High Pressure Studies of Superconductivity

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High Pressure Studies of Superconductivity

by

Narelle Jayne Hillier

A dissertation presented to the
Graduate School of Arts and Sciences
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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ABSTRACT OF THE DISSERTATION

High Pressure Studies of Superconductivity

by

Narelle Jayne Hillier

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Professor James S. Schilling, Chair

Superconductivity has been studied extensively since it was first discovered over 100 years ago. High pressure studies, in particular, have been vital in furthering our understanding of the superconducting state. Pressure allows researchers to enhance the properties of existing superconductors, to find new superconductors, and to test the validity of theoretical models. This thesis presents a series of high pressure measurements performed in both He-gas and diamond anvil cell systems on various superconductors and on materials in which pressure-induced superconductivity has been predicted. Under pressure the alkali metals undergo a radical departure from the nearly-free electron model. In Li this leads to a superconducting transition temperature that is among the highest of the elements. All alkali metals have been predicted to become superconducting under pressure. Pursuant to this, a search for superconductivity has been conducted in the alkali metals Na and K. In addition, the effect of increasing electron concentration on Li$_{1-x}$Mg$_x$ alloys has been studied. Metallic hydrogen and hydrogen-rich compounds are believed to be good candidates for high temperature superconductivity. High pressure optical studies of benzene (C$_6$H$_6$) have been performed to 2 Mbar to search for pressure-induced metallization. Finally, cuprate and iron-based materials are considered high-$T_c$ superconductors. These layered compounds
exhibit anisotropic behavior under pressure. Precise hydrostatic measurements of $dT_c/dP$
on $\text{HgBa}_2\text{CuO}_{4+\delta}$ have been carried out in conjunction with uniaxial pressure experiments by another group. The results obtained provide insight into the effect of each of the lattice parameters on $T_c$. Finally, a series of hydrostatic and non-hydrostatic measurements on $\text{LnFePO}$ ($\text{Ln} = \text{La, Pr, Nd}$) reveal startling evidence that the superconducting state in the iron-based superconductors is highly sensitive to lattice strain.
Chapter 1

Introduction

The 1908 liquefaction of helium by Heike Kamerlingh Onnes in his cryogenic laboratory at Leiden University was monumental in opening the doors to low temperature research. Small quantities of both nitrogen and oxygen had been independently liquefied about 30 years earlier by Louis P. Cailletet and Raoul P. Pictet, and James Dewar had succeeded in liquefying small quantities of hydrogen in 1898 [1]. \( \text{N}_2 \), \( \text{O}_2 \), and \( \text{H}_2 \) liquefy at 77 K, 90 K, and 20 K, respectively, so Onnes was able to reduce the lowest attainable temperature by a factor of about 10 when he liquefied \( \text{He} \) at 4.2 K and then further reduced the temperature to 1.7 K by pumping on the sample space to reduce the pressure. Along with the development of techniques to allow useful quantities of liquid helium to be produced (and maintained), this breakthrough opened the doors to a new realm of research opportunities for investigating the behavior of materials at extremely cold temperatures. As Onnes later stated so aptly in his 1913 Nobel lecture, the breakthrough allowed scientists to “\[lift\] the veil which thermal motion at normal temperatures spreads over the inner world of atoms and electrons” [2].

By the early 1900s, scientists already knew that the resistance of a metal decreased with
temperature. Electron scattering off vibrating atoms in the crystal lattice contributes to the resistance. As temperature decreases, so too do the vibrations of the atoms, thereby decreasing the resistance. Speculation, however, existed over what would happen at temperatures approaching absolute zero. Three possibilities were considered [3]:

- James Dewar believed that the resistance would continue to decrease smoothly, approaching zero at absolute zero.

- Mathiesson suggested that the resistance would approach a finite value at 0 K. This was based on the idea that, even at absolute zero, electron scattering off impurities would contribute to a finite resistance.

- Lord Kelvin proposed that the electrons would become frozen in place at low temperatures, causing a decrease in conductivity and a corresponding increase in resistance, which would approach infinite values at absolute zero.

The question of this low temperature behavior was particularly intriguing, as scientists hoped to be able to use the resistivity of metals as a secondary thermometer for other low temperature studies. Onnes knew that impurities would be a limiting factor in studying the temperature dependence. He and graduate student Giles Holst therefore chose to first study Hg, a room temperature liquid that could easily be distilled to ensure sample purity. Much to everyone’s surprise, they found that the resistance of Hg vanished abruptly at a finite temperature of 4.2 K [4, 5]. Experiments subsequently showed that this resistance is not just immeasurably small, but rather zero. Originally coined as *supraconductivity*, today this phenomenon is known as *superconductivity* and occurs below a critical temperature, $T_c$.

The discovery of superconductivity in Hg led to a flurry of research in an attempt to detect superconductivity in other materials and to understand the mechanism behind this novel
state of matter. In the past century, scientists have identified a wide array of superconducting materials. Early research centered on the discovery of superconductivity in single elements and in simple binary alloys and compounds. In 1957 Bardeen, Cooper, and Schrieffer finally developed a microscopic theory, known as BCS theory, that was able to explain superconductivity in these conventional superconductors in terms of electron-phonon coupling [6]. At the time the low critical temperatures of known superconductors severely restricted possible technological applications. For approximately 75 years following the discovery of superconductivity, the highest known critical temperature increased only very gradually, as seen in Fig. 1.1.

Finally, in 1986 Bednorz and Müller made a breakthrough with the discovery of superconductivity at about 30 K in a layered ceramic material, La:Ba:Cu:O (LBCO) [9]. Subsequent experiments by Chu et al., showing that $T_c$ of LBCO increased rapidly under pressure [10], led the group to replace La with Y, an isoelectronic element with smaller size, thereby inducing chemical pressure. The astounding result was the discovery of superconductivity in Y:Ba:Cu:O (YBCO) at 93 K, making it the first superconductor with $T_c$ above liquid nitrogen temperatures [11]. Today this class of materials, known as the cuprates, exhibit the highest known critical temperatures, with $T_c$ in one of the Hg-based materials reaching as high as 138 K at ambient pressures [12] and about 160 K under pressure [13].

The 2008 discovery of superconductivity in F-doped LaFeAsO at 26 K [14] motivated an investigation of a new class of iron-based superconductors. Superconductivity in these materials reaches as high as 55 K in SmFeAsO$_{1-x}$F$_x$ [15]. Like the cuprates, these iron-based materials are characterized by a layered structure and their superconducting critical temperature sensitively depends on both doping and applied pressure. Collectively the cuprates and
Figure 1.1: Highest observed superconducting critical temperatures since the discovery of superconductivity over a century ago. Critical temperatures are shown for conventional (●), cuprate (▲), and iron-based (◆) superconductors. Open symbols represent high pressure measurements. Data listed in bold font with two asterisks (**) indicate discoveries for which researchers later received the Nobel Prize in Physics: Kamerlingh Onnes in 1913 for low temperature research and the discovery of superconductivity; Bardeen, Cooper, and Schrieffer in 1972 for development of BCS theory; and Bednorz and Müller in 1987 for discovery of the cuprate superconductors. Figure based on Refs. [3, 7, 8].
iron-based superconductors are commonly referred to as *high temperature* superconductors (HTSC). They are considered *unconventional superconductors* in that they cannot be described by BCS theory.

Superconducting technology has already been widely adopted for several applications – from superconducting wire for creating large scale magnets in MRI machines and in particle accelerators to the use of SQUIDs for probing magnetism to Maglev trains in Japan; superconductors are even used to define the volt. Nevertheless, scientists still dream of one day finding a room temperature superconductor to revolutionize energy storage and transfer. As no theory has yet been developed to explain unconventional superconductivity and no reliable predictions can be made regarding a material’s critical temperature or even whether superconductivity exists, the quest to discover new superconductors remains largely one of systematic trial and error. The use of pressure is an invaluable tool for such systematic studies.

In addition to either increasing or decreasing the critical temperature of an ambient pressure superconductor, pressure may induce or suppress superconductivity. Of 53superconducting elements, 23 become so only under application of sufficient pressure. Application of pressure can significantly affect the electronic and lattice properties of a material and can induce structural changes that may favor the emergence of superconductivity. For some materials such as oxygen [16] and sulfur [17] that are non-metallic at ambient pressure, superconductivity appears at high pressure after metallization has been induced. A moderate pressure of 15 GPa applied to iron will destroy its magnetism and allow superconductivity to appear [18]. In many of the high temperature cuprate and iron-based materials, superconductivity emerges only upon application of pressure or upon doping. Pressure effects
give scientists vital information about the superconducting state and can provide clues for further enhancing $T_c$. The monumental discovery of YBCO occurred after researchers noticed a rapid increase of $T_c$ under pressure in LBCO [10,11]. In addition, pressure provides a means of pursuing the dream of a room temperature superconductor. It has been suggested that metallic hydrogen might be a room temperature superconductor [19] and experiments to extreme pressures have been carried out pursuant to this goal. Hydrogen-rich compounds have also been studied in the quest to metallize hydrogen with the idea that these materials may become metallic at lower pressures. Finally, comparing experimental results for the behavior of materials under pressure to theoretical predictions allows scientists to test the validity of these theoretical models [20,21].

Experimental studies of the behavior of materials under pressure would not have been possible without the technological improvements of the last century which have resulted in apparatuses capable of generating extreme pressures. Most notably, the advent of the diamond anvil cell enabled researchers to conduct experiments at static pressures extending into the multi-megabar regime. Availability of the ruby fluorescence technique as a simple pressure gauge has resulted in a significant increase in the number of laboratories capable of conducting high pressure research to study a wide range of material properties.

