C_p$ at the transition temperature and we believe the measurements were of sufficient accuracy to detect a $\Delta C$ of the order of magnitude predicted by Kwok et al. [1989].

The present measurements find that $\Delta \chi$ is also zero across the transition. Normal state susceptibility measurements show that BKBO is a normal state diamagnet. Given all of these factors, the hypothesis that BKBO exhibits a transition of an order higher than two is strong. The corresponding broadening of the transition may be associated with this higher order transition.

Our measured critical slope of $dH_{c1}/dT$ is $-17.2 \pm 0.66$ G/K as compared with the value of Batlogg et al. [1988] of $-4.5 \pm 0.5$ G/K. From this linear fit to the $H_{c1}$ data, we find that $H_{c1}(T=0)$ is $393 \pm 6$ G. However, it is not obvious that a linear function best represents the $H_{c1}$ dependence. Between
5 and 15 K the data is best fit by a second order polynomial with negative curvature. Around 15 K, $H_c(T)$ experiences an inflexion point and is fit to a function with positive curvature. Attempts were made to measure $H_{c1}$ at fields approaching $T_c$, but above 22 K the magnetization signal was too small to resolve with the SQUID measurement system. It appears that if $H_{c1}$ does not smoothly approach $T_c$, it might go to zero at some temperature less than $T_c$. This very low value of $H_{c1}$ is correlated with the very broad magnetic transitions observed in BKBO, even though the resistive transitions are sharp. $H_{c1}$ is the only measured thermodynamic critical field that does not diverge as the temperature goes to zero.

We observe the anomalous “fishtail” structure in our force magnetometer measurements also reported by Gatalskaya et al. [1996]. Figure 6.15 shows the fishtail in both the up and down sweeps and the fact that they are histeretic. These structures are not observed in the magnetization data taken with the SQUID magnetometer. This leads us to question the origin of these fishtails, specifically, whether they might be due to the measurement technique.

The first report of these fishtails in a HTSc material was by Daeumling et al. [1990] in small single crystals of YBCO using a vibrating sample magnetometer. They attributed the anomalous structure to flux pinning at oxygen deficient sites in the lattice. These oxygen deficient sites have a
Figure 6.15: A full sweep of the force magnetometer measurement showing the anomalous fishtail structure also observed by Gatalskaya et al. [1996]. A second hump of unknown origin is observed at higher fields than the initial fishtail.

lower $T_c$ and an applied field will suppress superconductivity in this region first. As the field increases, so does the pinning force per defect, leading to an increase in the magnetization. Daeumling et al. [1990] speculated that there were enough oxygen deficient regions in their sample to create “internal barriers” in the crystal, effectively imparting to it a granular character.

Daeumling et al. [1990] argue that two regions with different $H_{c2}$’s can give rise to a “fishtail”-like structure. Oxygen deficient regions in the lattice are not the only possible causes of this fishtail structure in BKBO. Two regions with different $H_{c2}$’s might arise in BKBO – one region would be associated with an ordered super-lattice of K and the other region would cor-
respond to regions of disordered K. The K-ordered and K-disordered regions might have different values of $T_c$ and $H_c$. As we go to higher temperature (above 17 K), the lower $T_c$ region is never superconducting, so the fishtail is not observed. In principle it should be possible to estimate the change in the superconducting volume fraction above and below 17 K from the initial slope of the $H_{c1}$ curves; however, to within the accuracy of our measurements we could not detect a change in the superconducting volume fraction at any temperature. From these measurements, it appears that the anomalous fishtail structure reported in BKBO is not due to two regions in the sample with different $T_c$'s.

The measurements of Gatalskiya et al. [1996] were taken with a vibrating sample magnetometer and a SQUID magnetometer, but no mention was made in their paper concerning a correlation between measurement method and the fishtails. It is possible that the fishtails are a residual effect of measuring the magnetization while continuously sweeping the applied magnetic field. If the sweep rate exceeds the relaxation rate [McHenry et al., 1989], unexpected results may occur. The SQUID measurements are made in static fields and after sufficient time for the vortex lattice to relax after changing the applied field. Although it is possible that the fishtails in BKBO represent some new physical phenomena, we believe that insufficient evidence exists to support this claim.
6.2.5 Conclusions

We have measured the normal state susceptibility from 31 K to 350 K and find that at temperatures below 150 K the susceptibility is not a zero slope linear function. At temperatures below 150 K the susceptibility becomes less negative, but does not take on a Curie-Weiss form; thus we rule out localized magnetic impurities as the cause of this behavior.

We report results of the first force magnetometer measurements of BKBO to fields up to 27 T. We have shown that the $H_{c2}$ and $H_r$ lines deviate from WHH theory [Werthamer et al., 1966], displaying a positive curvature at low temperatures. Our results are in general agreement with previous measurements, but show a marked enhancement of $H_{c2}$ and $H_r$. If the ambiguity of $H_{c2}$ is due to broadening of the mixed state to normal state transition, this suggests that Landau quantization effects may be a possible explanation. Additionally, the marked increase of $H_{c2}$ as zero temperature is approached suggests that BKBO might be a candidate material for experiments aiming to observe reentrant superconductivity (see Tesanovic et al. [1989]). Further measurements should be made at low temperatures and high fields to determine values for $H_{c2}(T=0)$ and $H_r(T=0)$.

Finally, we note that BKBO may exhibit a phase transition of thermodynamic order higher than two. This conclusion is based on measurements of the specific heat in the normal and superconducting state across the transi-
tion, on measurements of the susceptibility across the transition, and on the
fact that BKBO is a normal state diamagnet. The absence of a discontinu-
ity in the specific heat and the susceptibility at $T_c$ indicates a higher order
transition.