This thesis investigates the role of high pressure in a wide range of materials, focusing primarily on superconductivity in both known superconductors and in materials for which pressure is predicted to induce superconductivity. Measurements were performed using ac-susceptibility techniques. A brief theoretical introduction to superconductivity and the role of pressure in materials is contained in Chapter 2, while Chapter 3 gives a detailed description of the experimental techniques used to detect superconductivity, to produce and
measure high pressures, and to attain low temperatures. Experimental details of measurements are contained within Chapters 4–8, which also contain brief theoretical background information for the materials studied therein. In particular, Chapter 4 describes the search for superconductivity in the alkali metals Na and K, while Chapter 5 investigates pressure-induced superconductivity in Li(Mg) alloys for increasing Mg concentrations. In Chapter 6 high pressure optical measurements performed on benzene to search for metallization are described. Chapter 7 focuses on hydrostatic measurements on the single-layered cuprate material HgBa$_2$CuO$_{4+\delta}$ (Hg-1201) and in particular on how each lattice parameter should be varied to increase $T_c$. Chapter 8 focuses on the iron-based superconductors, in particular on $Ln$FePO ($Ln=$La, Pr, Nd) and how the degree of hydrostaticity in high pressure measurements significantly affects the pressure dependence of the critical temperature. Finally, Chapter 9 contains a summary of results.

The appendices include a brief discussion of measurements of the pressure dependence of the ferromagnetic Curie temperature in GdAgMg. Also contained are a brief overview of the optical set-up for the diamond anvil cell system, modifications made to enhance the LabVIEW measurement system, and information regarding the refurbishment of the cold head for the closed-cycle cryostat used in conjunction with the He-gas system.
Chapter 2

Background: Theory and Experiment

2.1 Superconductivity

In over a century since the discovery of superconductivity in Hg by Kamerlingh Onnes [4, 5], countless research papers have been published exploring this exotic state. Our understanding of superconducting properties and mechanisms has increased significantly. In order to aid in better understanding the material covered in subsequent chapters, this section will introduce many of the main concepts of superconductivity, including both theory and an overview of superconductivity’s characteristic properties. For more details it is suggested that the reader refer to several excellent textbooks on superconductivity [22–28].

When a material becomes superconducting, it undergoes a thermodynamic phase transition at a critical temperature, $T_c$, to an ordered state of electrons. Above this temperature, the material is in the normal state. Below $T_c$, however, the superconducting state exhibits the following striking features:

- Zero dc electrical resistivity
• Perfect diamagnetism, exhibited by the Meissner-Ochsenfeld effect

Superconductors exhibit perfect conductivity. As long as the current is below a critical value, the dc electrical resistivity drops abruptly to zero upon cooling through $T_c$. In fact, measurements have shown that the resistance is not simply negligibly small, but rather zero. If the resistance were finite, persistent currents established in superconductors would gradually decay over time due to energy dissipation. However, precise nuclear magnetic resonance measurements, which set an upper limit on the resistance, have shown that the decay time is at least 100,000 years [29].

Superconductors are distinguished from ordinary metals with perfect conductivity by the Meissner-Ochsenfeld effect, first observed in 1933 [30]. For a perfect conductor ($\sigma = \infty$), the magnetic field in the interior of the sample must be constant in time as given by Maxwell’s equation,

$$\nabla \times E = \frac{1}{c} \frac{\partial B}{\partial t}.$$  (2.1)

If a magnetic field is applied to a metal which is subsequently cooled below the critical temperature at which it becomes a perfect conductor, nothing occurs. When the magnetic field is removed, however, surface currents will be induced in the sample to maintain the magnetic field. On the other hand, if a magnetic field is applied to a perfect conductor, induced surface currents will prevent the penetration of magnetic flux into the sample. In both instances, eddy currents are induced so that the magnetic field within the perfect conductor remains constant. The magnetic response of a superconductor, however, is different. When an external field is applied while the material is in the normal state, the field will penetrate the sample. As long as the applied field is less than the critical field, upon cooling through $T_c$ a superconductor will expel the magnetic flux, as seen in Fig. 2.1. Eddy currents flowing
Figure 2.1: As a superconductor is cooled below $T_c$ in an applied magnetic field, the magnetic flux is expelled from the sample via the Meissner-Ochsenfeld effect.

at the surface of the superconductor shield the magnetic field from the bulk of the sample. This phenomenon is known as the Meissner-Ochsenfeld effect, often referred to simply as the Meissner effect. Similarly, if a magnetic field is applied below $T_c$, eddy currents screen the interior of the sample to exclude magnetic flux lines. Thus, regardless of the temperature at which an external magnetic field is applied, the bulk sample remains free of magnetic flux. Superconductors, therefore, are also perfect diamagnets\(^1\).

2.1.1 BCS Theory of Superconductivity

Following the discovery of superconductivity, scientists sought to understand the mechanism of superconductivity and to develop a microscopic theory. Early progress focused primarily on gaining a phenomenological understanding of superconductivity. In 1935 brothers Fritz and Heinz London developed a theory to explain the Meissner-Ochsenfeld effect [31]. The London equation effectively describes the screening out of the magnetic field inside a superconductor. F. London later showed that the infinite conductivity and suppression of thermal

\[^1\chi = -1\] in MKS units or \[\chi = -1/4\pi\] in cgs units.
conductivity characterizing the superconducting state could be explained in terms of Bose-Einstein condensation of bosonic charge carriers [32]. As metallic charge carriers are known to be electrons (fermions), however, it was unclear how this could occur. In 1950 Fröhlich proposed that superconductivity is mediated by the interaction between electrons and the crystal lattice through vibrational fields [33], while Ginzburg and Landau developed a phenomenological theory to describe superconductivity from a thermodynamic standpoint in terms of a superconducting order parameter [34]. It was later shown that this model could be derived from microscopic theory. At about the same time, the importance of the role of the crystal lattice in superconductivity was evidenced by discovery of the isotope effect [35–37]. Using stable Hg isotopes, scientists showed that $T_c$ depends upon the atomic mass of the ion, with heavier ions superconducting at lower temperatures. Subsequent experiments also verified this effect for isotopes of other compounds. Empirically, the isotope effect is given by $T_c \sim M^{-\alpha}$, where $M$ is the mass of the cation and $\alpha = 0.5$ for many simple superconductors. The realization that superconductivity must be mediated by electron-phonon coupling proved vital in the work of scientists at the University of Illinois. In 1957, almost half a century after Onnes’ discovery of this novel state of matter, Bardeen, Cooper, and Schrieffer finally developed a microscopic theory of superconductivity [6]. Today this theory is commonly referred to as the BCS theory and accurately predicts many of the properties of conventional superconductors.

Free electrons repel each other via the Coulomb force. However, in a crystal lattice, the effective Coulomb repulsion is reduced through screening. In fact, interaction with the crystal lattice can cause an attractive interaction between electrons! Suppose an electron with wave vector $k_1$ and corresponding energy $\epsilon_{k_1} = \hbar \omega_{k_1}$ is moving through the crystal lattice.
This electron excites a phonon with wave vector $q$ through lattice vibrations, leaving it in a new state, $k'_1 = k_1 - q$ by conservation of momentum. A second electron $k_2$ subsequently absorbs the phonon, resulting in the new state, $k'_2 = k_2 + q$. A Feynman diagram showing this interaction may be seen in Fig. 2.2(a). How does the interaction causing one electron to be indirectly scattered by another occur? As the first electron moves through the lattice, the phonon excitation produces vibrations of the lattice with frequency $\omega = |\epsilon_{k_1} - \epsilon_{k'_1}|/\hbar$. When, at a given moment, there is a localized region of negative charge, the surrounding cations will be attracted to this region, as seen in Fig. 2.2(b). Even after compensating for the increased charge density, motion of the ions will continue due to their large mass. As a result a region of excess positive charge will be created, which may then attract a second electron. These two electrons have an effective attractive interaction and constitute a bosonic Cooper pair.

Electrons are fermions, so by the Pauli exclusion principle the state $k'_i$ must be previously unoccupied for the state $k_i$ to scatter into it. These unoccupied states exist only near the Fermi surface, so the effective electron-electron attraction exists for electron energies within $\pm \hbar \omega_D$ of the Fermi surface, i.e.,

$$|\epsilon_{k_i} - \epsilon_F| < \hbar \omega_D,$$

(2.2)

where $\omega_D$ is the Debye frequency and $\epsilon_F$ is the Fermi energy. The attractive interaction makes a negative contribution to the total energy of the system, leading to a superconducting ground state. The most energetically favorable state occurs when the number of states participating in superconductivity is maximized. The total momentum $q_{tot} \equiv k_1 + k_2 = k'_1 + k'_2$ must be conserved. The shaded gray regions in Fig. 2.2(c) represent the electron states in the thin shell about the Fermi energy which can undergo Cooper pairing while maintaining conservation of momentum. The number of states participating in superconductivity is
Figure 2.2: Various representations of electron-phonon coupling leading to Cooper pairing of electrons in the superconducting state. (a) Feynman diagram of electron scattering in superconductivity. One electron, \( k_1 \), excites a phonon, \( q \), which is subsequently absorbed by another electron, \( k_2 \). (b) As an electron moves through the lattice, the cations are drawn from their equilibrium positions to compensate for the increased electron density. Motion of the massive ions continues after the excess charge density has been compensated for, resulting in a region of excess positive charge to which a second electron is attracted. The attractive interaction between electrons results in the formation of bound Cooper pairs. The small red central dot indicates the motion of the electron through the lattice. (c) Electron states participating in Cooper pairing are represented by the shaded gray regions where the total momentum, \( q_{tot} \), is conserved. When the spheres are concentric, i.e., \( q_{tot} = 0 \), the number of states participating in superconductivity is maximized, thereby minimizing the energy. Thus, Cooper pairing occurs for electron states of opposite momenta, \( k_1 = -k_2 \) in a thin shell about the Fermi surface. Note \( \Delta k/k_F \sim \hbar \omega_D/\epsilon_F \).
maximized when the spheres are concentric, i.e. when $q_{tot} = 0$. Thus, the most energetically favorable coupling occurs between electrons of opposite momenta: $k$ and $-k$ [38]. The resulting Cooper pairs are bosons and, as such, may undergo Bose-Einstein condensation.