6.3 $dHvA$ Measurements on BKBO

The results reported in this section were published in Goodrich et al.
[1993].

6.3.1 The Graebner-Robbins Effect

In 1975, Graebner and Robbins (GR) of Bell Laboratories made the first
measurements of the $dHvA$ effect in the mixed state of a superconductor
[Graebner and Robbins, 1976]. They observed no discrete change in the
phase or amplitude of the $dHvA$ oscillations across $H_{c2}$. Below the transition
temperature, the Dingle temperature and the frequency of the oscillations
increased. "These observations seemed to be consistent with the following
picture: a) the orbiting electrons still persist in the mixed state and the
oscillations arise from them; b) they feel the net magnetization, i.e. $H-4\pi M$,
and the flux lattice causes a dephasing of the oscillations or the increase of
the Dingle temperature." [Aoki et al., 1992]

GR measured oscillations well below $H_{c2}$ employing a field modulation
technique (see Section 3.3 similar to the technique we use at LSU). Anomalies
in their data at intermediate fields below $H_c^2$ suggest a broad transition to the superconducting mixed state. The broad transition is similar to results from measurements on BKBO presented above.

Some of the most interesting observations made by GR have to do with fluxon-electron interactions. The orbit of the electron extends through a great number of fluxons. As I will discuss in the following section, the field does not vary appreciably between fluxons due to the large Ginzburg-Landau parameter, $\kappa$. GR also point out that the deBroglie wavelength is 3 - 4 times the spacing of the lattice of flux lines, so that one might not expect the electron to respond to the spatial field perturbation very strongly. Microscopic fluctuations in the value of the field should not significantly disturb the orbiting electron.

It seems reasonable that a certain amount of phase smearing will take place due to variations in orbital area and the number of enclosed flux lines due to slight inhomogeneities in the sample. GR found that, to within an order of magnitude, the effects due to this mechanism agree with the observed Landau level broadening of the dHvA signal. This is what leads to the apparent increase in the Dingle temperature. When comparing the frequency of the dHvA oscillations above and below $H_c^2$, GR found a higher frequency in the super-conducting mixed state. It is not unusual for the magnetization

---

*A fluxon is another word for a flux vortex.*
to be changing rapidly in type-II superconductors so that $B$ is changing more rapidly than $H$. Since $H$ is the value of the applied field, $B$ can only be found if detailed knowledge of the magnetization is had. $d$HvA oscillations are periodic in $1/B$ so changes in frequency can be expected when $B$ is not changing in linear proportionality with $H$.

Measurements of the frequency across $H_{c2}$ in the HTcSs $V_3Si$ [Mueller et al., 1992] and BKBO [Goodrich et al., 1993] do not exhibit appreciable frequency shifts. Lack of experimental evidence of this in the HTScs of this frequency shift makes it difficult to speculate about the significance, but the steep magnetization curves for BKBO make the frequency shifting a valid concern in the mixed state.

6.3.2 Results of the Pulsed Field Measurements

Pulsed field measurements were made on a single crystal of BKBO in a 50 tesla magnet constructed in Leuven, Belgium by van Bockstal et al. [1991]. The measurements were made at LANL. The pulse shape of this magnet is shown in Figure 6.16. The peak field value can be adjusted by varying the voltage stored in the capacitor bank. The peak magnetic field is a linear function of the capacitor bank voltage.

Figure 6.17 shows a Fourier transform of a data set taken at 1.5 K and in a field range of 25 to 30 tesla. The values of the three largest peaks are listed in Table 6.1 together with the results of the measurements made at LSU.
Figure 6.16: Field profile of the 50 tesla pulsed field magnet constructed in Leuven, Belgium for use at the NHMFL pulsed field facility at LANL. The peak value of the magnetic field was varied by varying the charging voltage of the capacitor bank. This shot resulted from a 4 kV charge.

Figure 6.17: The power spectral density of the dHvA oscillations in BKBO at 1.5 K using a 50 T pulsed field magnet at the NHMFL at LANL. See Table 6.1 for values of the three largest peaks.
6.3.3 Results of the Field Modulation Measurements

dHvA measurements were made on a different BKBO single crystal at LSU in the 18 tesla superconducting magnet system, using the field modulation technique described in Section 3.3. Measurements were made at a temperature of 1.5 K and in fields from 14 to 16 tesla.

Figure 6.18 shows a Fourier transform of a data set taken between 15 and 16 tesla. At these fields, the BKBO sample used was definitely in the mixed state. Several peaks rise above the noise level. The three peaks shown are the ones we believe are significant. A peak at 1.7 kT might possibly be due to dHvA oscillations, but since the measurements were optimized for sensitivity to a 12 kT peak, this low frequency is somewhat obscured. The 11.6 kT peak in the LSU data is in good agreement with the 11.3 kT orbit predicted by band structure calculations.

6.3.4 Discussion

The results of the pulsed field and field modulation experiments on BKBO are listed in Table 6.1.

Table 6.1: dHvA frequencies for BKBO

<table>
<thead>
<tr>
<th></th>
<th>peak 1 (kT)</th>
<th>peak 2 (kT)</th>
<th>peak 3 (kT)</th>
<th>peak 4 (kT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>field modulation</td>
<td>1.7</td>
<td>3.4</td>
<td>4.7</td>
<td>11.6</td>
</tr>
<tr>
<td>pulsed field</td>
<td>1.7</td>
<td>3.4</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>band theory</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.3</td>
</tr>
</tbody>
</table>
Figure 6.18: The power spectral density of the dHvA oscillations in BKBO at 1.5 K using an 18 T superconducting magnet and field modulation at LSU. See Table 6.1 for values of the three largest peaks.

The data reported here were obtained from two different samples measured by two different methods. The pulsed field dHvA spectrometer was tested by measuring high purity samples of Au oriented along the [100] and [111]. A similar test was done with the field modulation spectrometer at LSU (see Section 3.9). Given that the two spectrometers yield a high coincidence of peak values, the results can be put forward with some degree of confidence. However, it is troubling that the pulsed field measurements did not resolve a peak around 11.6 kT. The absence of this highest peak in the pulsed field data is baffling since the disappearance of a peak at high fields cannot be explained away by some conventional mechanism like magnetic breakdown.
One would expect to introduce new frequencies at high fields if magnetic breakdown were occurring.

The observed 11.6 kT orbit nearly agrees with the frequency predicted by LDA band structure calculations; however, the presence of the three lower frequency peaks corresponding to larger pieces of Fermi surface is unexpected. Although it is possible that these extra peaks correspond to some different phase of the material, this seems unlikely based on the diffraction and magnetization measurements on these samples.

6.3.5 Future Work on BKBO

After the initial dHvA measurements on BKBO, many attempts were made to reproduce the results of this study using a new batch of samples prepared by M. L. Norton and on a batch of samples prepared at UC-Davis for their positron annihilation measurements of the FS of BKBO. No further signals were observed in these subsequent experiments. It is possible that the new batch of samples was in some way inferior to the original batch. It is puzzling that no results were extracted from the UC-Davis samples since they had high T_c's and strain free Laue patterns. Additionally, the UC-Davis group reported observing the 11.3 kT orbit in their BKBO sample by a positron annihilation method.

Recently, we attempted dHvA measurement on the spherical sample of BKBO fashioned for the magnetization work described above. We used the
same instrumentation and detection coil used for the measurements on CeB₆ and could not unambiguously resolve any dHvA signal that persisted as a consistent peak in all Fourier transforms. We have applied a simple statistical method for tallying the frequency of occurrence of peaks in multiple data sets. The results of this procedure are highly dependent on the selected bin width and therefore are unreliable until the noise spectrum of our measurement apparatus can be determined. The more preferred method would be to reduce the noise level or to increase the sensitivity by improving the measurement technique. We hope that the SQUID probe developed and described in Chapter 3 (see Section 3.5) will provide this increased level of sensitivity. Additionally, given that techniques exist for the fabrication of BKBO epitaxial films [Shiryaev et al., 1997], experiments on similar to the ones carried out on YBCO epitaxial films (described in the previous chapter) could be done on BKBO.

6.4 Conclusions

The results of our magnetization studies of BKBO suggest that \( H_{c2} \) is much higher than previously thought. The transition from the mixed to the normal state is not well defined, a fact that may be due to the effects of Landau quantization on the superconducting state. It seems that dHvA in the normal state of BKBO has yet to be carried out. However, the results
of the measurements presented here represent a remarkable observation of quantum oscillatory effects so far below $H_{c2}$. Taking a value of 60 tesla as $H_{c2}$ indicates that dHvA was observed in fields down to $H^* \sim H_{c2}/4$. 

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CHAPTER 7

Summary: Strongly Correlated Electron Systems in High Magnetic Fields

The unifying theme of this dissertation has been the magnetic properties of systems whose electrons interact strongly with a variety of lattice phenomena—other electrons, phonons, magnons, flux vortices, etc. The conceptual and mathematical model that the experiments described herein put to the test is the Fermi liquid theory. I have used the de Haas-van Alphen effect to probe the interaction of these Fermi liquid systems at low temperature and high magnetic fields, where these properties are most in evidence. A great deal of attention has been given to the effects of Landau quantization on the properties of Fermi liquids. In the limit of low temperatures and high magnetic fields, the semi-classical approximations upon which the foundational theories of this science have been built begin to break down. This physical regime provides an ideal testing ground to explore the quantum mechanical phenomena that challenge the semi-classical view. In particular, Landau quantization effects coupled with cyclotron mass renormalization in the heavy fermion, CeB$_6$, lead to a way to test experimentally for the polariza-
tion of that material's Fermi surface. The measurement of Landau quantum oscillations in the mixed state of the high $T_c$ superconductor, $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, provides important information about the superconducting pairing mechanism, the order parameter, the response of the electrons to the vortex lattice, etc. Additionally, Landau quantum oscillations in the upper critical field and in $T_c$ will provide useful measures of microscopic quantum effects in extreme type-II superconductors. The measurements of the critical points in BKBO reported in this dissertation indicate that the effects of Landau quantization at high fields and low temperatures cannot be ignored as a minor theoretical correction to an adequate semi-classical theory.

The choice of coupling a study of high $T_c$ superconductors with the study of heavy fermions is a natural one since the role of magnetism and weak-localization are important considerations in understanding the properties of both classes of material. Magnetism had been thought of as antagonistic to superconductivity, but in the superconducting ground state of many heavy fermions, magnetism seems to be a requisite component of the superconducting mechanism. In the theoretical studies outlined in this dissertation, it seems that when the effects of Landau quantization are included in the calculation, it can be shown that at very high fields a new superconducting phase which thrives on magnetism comes into being—with the superconductivity increasing as the field increases. The practical achievability of the fields
necessary for observation of this new phase of superconductivity is still questionable, but in certain materials such a phase might one day be observed. BKBO, with a possible $T^*$ as high as 10 K [Tesanovic et al., 1989] and values of $H_{c2}$ within reach of experimental technology, is an important system for the study of these effects. Its intermediate $T_c$ value makes it of more practical interest than the cuprate superconductors whose $T_c$'s and $H_{c2}$'s push the limits of available cryo-magnetic technology.