Only a small fraction of electrons participate in Cooper pairing. This is supported by observations of the change in entropy from the normal to superconducting state. Superconductivity is an ordered state of electrons, so entropy decreases when a material becomes superconducting. However, the entropy decrease is very small, indicating that only a small percentage of electrons contribute to superconductivity [25].

In the limit of weak electron-phonon coupling, BCS makes various predictions accurately describing the superconducting state. The critical temperature, $T_c$, is given by

$$T_c = 1.14 \left( \frac{\hbar \omega_D}{k_B} \right) \exp \left\{ -\frac{1}{N(E_F)V_{eff}} \right\},$$  \hspace{1cm} (2.3)

where $\omega_D$ is the Debye frequency, $k_B$ is the Boltzmann constant, $N(E_F)$ is the density of states at the Fermi level, and $V_{eff} > 0$ is the net attractive potential between electrons. Note that since $\omega_D \sim M^{-1/2}$, the isotope effect emerges from BCS theory. Finite energy is required to break the Cooper pairs formed by electrons near the Fermi level. Thus, an energy gap of $2\Delta$ exists in the electronic excitation spectrum. The size of this energy gap, which decreases with increasing temperature before finally vanishing at $T_c$, is well-described by BCS theory. Near $T_c$ the temperature dependence of the energy gap is given by

$$\Delta(T)_{T \to T_c} = 1.76 k_B T_c \left( 1 - \frac{T}{T_c} \right)^{1/2},$$ \hspace{1cm} (2.4)
and at absolute zero, the size of the energy gap is given by

\[
\frac{2\Delta(0)}{k_B T_c} = 3.52.
\]  

(2.5)

In a superconductor energy is required in order to establish the shielding currents necessary to screen the magnetic field from the bulk sample. At high enough fields, superconductivity no longer remains energetically favorable and the magnetic field penetrates the sample. BCS describes the temperature dependence of the critical field, \( H_c \), at which superconductivity is destroyed as

\[
H_c(T) \approx H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right],
\]  

(2.6)

where \( H_0 \) is the critical field at \( T = 0 \) K.

For a normal metal, the specific heat consists of a linear contribution from electronic excitations and a cubic term resulting from vibrations of the crystal lattice. At low temperatures the latter term is almost negligible. When a metal undergoes the thermodynamic transition to the superconducting state, the electronic contribution to the specific heat changes significantly, leading to a discontinuity in the specific heat at \( T_c \). The size of this discontinuity is given by BCS theory as

\[
\frac{c_s - c_n}{c_n} \bigg|_{T_c} = 1.43,
\]  

(2.7)

where \( c_s \) and \( c_n \) are the electronic specific heat in the superconducting and normal state, respectively. Below \( T_c \) the electronic specific heat of a superconductor decays exponentially to zero. Good agreement to the size of the discontinuity as predicted by BCS theory is found for weakly coupled superconductors.
2.1.2 Penetration Depth and Coherence Length

Two characteristic lengths describe superconductors – the London penetration depth \( \lambda_L \) and the coherence length \( \xi_0 \). Magnetic fields are excluded from the bulk superconductor. For this to be the case, the magnetic field at the external surface decays exponentially toward the interior of the sample. The field inside the superconductor as a function of the distance \( x \) from the surface is given by

\[
B(x) = B(0) \exp \left( \frac{-x}{\lambda_L} \right),
\]

(2.8)

where \( \lambda_L \) is the London penetration depth and \( B(0) \) is the field at the surface of the superconductor. The penetration depth is related to the density of superconducting electrons in the material by

\[
\lambda_L = \sqrt{\frac{mc^2}{4\pi ne^2}}
\]

(2.9)

where \( m \), \( n \), and \( e \) are the mass, concentration, and charge, respectively, of the superconducting charge carriers.

The coherence length, \( \xi_0 \), is defined as the distance over which the superconducting carrier density can not vary significantly. In BCS theory the coherence length is the size of the Cooper pair and is given by

\[
\xi_0 = \frac{2\hbar\nu_F}{\pi \Delta},
\]

(2.10)

where \( \nu_F \) is the electron velocity at the Fermi surface and \( \Delta \) is the superconducting energy gap. The coherence length is evidence of the presence of long range order in superconductors.

As first predicted by Brian Josephson, it is actually possible for a superconducting current to tunnel between two superconductors through a thin insulating layer known as a weak
Above a critical applied magnetic field, superconductivity no longer remains energetically favorable and the magnetic field penetrates the sample. The way in which the magnetic field penetrates a cylindrical sample differs between two classes of superconductors, as seen in Fig. 2.3. It is convenient to use the relationship between the penetration depth and the coherence length to characterize these classes. For a type I superconductor, $\lambda_L < \xi_0/\sqrt{2}$. Below a critical field, $H_{c1}$, magnetic flux is completely excluded from the sample. Above this critical field, superconductivity is destroyed and the sample reverts to a normal metal. In a type II superconductor, for which $\lambda_L > \xi_0/\sqrt{2}$, magnetic flux is completely excluded below a lower critical field, $H_{c1}$. Above an upper critical field, $H_{c2}$, the entire sample reverts to a normal state. For intermediate fields, however, partial penetration of flux becomes energetically favorable. The sample exists in a mixed state consisting of both superconducting and normal regions, with magnetic field lines penetrating the sample through vortices of quantized flux, $\Phi_0 = h/2e$. As the field increases, more and more of these fluxoids penetrate the sample. This phenomenon enables type II superconductors to withstand much higher fields before bulk superconductivity is destroyed at $H_{c2}$, making them more technologically useful for applications requiring high magnetic fields. Typically $H_c < 1$ Tesla for type I superconductors, while for type II superconductors, $H_{c2}$ may be as high as several hundred Tesla [8]. Most pure elements are type I superconductors, while alloys and compounds are usually type II.
Figure 2.3: Magnetization vs. applied magnetic field for type I and type II superconductors. In a type I superconductor (left) the field is completely expelled via the Meissner effect for applied fields less than a critical value, $H_{c1}$, above which superconductivity is quenched and the material exists as a normal metal. For a type II superconductor (right), a mixed state exists between lower and upper critical fields, $H_{c1}$ and $H_{c2}$, respectively. In this range, the magnetic field penetrates the sample through quantized flux vortices. Below $H_{c1}$ the field is completely excluded from the sample, while bulk superconductivity is destroyed above $H_{c2}$.

2.1.3 Strong Coupling

BCS theory is valid in the limit of weak coupling, i.e., when the electron-phonon interaction is weak. In some materials, however, deviations from the universal BCS equations are observed. Strong coupling is seen, for example, in lead where $2\Delta/k_BT = 4.3$ and $(c_s - c_n)/c_n = 2.6$ and in Hg($\alpha$) where $2\Delta/k_BT = 4.6$ [8, 26]. In each case, these values are significantly larger than the universal values predicted by BCS theory as seen in Eqs. 2.5 and 2.7. These deviations occur because the electron-phonon interaction is not always weak. For stronger coupling the universal parameters of BCS theory start to depend on characteristics of the phonon spectrum. It is important, then, to account not only for the effect of the phonons on the electrons, but also for the effect of electrons on the phonons. In 1960 Eliashberg developed a theory to account for strong coupling, giving a generalized formula for the strength of the
electron-phonon interaction in terms of a coupling constant [41]

$$\lambda = 2 \int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega. \quad (2.11)$$

The argument of this integral is sometimes referred to as the Eliashberg function and plays a central role in the theory of superconductivity; $\alpha(\omega)$ is the matrix element describing the effective interaction between the electron and lattice, while $F(\omega)$ is the phonon density of states. Weak, intermediate, and strong coupling are described by $\lambda \ll 1$, $\lambda \sim 1$, and $\lambda > 1$, respectively. It turns out that this function may actually be determined using tunneling spectroscopy data [42].

From the Eliashberg equation it is possible to determine the value of $T_c$ for arbitrary coupling strength, given by

$$T_c = \frac{0.25 \tilde{\omega}}{(e^{2/\lambda_{eff}} - 1)^{1/2}} \quad (2.12)$$

where $\tilde{\omega} = \langle \omega^2 \rangle^{1/2}$ is the characteristic phonon frequency and $\lambda_{eff}$ is an effective coupling constant given by

$$\lambda_{eff} = \frac{\lambda - \mu^*}{1 + 2\mu^* + \lambda\mu^*t(\lambda)}. \quad (2.13)$$

Here $\mu^*$ is the Coulomb pseudopotential which takes into account the screened Coulomb repulsion between the electrons and $t(\lambda)$ is a universal function [26].

For intermediate coupling strengths ($\lambda \lesssim 1.5$), $T_c$ has a slightly simpler dependence given by the McMillan equation [43, 44]:

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (2.14)$$
In the limit of weak coupling for $\lambda \ll 1$ these equations all reduce to those given by BCS theory. For a more in-depth summary of BCS theory as it is generalized for intermediate and strong coupling, refer to Diederichs [45].