A complete and up-to-date discussion of the theoretical aspects of dHvA and Landau quantization effects has been provided in Chapter 2. Special attention has been given to the Lifshitz-Kosevich theory and the various modifications to this theory due to the consideration of the effects of many-body interactions.

The experimental techniques used to carry out dHvA and magnetization measurements on heavy fermions and superconductors have been described in some detail in Chapter 3. Both pulsed and quasi-static magnetic fields were used in this study. Additionally, a SQUID detection system for doing dHvA has been built and tested for use in the 33 tesla resistive magnet at the National High Magnetic Field Laboratory in Tallahassee, FL. The data analysis techniques used to extract the results reported in this dissertation also were described in Chapter 3.
The results of a dHvA study on the heavy fermion compound CeB₆ has been described in Chapter 4. Evidence has been presented that indicates the Fermi surface of CeB₆ is polarized. This conclusion was reached based on careful measurements of the dHvA frequency as a function of field. Because the cyclotron mass is dependent on field, any polarization of the FS is seen as a change in the dHvA frequency as a function of field. Results of measurements in quasi-static magnetic fields using the field modulation technique have been combined with measurements made by Evert Haanappel in pulsed fields to show a decrease in dHvA frequency over the field range 7 to 50 tesla.

Extensive measurements have been made on epitaxial films of YBa₂Cu₃O₇. These measurements have been discussed in Chapter 5 along with a general discussion of the measurement of the dHvA effect in extreme type-II superconductors. Results of dHvA measurements in the mixed state of Nb₃Sn have been presented and compared with previous studies.

Magnetization and dHvA measurements on Ba₀.₆K₀.₄BiO₃ have been presented in Chapter 6. The magnetization measurements were made on several single crystal samples in a Quantum Design SQUID magnetometer. Additional measurements were made at the NHMFL up to 27 tesla using a force magnetometer. dHvA measurements on two single crystal samples were carried out in pulsed fields and in quasi-static fields. First observations of dHvA oscillations in the mixed state of BKBO have been reported. Four dHvA fre-
quencies were observed in the field modulation measurements, three of which correspond to the frequencies found by the pulsed field measurements, and the fourth and highest frequency corresponds to that predicted by LDA band structure calculations.

I intend to continue my collaboration with Roy Goodrich as I assume an assistant in research position in magnetometry at the National High Magnetic Laboratory in Tallahassee beginning in the Fall of 1997. dHvA measurements on \( \text{La}_{1-x}\text{Ce}_x\text{B}_6 \) have been planned in addition to the measurements on epitaxial films of YBCO using the SQUID detection system. Additional low temperature, high field measurements will be made on BKBO within the next two years. I hope to resolve the outstanding questions concerning the upper critical field of BKBO.
Bibliography


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Epitaxial growth of single crystal films of Ba$_{1-x}$K$_x$BiO$_3$ superconductors.  

D. Shoenberg.  page 74.  1960.


APPENDIX A

Proposal for a 500 G Modulation Coil for Use at the NHMFL

A.1 Introduction

Modulation of the magnetic field in the resistive magnets at NHMFL has been a problem. The limitations of the main power supplies do not allow for adequate modulation of the field. To get around this problem, in the past we have wound a small coil on the tail of one of the experimental cryostats and used a bipolar power amplifier to provide an oscillatory component to the main applied field of the resistive magnets. This coil proved to have too high a resistance to achieve the desired modulation fields with the available modulation power supply. To rectify partially this problem we have designed a modulation coil that can be wound directly on the dewar tail and has characteristics that provide us with higher modulation amplitudes when driven with the Kepco BOP 20-20 available in the NHMFL Instrumentation Shop.

The following is a description of the proposed coil and the results of a test performed on a prototype of the coil.
Table A.1: Modulation coil specification summary

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>wire diameter</td>
<td>0.584 mm (24 gauge)</td>
</tr>
<tr>
<td>coil diameter, D</td>
<td>29.595 mm (average for two layers)</td>
</tr>
<tr>
<td>coil length, H</td>
<td>29.595 mm</td>
</tr>
<tr>
<td>coil resistance, R</td>
<td>0.79 Ω (calculated)</td>
</tr>
<tr>
<td>total diameter, D</td>
<td>30.96 mm</td>
</tr>
</tbody>
</table>

A.2 Specifications

The two layer coil is to be wound out of 24 gauge copper wire on the room temperature tail of the dewar (diameter = 1.125 in.) so that the center of the coil will be at the field center when the dewar is placed in the magnet bore. The length, H, of the coil is equal to its diameter, D, for maximum field to power ratio. Each layer of the coil will have 50 turns. The calculated DC resistance of the coil at room temperature is 0.79 ohm." Taking 28.575 mm to be the diameter of the experimental cryostat, the total diameter of the dewar plus the coil is 30.963 mm. This leaves room for a layer of teflon tape to be wound on the coil to prevent shorts to the magnet bore. Also, a layer of teflon tape could be put down underneath the coil to insulate it from the dewar tail. † A summary of these specifications is given in Table A.1.

A coil length equal to the coil diameter is chosen to give the maximum field for the minimum power input. Given these dimensions, we have calculated that for a target amplitude of 500 gauss (peak) we will need a current

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*The strain introduced by winding the coil increases this value.
†The coil should be wound such that the leads come out at the bottom of the dewar tail.
of 16.4 amps. The operational impedance of the coil at 42 Hz to be approximately 1.2 ohms (including a contribution due to the inductance of the coil), the necessary voltage is 19.7 volts (peak). The Kepco BOP 20-20 can supply the necessary current at this voltage. The power dissipated in the coil will be 122 watts (rms), so some kind of cooling may be needed.

A.3 Results of Tests on the Prototype Coil

A coil conforming to the above specifications was wound on a 1.125 inch diameter form. The field to current ratio was measured with a calibrated pickup coil to be 30.85 gauss per amp. At 16.2 amps this coil yields a 500 gauss peak modulation which agrees well with the predicted required current of 16.4 amps for 500 gauss. Using a test coil wound on a copper pipe, we tested the calibration and the power requirements up to 7.2 amps (rms). The operational resistance calculated from a simultaneous voltage and current measurement was 1.56 ohms. The calculated power was 79 Watts (rms). This produced a temperature of greater than 170°C. Circulating air around the coil proved to be most effective at reducing the operating temperature of the coil.
A.4 Modulation Requirements

Tables A.2 and A.3 show the values of the peak modulation amplitude required to properly measure the de Haas-van Alphen (dHvA) effect with maximum sensitivity for a range of fields. Because of the advantages in eliminating direct pickup due to coil imbalance that are gained by detecting at second harmonic, the values listed in Table A.3 are the most important. In general, higher modulation fields are required for detection at harmonics higher than the fundamental. The dHvA frequencies of interest for our samples range from 0.5 kT to 12 kT. With the proposed 500 gauss modulation coil, we will have no problem measuring 12 kT dHvA frequencies up to 30 T for both harmonics. Signals due to dHvA frequencies below about 5 kT will not be maximized with a 500 gauss modulation coil at fields above 25 T and 20 T in first and second harmonic respectively. The lower the frequency we wish to measure the worse the situation gets. For frequencies on the order of 1 kT or less, it will be impossible to maximize the amplitude for detection at fields in excess of 10 T with this 500 gauss coil. Maximization of the modulation amplitude is necessary to maximize the voltage output of the sample pickup coil. A factor of two drop in the modulation amplitude results (roughly) in a factor of 4 drop in the voltage output of the pickup coil. Table A.4 shows the expected fraction of dHvA signal measurable if 500 gauss peak is the maximum possible modulation. When we are attempting to measure
nanovolt signals, this signal loss can become substantially detrimental to our ability to distinguish signal from noise. The modulation amplitudes (around 50 gauss peak) available to us heretofore have resulted in nearly a factor of 1000 loss in signal for most of our low frequencies at the highest fields. (See Table A.5.) Compare these calculations with the expected fraction of signal from a theoretical 2500 gauss modulation coil (Table A.6). Given such a coil we would be able to measure the lowest frequencies in most of our samples up to 30 T without substantial loss in the signal. Clearly, it is desirable to have higher modulation capacity built into the system for these experiments.
Table A.2: Chart of the optimum modulation amplitudes for first harmonic in gauss (peak) as a function of field and dHvA frequency $F$.

<table>
<thead>
<tr>
<th>$F$ (kT)</th>
<th>5.0 (T)</th>
<th>10.0 (T)</th>
<th>15.0 (T)</th>
<th>20.0 (T)</th>
<th>25.0 (T)</th>
<th>30.0 (T)</th>
<th>35.0 (T)</th>
<th>40.0 (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>143</td>
<td>372</td>
<td>1287</td>
<td>2288</td>
<td>3575</td>
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Table A.3: Chart of the optimum modulation amplitudes for second harmonic in gauss (peak) as a function of field and dHvA frequency $F$.

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Table A.4: The table below shows the ratio of detected signal loss to optimum signal in the dHvA effect at various fields with the modulation amplitude adjustable up to 500 G\textsubscript{peak} for second harmonic detection.

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<tr>
<td>12</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.847</td>
<td>0.854</td>
<td>0.819</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.847</td>
<td>0.854</td>
<td>0.852</td>
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<td></td>
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<tr>
<td>13</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.847</td>
<td>0.854</td>
<td>0.883</td>
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<td></td>
</tr>
<tr>
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<td>1</td>
<td>0.847</td>
<td>0.854</td>
<td>0.911</td>
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<td></td>
</tr>
<tr>
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<td>0.854</td>
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<td></td>
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<tr>
<td>14.5</td>
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<td>1</td>
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<td>0.847</td>
<td>0.854</td>
<td>0.959</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A.5: The table below shows the ratio of detected signal loss to optimum signal in the dHvA effect at various fields with the modulation amplitude adjustable up to 50 G<sub>peak</sub> for second harmonic detection.