### 2.1.4 Unconventional Superconductivity

The microscopic BCS theory, and its extension to stronger coupling, effectively describes *conventional* superconductors, which include many elements as well as many metallic compounds and alloys. However, several classes of superconductors can not be explained by BCS theory and are referred to as *unconventional* superconductors. Among these are heavy fermion and some organic superconductors, along with the high temperature cuprate and iron-based superconductors.

These unconventional superconductors have a different ground state symmetry than the BCS ground state. The pairing mechanism in these superconductors remains unclear and may not be due to electron-phonon coupling. Whether the pairing mechanism is even the same among the various unconventional superconductors remains controversial.

The cuprate and iron-based superconductors will be discussed in more detail in Chapters 7 and 8, respectively. For more detailed information on unconventional superconductivity, refer to Refs. [46–50].

### 2.2 High Pressure

Pressure, like temperature, is a thermodynamic variable. Application of pressure to a material can cause significant changes to its electronic, magnetic, and structural properties. By studying the behavior of materials over a wide range of pressures, we gain invaluable insight
into the physics of this condensed state.

Our own everyday experiences with pressure center on a very narrow region about atmospheric pressure\(^2\). For example, a person diving underwater to a depth of \(\sim 10\) m would experience a pressure of \(\sim 2\) bar, while the thin atmosphere at the top of Mt. Everest is \(\sim 0.33\) bar. Humans are able to withstand about 10 bars, while some lifeforms have adapted to survive at pressures up to at least 1086 bar at the bottom of the Mariana trench. Pressures in nature, however, extend over a much wider range – from \(\sim 10^{-27}\) bars in intergalactic space to \(\sim 1.6 \times 10^{30}\) bars at the center of a neutron star, with pressures in a black hole even higher. Within this pressure regime we find the pressure at the center of the earth (\(\sim 3.6 \times 10^6\) bars) and at the center of the sun (\(\sim 2.5 \times 10^{11}\) bars).

Over time scientists have developed various techniques to study matter over this wide range of pressures. Early research was limited to low pressures due to the inability of apparatuses at that time to withstand high pressure. One of the first high pressure questions to be investigated was whether water was compressible, a matter finally affirmed by John Canton in 1762 [51]. In the 1880s French physicist Émile Amagat designed a hydraulic manometer that could regularly produce pressures exceeding 3 kbar [52]. It was not until 1905, however, when a doctoral student at Harvard University named Percy Williams Bridgman began developing better high pressure techniques, that interest in high pressure research started to really increase. A series of 1909 papers [53–55] marked Bridgman’s entry into the world of high pressure physics. His design for a system of opposed anvils, which became known as the Bridgman anvil, allowed him to regularly reach pressures of up to 100 kbar (10 GPa), thereby extending the upper limit for static pressures. His pioneering

\(^2\)1 atm \(\sim 1\) bar. In this thesis pressure units of kbar, GPa, and Mbar will typically be used. \(10\) kbar = 1 GPa and \(100\) GPa = 1 Mbar.
work in the field of high pressure research earned him the 1946 Nobel Prize in Physics. In the late 1950s scientists working at the National Bureau of Standards constructed the first diamond anvil cell (DAC) [56]. Designed by Charles E. Weir, Alvin Van Valkenburg, Ellis R. Lippincott, and E. N. Bunting, this cell was basically an extension of the Bridgman anvil using diamonds rather than tungsten carbide (WC) as anvils. Single crystal diamond is the hardest known material, so its use as an anvil allows static pressure in the multi-megabar regime to be reached. The wide optical transparency range of diamonds over the electromagnetic spectrum from infrared to gamma rays makes DACs suitable for spectroscopic and crystallographic studies. The subsequent discovery in the 1970s of the ruby fluorescence gauge as an *in situ* pressure manometer [57–59] revolutionized high pressure research, allowing widespread use of the DAC as an experimental tool in laboratories. More recently the first order Raman vibron line of diamond has been calibrated as an alternative pressure gauge valid to $\sim 4$ Mbar [60,61]. This pressure gauge is particularly useful for measurements above 1 Mbar. Today, DACs can be used to reach static pressures exceeding 3 Mbar [61–65].

Design of an individual diamond anvil cell varies significantly depending on the type of measurement that is being performed. Suitability of a cell for a particular measurement is based on considerations such as the desired temperature range of the experiment, optical access to the sample space, dimensions of the cell, sample size, pressure limit, and magnetic properties of the cell. In each case, however, pressure is generated between the tips (culets) of two high-quality, opposing diamond anvils, as seen in Fig. 2.4. The culets are ground parallel to the base of the diamond (commonly referred to as the diamond table). Pressure may be applied to the diamonds either mechanically or through a gas-loaded membrane. A gasket (typically a metal foil) between the diamond culets helps to support the diamonds
Figure 2.4: Pressure in a diamond anvil cell is generated between the culets of two opposing diamonds. A hole drilled through the center of a pre-indent ed gasket forms the sample space containing the sample, pressure medium, and pressure calibrant such as a small ruby sphere.

Figure 2.5: Both flat (left) and bevelled (right) diamond anvils may be used for high pressure experiments. The design of the bevelled anvils, along with their smaller culet size, allows higher pressures to be attained.

and contains the sample, pressure medium, and pressure calibrant. The maximum pressure in the cell depends on the culet size, with smaller culets able to generate higher pressures. The diamonds are cut in such a way as to maximize pressure while minimizing stresses and strains. The culets, which resemble truncated cones, may be either flat or bevelled, as seen in Fig. 2.5. Bevelled anvils, which typically have smaller culets, are used to reach multi-megabar pressures. However, upon releasing pressure bevelled diamonds usually develop
shallow ring cracks that must be ground off before the diamonds can be reused. Flat anvils, on the other hand, can often be reused many times to reach high pressures, albeit normally less than those attainable with bevelled anvils.

High pressures are possible due to the hardness of the diamond anvils. Even so, stresses and strains within the diamond caused by the pressure distribution can cause catastrophic failure of diamond anvils. Under pressures of 50–100 GPa, the diamond deforms [66] and the culet becomes cupped. Specific details on the DAC and pressure measurement techniques may be found in Secs. 3.1.2 and 3.3, respectively.

2.2.1 Equation of State

When pressure is applied to a material, the atoms are brought closer together, thereby decreasing the volume and increasing the density. As the distances between the atomic cores decrease, less volume is available to the conduction electrons and there is increased orbital overlap. This induces significant changes in the electronic, magnetic, and structural properties of a material. Application of pressure may lead to electron transfer from the s- and p-orbitals to the d-orbital, as seen, for example, in the heavy alkali metals, the transition metals, and the actinides [67–69]. Increasing pressure generally broadens bands, leading to a decrease in the size of energy gaps. This favors the metallic state over the insulating state.

A material’s resistance to compression is given by its bulk modulus, $B_o = -V(\partial P/\partial V)$. As the pressure increases, the compressibility of a material, which is given by the inverse of its bulk modulus, usually decreases (lattice stiffening). One of the most useful ways to describe the response of a material to pressure is using its equation of state (EOS). Several equations of state are commonly used, among these the Murnaghan, the third-order Birch-Murnaghan,
and the Vinet equations of state [70–72]. Seen below, the Murnaghan equation of state is particularly useful in that it gives a simple relationship between volume and pressure in terms of only the bulk modulus and its pressure derivative, $B'_o$:

$$P(V) = \frac{B_o}{B'_o} \left[ \left( \frac{V_0}{V} \right)^{B'_o} - 1 \right].$$  \hspace{1cm} (2.15)

If the pressure is known, a material’s equation of state can be used to determine its volume. Conversely, if the volume of a material is known, for example using x-ray or neutron diffraction techniques, then the EOS may be used to determine pressure. In fact, before the advent of the ruby fluorescence technique, the most common way to determine high pressure was to first measure the lattice volume of a pressure calibrant such as NaCl that was placed inside the sample space and to then use its EOS to determine the pressure. This technique is still widely used today.

The pressure dependence of the volume also gives information about structural changes in a material. The presence of a structural transition is often indicated by a sudden decrease in the volume or by a more subtle change in the EOS.

### 2.2.2 Superconductivity under Pressure

Ever since superconductivity was first studied under pressure in 1925 by Sizoo and Onnes, who discovered a negative pressure dependence $dT_c/dP$ of Sn and In to 300 bar [73], pressure has played a vital role in the study of superconductivity. Application of pressure affects both the lattice and electronic properties of a material, both of which influence critical temperature. It is therefore not surprising that pressure can profoundly alter the superconducting behavior of a material. In many materials application of pressure may even induce supercon-
Figure 2.6: Periodic table of superconductivity. At ambient pressure 30 elements have been found to become superconducting (yellow). The application of pressure induces superconductivity in an additional 23 elements (light green with bold outline). $T_c(K)$ is the critical temperature for those elements which superconduct at ambient pressure. The highest observed critical temperature, $T^{\text{max}}_c(K)$, occurs at the pressure $P(\text{GPa})$. Figure adapted from Ref. [75].

ductivity. Consider the periodic table of the elements seen in Fig. 2.6. At ambient pressure 30 elements are superconducting. With the application of sufficiently high pressure, an additional 23 elements become superconducting. For a review of superconductivity among the elements, refer to Ref. [74].