<table>
<thead>
<tr>
<th>F (kT)</th>
<th>5.0 (T)</th>
<th>10.0 (T)</th>
<th>15.0 (T)</th>
<th>20.0 (T)</th>
<th>25.0 (T)</th>
<th>30.0 (T)</th>
<th>35.0 (T)</th>
<th>40.0 (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.091</td>
<td>0.006</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.33</td>
<td>0.023</td>
<td>0.005</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>0.625</td>
<td>0.032</td>
<td>0.01</td>
<td>0.003</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.871</td>
<td>0.061</td>
<td>0.018</td>
<td>0.006</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>2.5</td>
<td>1</td>
<td>0.14</td>
<td>0.029</td>
<td>0.009</td>
<td>0.004</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.197</td>
<td>0.047</td>
<td>0.013</td>
<td>0.003</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>3.5</td>
<td>1</td>
<td>0.261</td>
<td>0.068</td>
<td>0.018</td>
<td>0.007</td>
<td>0.004</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
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<td>0.33</td>
<td>0.073</td>
<td>0.023</td>
<td>0.01</td>
<td>0.005</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>4.5</td>
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<td>0.403</td>
<td>0.091</td>
<td>0.03</td>
<td>0.012</td>
<td>0.006</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>5</td>
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<td>0.477</td>
<td>0.112</td>
<td>0.038</td>
<td>0.015</td>
<td>0.007</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>5.5</td>
<td>1</td>
<td>0.552</td>
<td>0.134</td>
<td>0.044</td>
<td>0.018</td>
<td>0.009</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.625</td>
<td>0.158</td>
<td>0.052</td>
<td>0.022</td>
<td>0.01</td>
<td>0.008</td>
<td>0.003</td>
</tr>
<tr>
<td>6.5</td>
<td>1</td>
<td>0.695</td>
<td>0.184</td>
<td>0.061</td>
<td>0.025</td>
<td>0.012</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>7</td>
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<td>0.76</td>
<td>0.211</td>
<td>0.07</td>
<td>0.029</td>
<td>0.014</td>
<td>0.008</td>
<td>0.005</td>
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<tr>
<td>7.5</td>
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<td>0.819</td>
<td>0.238</td>
<td>0.08</td>
<td>0.034</td>
<td>0.016</td>
<td>0.009</td>
<td>0.005</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0.871</td>
<td>0.268</td>
<td>0.091</td>
<td>0.038</td>
<td>0.019</td>
<td>0.01</td>
<td>0.006</td>
</tr>
<tr>
<td>8.5</td>
<td>1</td>
<td>0.916</td>
<td>0.299</td>
<td>0.103</td>
<td>0.043</td>
<td>0.021</td>
<td>0.011</td>
<td>0.007</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0.955</td>
<td>0.33</td>
<td>0.114</td>
<td>0.048</td>
<td>0.023</td>
<td>0.013</td>
<td>0.007</td>
</tr>
<tr>
<td>9.5</td>
<td>1</td>
<td>0.989</td>
<td>0.362</td>
<td>0.127</td>
<td>0.053</td>
<td>0.026</td>
<td>0.014</td>
<td>0.008</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0.395</td>
<td>0.14</td>
<td>0.059</td>
<td>0.029</td>
<td>0.016</td>
<td>0.009</td>
</tr>
<tr>
<td>10.5</td>
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<td>1</td>
<td>0.428</td>
<td>0.153</td>
<td>0.065</td>
<td>0.032</td>
<td>0.017</td>
<td>0.01</td>
</tr>
<tr>
<td>11</td>
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<td>1</td>
<td>0.461</td>
<td>0.167</td>
<td>0.071</td>
<td>0.035</td>
<td>0.019</td>
<td>0.011</td>
</tr>
<tr>
<td>11.5</td>
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<td>1</td>
<td>0.494</td>
<td>0.182</td>
<td>0.076</td>
<td>0.038</td>
<td>0.021</td>
<td>0.012</td>
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<tr>
<td>12</td>
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<td>1</td>
<td>0.527</td>
<td>0.197</td>
<td>0.084</td>
<td>0.041</td>
<td>0.022</td>
<td>0.013</td>
</tr>
<tr>
<td>12.5</td>
<td>1</td>
<td>1</td>
<td>0.56</td>
<td>0.212</td>
<td>0.091</td>
<td>0.045</td>
<td>0.024</td>
<td>0.014</td>
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<td>0.583</td>
<td>0.228</td>
<td>0.098</td>
<td>0.048</td>
<td>0.026</td>
<td>0.015</td>
</tr>
<tr>
<td>13.5</td>
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<td>0.625</td>
<td>0.244</td>
<td>0.106</td>
<td>0.052</td>
<td>0.028</td>
<td>0.017</td>
</tr>
<tr>
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<td>1</td>
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<td>0.113</td>
<td>0.056</td>
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<tr>
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<td>1</td>
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<td>0.121</td>
<td>0.059</td>
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<td>0.019</td>
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<tr>
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<td>1</td>
<td>0.717</td>
<td>0.295</td>
<td>0.129</td>
<td>0.064</td>
<td>0.033</td>
<td>0.021</td>
</tr>
</tbody>
</table>
Table A.6: The table below shows the ratio of detected signal loss to optimum signal in the dHvA effect at various fields with the modulation amplitude adjustable up to 2500 G_{peak} for second harmonic detection.

| $F$ (kT) | 0.5 (T) | 1.5 (T) | 2.5 (T) | 3.5 (T) | 4.5 (T) | 5.5 (T) | 6.5 (T) | 7.5 (T) | 8.5 (T) | 9.5 (T) | 10.5 (T) | 11 (T) | 12 (T) | 12.5 (T) | 13 (T) | 13.5 (T) | 14 (T) | 14.5 (T) | 15 (T) |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 10.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 15.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 20.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 25.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 30.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 35.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| 40.0 (T) | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
A.5 Conclusion

The modulation coil design presented here will enable us to carry out measurements under substantially improved measurement conditions for a large number of frequencies and fields. But this coil does not represent the ideal; it is merely the optimum design given available equipment and materials.

Ultimately, a coil capable of producing 2500 gauss peak or higher will be necessary to make the most sensitive measurements at low dHvA frequencies.
APPENDIX B

Simulation of dHvA peaks using the LK equations

For convenient comparison of actual data to the LK equations a short function was composed in Igor's built-in programming language to generate the LK equations. The following is a listing of that function.

```
Function dHvA(F, effm, effm2, gfac, dng, T, H, B1, plimit, Pts, WaveName)
Variable F, effm, effm2, gfac, dng, T, H, B1, plimit, Pts
String WaveName

   Vars/F=(Pts)/3/0 @Wname = "Up"
   Vars v1 = @Wname + "Up"
   Vars/F=(Pts)/3/0 @Wname = "Down"
   Vars v2 = @Wname + "Down"
   Vars/F=(Pts)/3/0 @Wname = "Base"
   Vars v3 = @Wname + "Base"

   Variable i = 0, N, effm.phase, effm, maser
   Variable A = 37, delta = 9.3
   VariableO outfile

   F = F*1000
   dH = (G1-B0)/Pts
   B = B0

   maser = effm
   maser = (effm - effm2)/Pts
dc
   if (effm == 0)
      maser = (A*delta^2)/(delta^2) + (B + 7)^2
   endif
   phase = (pi/2) + maser + gfac
   u1[i] = ThreeOccEng(F, maser, gfac, dng, T, H, phase + (pi/2), plimit)
   u2[i] = ThreeOccEng(F, maser, gfac, dng, T, H, -(pi/2), plimit)
   u3[i] = maser
   i = i + 1
   if (i < N)
      while (B < B1)
         WriteField(G1-B1, Pts, "Field.T")
         Vars/F=(Pts)/3/0 @Wname
         Vars B = @Wname
      endwhile
      B = B + 2
   End

   Function ThreeOccEng(F, effm, gfac, dng, T, H, phase, plimit)
   Variable F, effm, gfac, dng, T, H, phase, plimit

   VariableO G, Beta, L, Single, Amp, dH, dH1, dH2, dH3, Temp8
   Variable eq = 1.60217736*10^-19 | electron charge in Coulombs
   Variable m = 9.109389851 | mass of electron in kg
   Variable h = 1.0540008833 | Bohr magneton constant in J/T

```

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Variable c = 399795058 | speed of light in m/s
Variable hbar = 1.06487268e-34 | reduced Planck constant in m·s
Variable tau_e = 1e-11 | electron relaxation time in sec

Variable g_Lande = 2
Variable p = 1

Beta = (sqrt(hbar)/(2*G*m*c))
I = (2*(PI^2)*hbar)/(c*Beta*e)
Simple = hbar/(2*PI*e*tau)
G = (PI/2)*G*e*sqrt(hbar)

Amp = (2*sqrt(2*beta))/((hbar+sqrt(hbar))
sh = 0
TempE = 0
do
sh1 = exp(-2*Sigma*p)
sh2 = sin(2*Sigma*p)/p + phase
sh3 = sinh(2*Sigma*p)
sh = (1/sqrt(p))*sin(sh1+sh2)/sh3
TempE = TempE + sh
p = 0.1
while(p < plimit)
dh = Amp * TempE
return dh
End

Function ElseField(X0, E1, Pt, WaveName)
Variable E0, E1, Pt
String WaveName

Variable H = E0, dh, i
RhsX = Pt/3/D/0 WaveName
Wave field = @WaveName
dh = (E1 - E0)/Pt

do
field[i] = h
i = i + 1
h = dh
while(H < E1)
RhsX = Pt/3/D/0 InvH
InvH = 1/field
End

End
APPENDIX C

C Code for DFT XOP

The following is a listing of the C language computer code for the DFT routine used for the determination of dHvA amplitudes and frequencies. This code was implemented and debugged by Steven Mitchell, an undergraduate student who assisted in the development of the data acquisition and analysis software used in this dissertation.

```c
/*
 * Discrete Fourier Transform (DFT) XOP
 * Version 1.0
 * Louisiana State University
 * DFT source, source, destination, destination, frequency, frequency2
 * source, source Source x and y waves
 * destination, destination Destination x and y waves
 * frequency, frequency Frequency range for destination waves
 * Notes:
 * Source waves must have the same number of points. Destination waves must have the same number of points. The number of points in the output range is determined by the number of points in the destination waves. All waves must be double precision.
 */
#include <ctype.h>
#include <string.h>
#include <stdio.h>
#include <math.h>
#include "igxip.h"
#include "DOP.h"
#include "DOPSupport.h"
#include "DFT consultation.h"

/* All structures are 64000-aligned. */
#ifdef(__power) || defined(__powerpc)
#undef if
#endif

/* Global Variables (none) */

DOUBLE trap (DOUBLE x, DOUBLE y, long x, long y)
{
    long j;
    DOUBLE delta, e;
```
```c
// Set DPT Parameters */
result = GetUsername(srcn);
if (result)
    return(result);
result = GetUsername(scry);
if (result)
    return(result);
result = GetUsername(desta);
if (result)
    return(result);
result = GetUsername(desty);
if (result)
    return(result);
result = GetDum(RepeatStart);
if (result)
    return(result);
result = GetDum(RepeatD);
if (result)
    return(result);
result = CheckTerm();
if (result)
```
return(result);

/* Error Checking */
if (strcmp(scrn, scrp) == 0 || strcmp(scrn, destx) == 0 || strcmp(scrn, desty) == 0) {
    return(ERR_INVALID_INPUT);
}

scrn = FetchResource(scrn);
scrp = FetchResource(scrp);
destx = FetchResource(destx);
desty = FetchResource(desty);

if (IS_VAR(scrn)) {
    return(ERR_INVALID_INPUT);
}

if (strcmp(scrn, NULL) == 0) {
    return(ERR_INVALID_INPUT);
}

result = dtc(scrn, scrp, destx, desty, fstart, xon, on, off, xoff);
    
    } /* Main */

*/

This is the entry point from the host application to the LDP when the message specified by the
host is other than INIT.