To better understand the effect of pressure on superconductivity, let us consider the BCS equation for critical temperature, given by Eq. 2.3. Using the fact that $\omega_D \sim \sqrt{k/m}$, where $k$ is the lattice spring constant and $m$ is the mass of the cation, for weak coupling the critical
temperature may be rewritten as
\[ T_c \approx \sqrt{\frac{k}{m}} e^{-k/\eta}. \] (2.16)

Here \( \eta \equiv N(E_F) \langle I^2 \rangle \) is a purely electronic term known as the Hopfield parameter\(^3\). For a more detailed explanation of this derivation, refer to James Hamlin’s thesis [76]. Note that any effect of a change in \( T_c \) as a function of \( k \) is dominated by the exponential factor \( e^{-k} \), which overwhelms the prefactor of \( \sqrt{k} \). Thus, the pressure dependence of \( T_c \) may be determined by the relative pressure changes in \( k \) and \( \eta \), which relate to the lattice and electronic properties of the material, respectively. Under pressure \( k \) increases due to lattice stiffening, while \( \eta \) also usually increases.

In simple s- and p-electron metals such as Al, Zn, In, Sn, and Pb, \( k \) increases more rapidly than \( \eta \), leading to a rapid decrease in \( T_c \). For the transition metals, the pressure-dependence is not as clear cut, with \( T_c \) either increasing or decreasing depending on the relative change in \( \eta \). Pressure can induce electronic, structural, and magnetic transitions that favor the appearance of superconductivity in elements that do not superconduct at ambient pressure. In Fe and Ce, for example, superconductivity emerges after magnetism has been destroyed by pressure. Elements such as O, P, S, Se, Br, and I that are nonmetallic at ambient pressure can become superconducting under pressure following an insulator-metal transition.

For elemental superconductors, higher critical temperatures are generally found among the lighter elements. This is clearly observed by comparing the maximum \( T_c \) values of the superconducting elements among the alkali metals in column I of the periodic table – 1.3 K in Cs vs. 14 K in Li – and those of the alkaline-earths in column II – 5 K in Ba, 7 K in Sr, and 25 K in Ca. At ambient pressure the alkali metals are considered to be quintessential

\[^3\]N\((E_F)\) is the electron density of states at the Fermi level and \( \langle I^2 \rangle \) is the mean-square electron phonon matrix element.
models of simple metals and of nearly-free-electron behavior. Of these elements, only Li is superconducting at ambient pressure, albeit at an extremely low temperature. However, under pressure all the alkali metals exhibit complex behavior and are predicted to become superconducting. The pressure dependence of these materials will be explored in detail in Chapter 4 with a particular emphasis on Na and K. Looking at the alkaline-earths, only Mg and Ra have not been found to become superconducting. Due to its light mass, one might expect a high $T_c$ value in Mg. An investigation of pressure-induced superconductivity in Li(Mg) alloys is presented in Chapter 5.

Under sufficient pressure hydrogen is expected to become metallic and has even been predicted to become a room temperature superconductor [19]. Hydrogen-rich compounds have also been investigated in the hope that these materials may metallize at lower pressures and be high temperature superconductors. Chapter 6 focuses on the search for pressure-induced metallization in one of these hydrogen-rich compounds – benzene (C$_6$H$_6$).

In the high temperature cuprate and iron-based superconductors the pressure dependence can be quite complex. Often $T_c$ initially increases with pressure before passing through a maximum. In the iron-based superconductors, hydrostaticity of the pressure medium has been shown to significantly affect the pressure dependence. Chapter 7 includes more details on the pressure dependence in the cuprates, focusing in particular on HgBa$_2$CuO$_{4+\delta}$, commonly referred to as Hg-1201. Chapter 8 will subsequently give more details on superconductivity and its pressure dependence in the iron-based materials, focusing on LnFePO ($Ln=$La, Pr, Nd).

The effects of pressure on the superconducting critical temperature can give vital information about the superconducting state. In addition to inducing superconductivity in
some materials, information gained in pressure studies can help researchers to improve the properties of known superconductors and aid in the discovery of further superconductors. High pressure studies also allow theoreticians to test models and provide a path to finding superconductors with even higher $T_c$ values. For an extensive review of superconductivity under pressure refer to Ref. [75, 77–79].
Chapter 3

Experimental Techniques

3.1 High Pressure Devices

Two main systems were used to generate high pressure over the course of this thesis work. The first, a He-gas system, can generate hydrostatic pressures up to 14 kbar. To obtain higher pressures, up to 2 Mbar, a diamond anvil cell (DAC) system was used.

3.1.1 Helium Gas System

The He-gas system is ideal for lower high-pressure measurements. Helium is used as a pressure medium to generate hydrostatic pressures up to 14 kbar in a high pressure cell (Unipress). To preserve the life of the system, however, pressures were kept below 9.5 kbar over the course of this thesis work.

Pressure is applied using ultra-high purity helium. A two stage compressor (Newport Scientific) is used to increase the pressure to $\sim 20,000$-$25,000$ psi$^1$ (1.4–1.7 kbar). An intensifier (Harwood Engineering) is then used to further increase the pressure to as high as 14 kbar.

\footnote{1 psi (pound per square inch); 1 bar = 14.7 psi}
Figure 3.1: The pressure of ultra-high purity He is increased first through a two stage compressor and then through an intensifier. High pressure valves, indicated on the figure by X-(number), allow the user to control the application of high pressure to the He-gas system. More details on the system can be found in the text.

The high pressure gas is transmitted to the sample space via a flexible copper beryllium capillary with an inner and outer diameter of 0.3 mm and 3.0 mm, respectively. A schematic of the pressure application system may be seen in Fig. 3.1. Pressure can be applied at any temperature above the melting curve of helium and is determined via a manganin gauge at room temperature. Note that below the melting curve of helium, it is important to use helium isochore\textsuperscript{2} tables [80] to determine sample pressure. The sample itself is contained within a CuBe high pressure cell, seen in Fig. 3.2. Two retaining screws are screwed into the cell body. The capillary runs through a plug on the upper side of the cell, while an electrical feed-through runs through a lower plug. The sample holder, generally either a coil

\textsuperscript{2}On a phase diagram, an isochore is a line of constant volume.
Figure 3.2: The Unipress high pressure cell for the He-gas system is made of CuBe. A sample holder is attached to an electrical feed-through for susceptibility and resistivity measurements. He-gas pressure is supplied through a CuBe capillary with an inner diameter of 0.3 mm. The cell is sealed using indium-coated CuBe gaskets. An alumina filler is placed in the cell to reduce the dead volume, thereby helping to reduce the temperature dependence of the pressure.

For ac-susceptibility measurements or a resistivity holder, is screwed onto the lower plug and attached to the electrical feed-through, which brings 12 wires into the high pressure cell. During the course of this research, ac-susceptibility measurements were performed in the He-gas system. A detailed description of the coil system may be found in Sec. 3.4. Upon cooling, the pressure gas contracts by the ideal gas law. To minimize the pressure reduction upon cooling, it is necessary to increase the volume of gas at room temperature and to decrease the low temperature gas volume. To do so, an additional volume of gas (3.6 cm$^3$) is kept at room temperature, while an alumina filler is placed in the cell to decrease the low temperature volume of gas. Gaskets located between the cell body and the plugs ensure that the cell is sealed under high pressure. These gaskets, purchased from Unipress, are coated with indium. As indium is quite soft, it helps the cell to seal at lower pressures, below that at which the CuBe deforms. It has been found, however, that recoating the gaskets with more indium significantly helps to seal the cell at high pressure. Without the extra indium, the pressure often leaks, sometimes leaking more as the temperature decreases. For the
procedure on how to coat the gaskets with indium, see the He-gas manual and A.-K. Klehe’s thesis [81,82].

Sample temperature is measured using four thermometers: a germanium resistor and a platinum resistor at both the top and bottom of the cell. The germanium resistor, a semiconductor, is used for temperatures below \(~40\) K, while the platinum resistor is used at higher temperatures. A small amount of Apiezon N grease is used to hold the thermometers in place and to help ensure good thermal contact. Temperatures may be controlled in part by 50 \(\Omega\) heaters wrapped around the top and bottom of the cell and by a 60 \(\Omega\) heater wrapped around the capillary. Additional temperature control is attained using heaters found in the cryostats, as described in Sec. 3.2. Temperature gradients across the cell are kept as small as possible during measurements, typically below \(~50\) mK.

When cooling (or warming) through the melting curve, it is vital that the temperature gradient be such that the coldest temperature is at the bottom of the cell, and the warmest temperature is at the capillary. This ensures that the helium in the system freezes from the bottom up (or melts from the top down), thereby preventing a possible situation in which expanding helium has nowhere to expand because of frozen helium above it in the line. Typical gradients upon passing through the melting curve are about 1-2 K between the top and bottom of the high pressure cell, while the capillary is kept at a temperature about 20 K above that of the cell. Cooling (and warming) slowly through the melting curve also helps to minimize shocks to the sample and to the ac-susceptibility coil or to resistivity contacts on the sample.
3.1.2 Diamond Anvil Cell System

To generate pressures higher than those attainable in the He-gas system, a diamond anvil cell made of a hardened CuBe alloy was used. A cross-section of this cell, designed by J. S. Schilling, may be seen in Fig. 3.3 [83]. Diamonds are glued onto backing pieces with epoxy (stycast 2850 FT Black and catalyst 24 LV). A piece of Zr foil (25 µm) is typically placed between the diamond and the backing piece to help minimize local stresses on the diamond table under pressure. After the diamonds are glued in place, they are aligned in the lateral direction by using three set screws to move the backing plate onto which the body diamond is glued. Angular alignment is achieved by adjusting the tilt of the hemisphere at the top of the piston until both diamonds are parallel, as indicated by the absence of interference.
fringes when the diamonds are slowly brought together. Ensuring proper alignment of the diamond anvils is vital in performing a successful experiment. The piston should fit snugly within the bore of the cell, with a tolerance of no more than 5-10 µm. Over time, wear on the piston will make the fit looser. This can be corrected by copper-plating the piston and then polishing it with diamond powder ∼ ¼ µm in size until the fit is once more snug. Details on the alignment and copper-plating procedures for the cell used over the course of this dissertation may be found in the DAC manual [84].

Success of an experiment depends in a large part on the quality of the diamonds and on their precise alignment. Diamonds used over the course of this dissertation research were ¼ carat with either 8 or 16 facets. Both flat and bevelled diamonds were used. Culet sizes for flat anvils were 0.3, 0.5, and 0.9 mm, while bevelled culets with diameters of 0.18 mm and 0.10 mm were used (bevelled at a 7° angle from 0.35 mm and 7.5° from 0.30 mm, respectively).

Diamonds were purchased from both d’Anvils and Almax. To withstand the highest pressures, diamonds should be free of inclusions and defects. Localized stresses and strains in the diamond resulting from defects or from the diffusion of the pressure medium into the defects may cause diamond failure. Using two cross-polarizers under a microscope allows defects to be observed. The diamond, illuminated from below, is placed between the two polarizers. When these polarizers are 90° out of phase with each other, any observable features are indicative of defects. Fig. 3.4 shows an image of several diamonds through the cross-polarizer.

Typically metal foils are used as gasket materials, as they can provide suitable hardness and ductility. A detailed explanation of how to choose the correct gasket material will be
Figure 3.4: Viewing diamonds through cross-polarizers allows defects to be observed. Features visible in the first two diamonds indicate defects, while the image of the third diamond is clear, indicating that it is free of defects.

given later. During this research, gaskets with a 2.7 mm diameter were typically punched from a foil with an initial thickness 250–300 µm. In one case, the initial gasket thickness was 400 µm. Before performing an experiment, the gasket is pre-indented to the required thickness. This is done gradually to prevent cold-welding of the diamond to the gasket. A hole is then drilled through the center using an EDM (electrical discharge machine). The ideal preindentation thickness and hole diameter are related to the behavior of the gasket under application of pressure in an anvil cell [66, 85]. Typically, at the highest pressure, the desired hole diameter is $\frac{1}{3}$ of the culet diameter, while the gasket thickness is $\frac{1}{3}$ of the hole diameter, i.e., $\frac{1}{9}$ of the culet diameter. Under pressure the gasket becomes thinner and the hole size decreases, especially when helium is used as a pressure medium, since it is so compressible. Thus, the hole size is usually initially drilled to about $\frac{1}{2}$ of the culet, while the gasket is pre-indented to about twice the thickness desired at the highest pressure.

Measurements carried out during this research were performed either with a hydrostatic He pressure medium or with no pressure medium at all (i.e., the anvils pressed directly on the sample). When using He as a pressure medium, it is important that it be sealed inside the gasket when pressure is applied. Even microcracks and scratches on the gasket can
prevent the gasket from sealing. To minimize this possibility, the gaskets are coated with a thin layer of gold using a sputtering unit. In addition, use of a He pressure medium presents challenges in that the small He atoms can diffuse into the diamond, causing diamond failure. This effect becomes much more pronounced at higher temperatures, so the cell is kept below \( \sim 150 \text{ K} \) after pressure has been applied.

Pressure is applied to the sample space by increasing the pressure in a membrane. A needle valve allows fine control of the pressure to the membrane, which is attached via a thin capillary to ultra-high purity He gas. This membrane, made of stainless steel, is a diaphragm. As pressure in the diaphragm increases, it puffs up slightly thereby increasing the load on the diamonds, and the sample pressure. Membrane pressure may be measured either with an analog gauge or with a digital gauge. For pressure to be measured digitally, \( \sim 20 \text{ V} \) should be applied to a digital transducer; the output voltage, in volts, is then given by [86]

\[
P(\text{bar}) = 1 + \frac{(300 - 14.5) \times (V - 1.002)}{14.5 \times (11 - 1.002)},
\]

The membrane system allows pressure to be applied \textit{in situ} in the cryostat at any temperature above the melting curve of helium. This is a significant advantage over mechanically loaded DAC systems, which require that the cell either be removed from the at room temperature before pressure can be changed or that a low-temperature gear box be used. A gas reservoir kept at room temperature is connected to the capillary and membrane system to reduce the pressure decrease in the membrane upon cooling. Changes in the membrane pressure should be performed slowly to reduce stresses and strains on the diamonds and to allow the anvils and the gasket time to relax after pressure application. Typically, membrane pressure is increased no more than 1–2 bars every ten minutes. At higher pressures (relative to the
maximum pressure typically withstood by the diamond size), pressure should be increased more slowly to minimize the chance of catastrophic diamond failure. When loading a He pressure medium for hydrostatic measurements, the cell is cooled at ambient pressure below the lambda point of LHe ($\sim 2.2$ K). First, LHe is loaded into the cryostat so that the cell is completely submerged. A small gap between the gasket and diamonds allows superfluid liquid He to flow into the sample space. The membrane pressure is then increased. The size of the hole in the gasket typically decreases initially. After sufficient pressure has been applied, the gasket seals – the size of the sample hole should stabilize, and pressure in the sample space should begin increasing. Upon increasing the temperature, the helium remains trapped in the sample space, providing a hydrostatic pressure medium. The relationship between sample and membrane pressure varies depending on the size of the diamond culet and the gasket material being used. A typical plot of membrane versus sample pressure may be seen in Fig. 3.5.

**Backing Pieces**

The backing pieces onto which the diamonds are mounted are vital in ensuring adequate support for the diamonds. Backing materials need to be hard enough to withstand the high pressure generated at the diamond table yet ductile enough that cracks do not occur. The backing pieces are polished using diamond grinding paper (grain size $\sim 10 \, \mu\text{m}$) to remove imperfections in the surface, as these add unnecessary stress and strain to the diamond. Backing pieces should also be nonmagnetic so that their temperature dependent susceptibility signal does not obscure the small superconducting signal of the sample when ac-susceptibility measurements are being performed. Two materials have been utilized for backing pieces – tungsten carbide (WC), and a Ni:Cr(39-41% at.):Al(3-4% at.) alloy, also known as ‘Russian
Figure 3.5: Sample vs. membrane pressure is shown for various culet sizes. Unless otherwise noted, a Re gasket is used. Some of the data are taken from [76].
Alloy’. Hereafter, this material will be referred to simply as NiCrAl. Previously, the backing pieces contained a 1 mm wide bore through the center of the material, allowing optical access through the diamonds to the sample space. In order to increase the amount of transmitted light and to improve optical measurements, a large aperture was added to the backing material. The current design of the backing pieces therefore adds a 15° half-angle cone to the 1 mm bore. A schematic may be seen in W. Bi’s thesis [86]. WC backing pieces (ROCTEC 500) with this design were ordered from Kennametal. These backing pieces have proven to be quite brittle, so extreme caution needs to be taken when removing them from the cell in order to polish them. In addition to the WC backing pieces, three NiCrAl backing pieces with the new design were made at Washington University. The backing pieces were hardened after Uwatoko et al. [87]. The material was first annealed at 1200°C for one hour before quenching in water. Optimal mechanical properties were then attained by hardening the material at 700°C for 2 hours, resulting in a hardness of 57 HRC. To make the backing pieces, a disk ~ 5 mm thick was cut from a rod with a 20 mm diameter using a low speed diamond wheel saw (South Bay Technology, Model 650). When using a diamond wheel, the blade often got stuck in the material while cutting it, and occasionally broke. Therefore, instead of using a diamond wheel, we used a cBN wheel (South Bay Technology, NWL4121), which is better for cutting iron, nickel, and lead based alloys. This wheel proved much more effective at cutting the NiCrAl alloy, although care still had to be taken to restart the wheel whenever it started to get stuck. Next, this disk was cut into three wedges of approximately the same size. The outer dimensions of the backing pieces, including the 1° angle, must be very precise so that the backing pieces fit snugly in the holders. Upon hardening, the material dimensions change slightly by ~ 1–2% so it is not possible to machine the entire

\(^4\text{HRC is the Rockwell hardness “C” scale}\)
piece while the material is soft. On the other hand, it takes much longer to machine the harder material, and machining the center bore would require a special carbide countersink. As the dimensions of the cone-shaped bore through the center of the backing piece are not as critical, it was decided to machine the backing pieces in two stages. First, the annealed sample was given to the machine shop. They machined the backing pieces, leaving the outer dimensions slightly larger than the desired final dimensions. A cone-shaped bore with a $15^\circ$ half angle was drilled through the center of the backing piece. The material was then hardened in the box furnace for 2 hours at $700^\circ$C. Finally, the hardened pieces were returned to the machine shop to precisely cut the backing pieces to the correct dimensions.

**Gasket Materials**

In performing high pressure experiments in a DAC, the choice of a suitable gasket material is extremely important. The gasket supports the diamond culets and encloses the sample space, containing the sample, ruby spheres, and pressure medium. The gasket must be both hard and ductile. The ductility of a material refers to its ability to deform under stress. Hardness and ductility are generally inversely related. If the gasket material is not hard enough, it will not be able to withstand the high pressures generated during an experiment. On the other hand, if the ductility is too low, the gasket may become brittle, developing cracks under pressure, leading to diamond failure.