*/

static void
LDPEnd(void)
{
    
    switch (GetIDPMessage()) {
    case CB: /* command passed to LDP */
        result = Begin(); /* examine parameters and process them */
        SetIDPMessage(CB); /* LDP has done its job, it can be discarded */
        break;
    case EXE: /* LDP's main item selected */
        result = ExecList();
        SetIDPMessage(EXE); /* LDP is done now */
        break;
    }
    SetIDPError(result);
    
    /* maintainIDPHandle */

    This is the initial entry point at which the host application calls LDP.
    The message sent by the host must be INIT.
    main() does any necessary initialization and then sets the IDPEnd field of the
    IDPEndHandle to the address to be called for future messages.

    */

    main(IDPEndHandle inIDPEndHandle)
    {
    ifdef applc /* for MV C only */
    void DATAENTRY(void);
    DATAENTRY(); /* for MV C only */
UnloadSeg(_DATAINIT);
#endif

#define IIDP_GLOBALS_ARIA_44_BASED
#define __WINS__
SetCurrentApp(); // Set up correct 44. This allows globals to work. */
SendSIDP44Tagger(_inahelloThreadId, 0); // And communicate it to iger. */
#endif
#endif

IIDLInit(_inahelloThreadId); /* do standard IIDP initialization */
SetIIDPEntry(_IIDPEntry); /* see entry point for future calls */
SetIIDPHistory(0L);
}

#ifdef(powered) && defined(__powerc)
#endif
#endif

/* All structures are 68000-aligned */
APPENDIX D

Sample Rotator

The design of this rotator is based on a similar instrument constructed by D. H. Lowndes. The rotator was machined from 1266 clear epoxy manufactured by Emerson and Cumming, Inc.* When machining, it is important to put a 0.015 in radius on all edges to prevent the epoxy from cracking as it is cooled to 4.2 K. Cracks form in 1266 epoxy at sharp edges upon rapid coiling. The moving parts can be lubricated with any sort of graphite-like material; we used MoS₂.

An overview of the rotator body is given in Figure D.1. This body is coupled to a probe fashioned out of a length of G-10 tube. Using a G-10 tube helps prevent heating when using pulsed fields. A stainless probe is best if rapid cooling is desirable and quasi-steady applied fields are to be used. A detail of the shaft to which the spiral gear is attached is given in Figure D.2. Details of the gear ball and its assembly are given in Figure D.3 and D.4.

*77 Dragon Court, Woburn, MA 01888

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Figure D.1: Diagram cross-section of the small sample rotator machined at LSU.

Shaft center drilled 0.078 from body center.

Hole for lubrication

Groove cut 0.040" deep
Figure D.2: The shaft is attached to a rod that runs up the probe to room temperature to facilitate in situ rotation. A spiral gear is attached to the end of the shaft. As this gear turns the gear ball is rotated in the z-x plane.
Figure D.3: This is a detail showing how the rotation axle of gearball is to be machined and installed.
Figure D.4: The detection coil is mounted in the gear ball. The twisted pair leads run out through the axle. All loose wires should be secured with GE-varnish to prevent them from vibrating in the field.
VITA

Donavan Weslee Hall was born the second son of Danford Austin Hall and Patricia May (Lyman) Hall on the thirty-first of January 1969, in Oklahoma City, Oklahoma. Hall spent his childhood on the farm homesteaded by his great-grandfather, whose own father had made the Cherokee Outlet landrun of 1892. His family still lives on that farm to this day.

Hall showed an early interest in music and at a young age mastered both the piano and violin. He began voice training at the age of nine. He competed in state and local arts competitions, securing many honors. During his High School education in Hobbs, New Mexico, Hall continued his musical interests through the formal study of music composition. During Hall's senior year, shortly after being awarded the J. L. Burke prize for poetry, he decided to major in physics upon going to college.

At the University of Dallas, Hall began work on a Bachelors of Science in physics. He became a laboratory assistant for the general physics, the modern physics, and the astronomy labs. He tutored fellow students nightly at the physics department "Help Lab" where he met his future wife, Denise. After five months of traveling during his sophomore year throughout Europe, with a copy of the complete works of Aristotle, Hall became interested in computational physics and began working on computer simulations of space.
filling topological structures. For his work on this problem, he was awarded an undergraduate research opportunity at Argonne National Lab to work with Kathrine Strandburg and Nick Rivier. There he continued work on grain growth and on Monte Carlo simulations of the Surface Magneto-Optical Kerr Effect. This work comprised the bulk of his undergraduate thesis work, jointly directed by Strandburg and Richard P. Olenick of the University of Dallas physics department.

After completing his studies at the University of Dallas, Hall abandoned computational physics for experimental low temperature physics in high magnetic fields under the direction of Professor Roy Goodrich of Louisiana State University. Hall has worked as a research assistant for the last six years, measuring magnetic properties of and the de Haas - van Alphen effect in a variety of strongly correlated materials. In his capacity as research assistant, Hall has had the opportunity to work at a number of premier facilities including the National High Magnetic Field Laboratory in Tallahassee, Florida and at the pulsed field facility located at Los Alamos National Laboratory, and at Oak Ridge National Laboratory. Hall has collaborated with Douglas Lowndes, Fred M. Mueller, and Joseph Vuillemin. Hall earned his master's degree in physics in 1993 and hopes to complete his doctor of philosophy degree before his twenty-ninth birthday.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Donavan Hall
Major Field: Physics
Title of Dissertation: Magnetic Measurements on Superconductors and Heavy Fermions

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: September 5, 1997