For resistivity measurements, the sample is electrically insulated from the gasket, so choice of a gasket material is limited to its hardness and ductility. For ac-susceptibility measurements, however, magnetic and superconducting properties of the material must also be taken into consideration. A small superconducting transition from the sample is difficult to detect if the temperature dependence of the gasket’s magnetic response is too steep. In ad-
dition, the gasket must be non-superconducting over the measured temperature range. The gasket is several orders of magnitude larger than the sample, so any superconducting transition in the sample which occurs below the temperature at which the gasket superconducts will be completely obscured.

Among the various gasket materials used over the course of this research, Re was used most frequently due to its high hardness (51 HRC) and low magnetic response. At ambient pressure, however, Re superconducts at \(\sim 1.7 \text{ K} \) [88]. Under strain, \(T_c\) increases to \(\sim 4 \text{ K}\), limiting measurements of superconductivity to temperatures above 4 K. For measurements as low as 1.3 K, a non-superconducting material, usually Cu:Be was utilized. Cu:Be has an initial hardness of 25 HRC. After annealing it at 315°C for 3 hours, the hardness increases to 41 HRC. As Cu:Be is softer than Re, it becomes much thinner under application of pressure. However, pressures as high as 142 GPa have still been achieved using bevelled 0.18 mm anvils. A W:(Re 25% at.) alloy, with a hardness of 57 HRC has also been used. Ac-susceptibility measurements are limited to temperatures above \(\sim 5.2 \text{ K}\), the temperature at which this alloy superconducts. Pressures as high as 174 GPa have previously been attained using this gasket material [76]. However, when used during the course of this research, pressures were increased at about 30–50 K. In both cases, diamond failure occurred when gasket cracks developed. Upon taking the cell apart, the W:Re gasket was in multiple pieces, and deep cracks could be seen on the remainder of the gasket. No cracks were visible after preindentation. It is believed that at low temperatures, the ductility of the W:Re gasket is relatively low, so cracks can develop. At higher temperatures, the higher ductility allows the gasket to deform under application of pressure rather than develop cracks. For several experiments, a non-magnetic, non-superconducting Ni:Mo(15.3% at.) alloy was used as a
gasket material. These gaskets were brought to our lab by V. Tissen during his visit. Finally, a NiCrAl alloy has been considered as a possible gasket material for use to temperatures as low as 1.3 K. To prepare the gaskets, an \( \sim 600 \mu m \) thick disk was cut from a 20 mm diameter NiCrAl rod. Using the diamond grinding paper, the disk was polished on each side to 520 \( \mu m \). Samples were annealed and hardened using the same procedure as for the NiCrAl backing pieces [87]. After each step, the disk was polished to remove oxidation on the surface. Gaskets were punched from the metal sheet, with a hardness of about 52.5 HRC. These gaskets have not yet been used in high pressure experiments, as initial preindentation using 0.5 mm anvils was not uniform for either hardened or annealed gaskets. Wrinkles and tears could be seen.

3.2 Cryostats

The ability to achieve low temperatures is vital in order to study superconductivity. Pursuant to this goal, three types of cryostats were used in the course of this research to generate temperatures as low as 1.35 K. Two of these cryostats utilize LHe. In order to reach pressure temperatures below that of LHe (4.2 K), the pressure cell is submerged directly in LHe. Pumping on the sample space removes the faster molecules at the surface of the liquid. The remaining molecules equilibrate thermodynamically, thereby lowering the temperature of the LHe. In this way the temperature decreases as the sample space pressure decreases. A larger, more powerful pump can be used to obtain lower pressures, and hence lower temperatures.
3.2.1 Balzers Closed-Cycle Refrigerator

A two-stage Balzers closed-cycle system (UCH 130) is typically used with the He-gas system to cool down the sample. One major advantage with this system is that no cryogenic fluids are used, thereby reducing the cost. The sample is placed in a cryostat (Cryo Industries of America, Inc.), and the sample space is filled with helium, which acts as an exchange gas. The cryogenic refrigerator acts much like a typical household refrigerator, except that helium is used as the refrigerant. High pressure ($\sim 300$ psi) helium gas is delivered from the compressor to a 2-stage cold head, where it expands, leading to cooling. With the pressure cell in place, temperatures as low as 6.5 K may be reached (low enough to calibrate the coil using the superconducting lead transition at 7.2 K), but well-reproducible measurements can really only be made above $\sim 10$ K, where the temperature can be controlled more accurately. The coldest part of the cryostat is located near the cold head, about 20 cm above the top of the pressure cell. Temperature is regulated through the use of heaters attached near the cold head. Initially, a single 50 $\Omega$ heater, referred to as the second stage heater, was used. It consists of two ribbon heaters that have been placed around the heat exchanger. With a maximum power of 25 Watts, the temperature could be controlled up to about 70 K while the compressor was still running. In 2008, an additional 150 $\Omega$ heater (referred to as the block heater) was attached to provide additional heating power. Simultaneous use of these heaters allows accurate temperature control up to about 100 K, with gradients across the cell as low as 20-50 mK.
3.2.2 Janis Supervaritemp Bath Cryostat

For measurements in the He-gas system that require temperatures below $\sim 10$ K, the Janis supervaritemp bath cryostat is used, seen in Fig. 3.6. Two reservoirs hold cryogenic liquids, thereby allowing the low temperature regime to be accessed. The reservoirs are separated from each other and from the sample space via vacuum chambers. The outer reservoir is filled with nitrogen, forcing the temperature to drop to $\sim 130$–160 K overnight. The next morning, liquid helium is transferred into the inner reservoir via a transfer tube. A small cold valve between the helium reservoir and the sample space can be opened to allow liquid helium or cold helium gas to flow into the sample space. This is achieved through a pressure gradient, either by maintaining an overpressure in the LHe reservoir or by pumping on the sample space. Adjusting the power of a diffuser/vaporizer heater allows the user to control the temperature (monitored using a Si-diode thermometer) of the cryogenic fluid entering the sample space, thereby allowing accurate control of heating and cooling rates of the sample in the high pressure cell. The bottom of the cell is located about 4” above the diffuser. Temperatures below 4.2 K, as low as $\sim 1.5$ K, can be achieved by loading LHe into the sample space, closing the cold valve, and then slowly pumping on the sample space through a needle valve. From 4–20 K, accurate warming measurements with a small temperature gradient are possible by keeping the temperature at the diffuser $\sim 0.5$ K above the cell temperature. The liquid helium level in the reservoir is measured using a He level meter. The reservoir holds about 3.5 liters of LHe, which is usually enough He to conduct experiments for one day. More details on the operation of the Janis cryostat may be found in the He-gas manual [81].
Figure 3.6: Schematic of the Janis helium bath cryostat (not to scale). Colors are added to make it easier to distinguish distinct parts of the cryostat.
Figure 3.7: An Oxford continuous flow cryostat is used to obtain temperatures as low as 1.35 K in the DAC system. Also shown are the pump and LHe dewar. The cell is optically accessible through windows at the bottom of the cryostat. Figure from Ref. [76].

3.2.3 Oxford Continuous Flow Cryostat

An Oxford continuous flow cryostat, seen in Fig. 3.7, is used to obtain temperatures as low as 1.35 K in the diamond anvil cell system. Three windows at the base of the cryostat (one sapphire and two quartz) permit optical access to the cell for reflected light and for measurements of pressure using ruby fluorescence. A fiber optic cable guided to the diamonds enables transmitted light to pass through the sample space. Temperature is monitored using a thermometer located near the sample. Previously, a platinum (> 40 K) and germanium...
(<40 K) thermometer were used. The wiring near the germanium thermometer, however, was very delicate, and connections often had to be repaired. To alleviate this problem, the thermometers were replaced with a single Cernox resistor for measuring temperatures over the entire temperature range. Each of these thermometers was used over the course of this research.

To cool the cell, a LHe dewar is attached to the cryostat via a transfer tube. A cold valve (generally open 4 turns during cooling) controls the flow of helium, while a membrane pump is used to create a pressure gradient between the dewar and the sample space. As the cryogenic fluid is transferred to the cryostat, the cell cools to \( \sim 4 \) K, typically over two hours. Above liquid helium temperatures, accurate measurements can be obtained in two ways. First, the sample may be allowed to warm naturally after shutting off the pump and closing the cold valve to the transfer tube – this is typically referred to as drift warming. Alternatively, slow warming (cooling) may be achieved by slowly increasing (decreasing) a heating current to counter the cooling effect from the transfer of LHe to the dewar. This technique is optimal for temperatures \( \sim 3.5–10 \) K. In ac-susceptibility measurements, this is especially advantageous near 4.2 K, as LHe effects are eliminated. These effects are typically visible in drift warming measurements, and may obscure or be mistaken for small superconducting transitions. Temperature control is achieved using a current ramping control unit [84]. This device allows the current to be changed linearly at one of several rates. While the membrane pump is running (i.e., the system is cooling), the cold valve on the transfer tube should be closed most of the way to reduce the flow of helium. A heating current is turned on, and the temperature is allowed to stabilize at about 10–15 K. Typically, this corresponds to the cold valve being open between \( 1/4 \) and \( 3/4 \) of a turn. After the temperature stabilizes,
the current ramping device is set to slowly decrease the pressure. As the current decreases, so too does the temperature. After reaching the lowest temperature, usually about 3.5 K, slow warming measurements can be obtained by simply reversing the setting on the current control unit so that current increases linearly. For measurements performed over the course of this dissertation, the maximum heater current was set to 0.27 A, while the rate was set to position # 8. With this setting, the current increases (or decreases) by 5.4 mA/minute.

For measurements below 4.2 K, LHe is filled into the cryostat so that the cell is completely submerged. After cooling to liquid helium temperatures as normal, the membrane pump is allowed to continue running for about 25–30 minutes, thereby transferring LHe into the cryostat until the liquid level is ~ 8-10 inches above the top of the cell, as measured using a helium level meter. The pump is then shut off and the transfer tube is disconnected from the cryostat. Temperature can be controlled for cooling or warming measurements by slowly opening or closing a two-stage valve connecting a Balzers fore pump to the sample space. The Balzers pump allows temperatures to reach 1.6 K, while the addition of a more powerful roots pump enables temperatures as low as 1.35 K to be obtained.

3.3 Pressure Determination

Use of diamond anvil cells necessitated the development of a reliable and practical method for in situ pressure measurements. In early work with the diamond anvil cell, pressures were often estimated from the applied load. This is, however, particularly unreliable when a gasket is used, as an unknown load is absorbed by the gasket. X-ray diffraction techniques employing the pressure dependence of lattice constants and equation of state (EOS) of various materials, particularly in NaCl, were also used, but the time-consuming nature of
x-ray measurements and the impracticality of its use in many experiments and laboratories prevented its widespread use. Development of an optical pressure measurement technique using a ruby gauge allowed for reliable and routine pressure determination, thereby spurring research using diamond anvil cells. More recently, development of a diamond anvil Raman vibron gauge has enabled pressure determination in the multimegabar pressure regime.

During the course of this research, both the ruby fluorescence and diamond Raman gauges were used to determine pressure. These techniques are described in the following sections. A description of the optical system used during the course of this dissertation research may be found in App. B. Whenever possible, pressure was measured in the temperature range at which superconductivity or some other property was observed. This is due to the fact that the pressure in a diamond anvil cell generally can vary with temperature.

3.3.1 Ruby Fluorescence

The ruby gauge is by far one of the most widely used methods for determining pressure in diamond anvil cells. Use of the ruby (Cr$^{3+}$ doped $\alpha$-Al$_2$O$_3$) as a pressure gauge was first proposed in the 1970s [57–59]. The Cr$^{3+}$ ions substitute for the Al$^{3+}$ ions upon doping, resulting in an expansion of the host lattice due to the slightly larger size of the Cr$^{3+}$ ions. The ruby fluorescence technique utilizes the excited states of the Cr$^{3+}$ ion in ruby, as seen in Fig. 3.8. Optical pumping using a blue or green laser excites electrons into the broad $U$ (centered at about 18,200 cm$^{-1}$) or $Y$ (centered at about 24,800 cm$^{-1}$) absorption bands. The metastable $^2E$ states are then populated by non-radiative decay (phonon emission). Slower, radiative decay from the $^2E$ states subsequently leads to the ruby fluorescence in the form of $R_1$ and $R_2$ lines. At room temperature and ambient pressure, these lines occur
Figure 3.8: Excited states of Cr$^{3+}$ in ruby. Optical pumping to the $U$ and $Y$ absorption bands populates the metastable $^2T_1$ and $^2E$ by non-radiative decay. The $R_1$ and $R_2$ fluorescence lines are then produced via radiative decay from the $^2E$ state. Figure taken from [89].

at 694.25 and 692.86 nm, respectively. These sharp, high intensity fluorescence peaks shift monotonically with pressure. They are therefore ideal for measuring pressure as small ruby chips on the order of 1% of the sample space may be used, thereby minimizing any effects on the sample itself.

The intensities of the $R_1$ and $R_2$ peaks at room temperature are comparable, as the population of the $^2E$ states is governed by a Boltzmann distribution, $\exp(-\Delta E/k_B T)$. These states are separated by approximately $29 \text{ cm}^{-1} = 3.6 \text{ meV}$ (room temperature $\approx 25 \text{ meV}$), with the state corresponding to the $R_2$ line having a higher energy than the state corresponding to the $R_1$ line. Thus, as the temperature decreases, the lower energy state is favored,
leading to a decrease in the intensity of the $R_2$ line relative to the $R_1$ line. The $R_1$ line is therefore generally used for pressure measurements. With decreasing temperature, the line-widths of the $R_1$ and $R_2$ lines decrease, and the lines shift to slightly higher energy. For the $R_1$ line below 300 K, the frequency shift with temperature, $\nu_0(T)$ is described by

$$
\nu_0(t) = 14422.0 - 36.612t^{3/2} + 169.77t^3 - 264.54t^{5/2} + 112.14t^3,
$$

(3.2)

where $t = T/300$ K is the reduced temperature, and $\nu_0(T)$ is given in cm$^{-1}$ [90]. This temperature dependence can be seen in Fig. 3.9.

![Figure 3.9: Temperature dependence of the $R_1$ ruby fluorescence line in ruby [90]. Frequency in cm$^{-1}$ from the equation has been converted to $\lambda$(nm) for purposes of the plot. As the temperature decreases, the $R_1$ line shifts to higher energy (lower wavelength). Below $\sim$ 70 K, the fluorescence wavelength remains relatively constant.]

With increasing pressure the $R_1$ and $R_2$ ruby fluorescence lines are red-shifted as the
$^2E$ state shifts to lower energy. It is this shift which can be used to determine pressure. The pressure dependence of the ruby fluorescence is relatively linear to $\sim 20$ GPa [59]. At higher pressures, however, the pressure dependence becomes significantly non-linear [91,92]. The 1986 calibration to $\sim 80$ GPa by Mao et al., known as the quasi-hydrostatic scale, served as the most widely used scale for many years. Since then, the calibration has been extended to higher pressures. A 2008 review article by Syassen et al. provides an excellent comparison of various calibrations and indicates that recent calibrations agree within about 2% at 150 GPa [89]. Throughout the course of this dissertation, a calibration to 150 GPa by Chijioke et al. [93] that takes into account various calibrations in quasi-hydrostatic media was used. Pressure is given in terms of the wavelength, $\lambda$, of the $R_1$ line by the expression

$$P(\text{GPa}) = \frac{1876}{10.71} \left[ \left( \frac{\lambda}{\lambda_0} \right)^{10.71} - 1 \right],$$

where $\lambda_0$ is the wavelength of the ambient pressure $R_1$ line.

Due to the slight temperature variation in the $R_1$ line, it is important to always measure the pressure in terms of the shift from the ambient pressure line at that temperature. Otherwise, the temperature shift may be mistaken for a variation in the pressure. The position of the ambient pressure $R_1$ line may be determined by measurement of a reference ruby kept at the same temperature, yet positioned outside the pressure cell.

Calibrations of the $R_1$ ruby fluorescence line have generally been carried out at room temperature. Generally, the temperature and pressure dependences have been considered to be independent, although only a few experiments have been carried out to verify this. The effect of temperature on the $R_1$ and $R_2$ lines under both low temperature and high pressure was first studied by Adams et al. in 1977, who showed that the pressure dependence of
the shift of the $R_1$ line under pressure is virtually unchanged at 166.8 K compared to room temperature [94]. A study by Noack and Holzapfel confirmed this independence only to approximately 1 GPa [95]. A calibration of the $R_1$ ruby fluorescence line was carried out at 10 K and 77 K up to 22 GPa by Nakano et al. using the equation of state of NaCl [96]. The group showed that the pressure coefficient of the $R_1$ ruby line is the same at low temperature as at room temperature. A recent study, however, points out that the calibration by Nakano et al. used a temperature independent bulk modulus for the EOS of NaCl, which is likely incorrect [97]. Feng et al. calibrated the ruby pressure gauge at 4.5 K against the lattice constant and known EOS of silver to 15.8 GPa. Over this pressure range, a linear relationship between the $R_1$ ruby wavelength and pressure was observed, given by

$$P = A_0 \ln \left( \frac{\lambda}{\lambda_0} \right),$$  \hspace{1cm} (3.4)

where $A_0 = 1762 \pm 13$ GPa [97]. This pressure coefficient is almost 6\% lower than the linear pressure coefficient $A_0 = 1868 \pm 30$ GPa at room temperature summarized in the review article by K. Syassen [89]. Near 16 GPa, the low temperature calibration yields a pressure about 10\% lower than the pressure based on the non-linear calibration by Chijioke et al. (see Eq. 3.3) used in this dissertation. Many of our ruby pressure measurements are performed at low temperatures near superconducting transitions. However, as most of our measurements extend to pressures above 16 GPa, we still use the calibration by Chijioke et al., as the low-temperature calibration has only been performed at low pressures. At higher pressure, one would expect that the calibration becomes non-linear. If the low-temperature calibration is later extended to higher pressure, it would be possible to correct the low-temperature pressures measured in the course of this dissertation.
Ruby fluorescence is extremely sensitive to pressure conditions. Under non-hydrostatic conditions, the ruby fluorescence peaks broaden, and the separation between $R_1$ and $R_2$ increases. For more information on this phenomenon, please refer to Refs. [76, 89, 98, 99].

At pressures above 1 Mbar, measurements of the ruby fluorescence line become increasingly difficult. First, the intensity of the ruby luminescence decreases with pressure as the $U$ and $Y$ absorption bands shift to higher energies. Consequently, optical pumping into these bands using a blue or green laser becomes less efficient. At $\sim 50$ GPa, the $U$ band has a higher energy than the Ar-ion laser line ($\lambda = 514$ nm). A higher energy laser line, such as that from a He-Cd laser (441.6 nm) can be used to measure higher pressures.

Finally, smaller culets are needed to attain higher pressures. The smaller sample space size limits the amount of ruby that can be put into a cell, thereby reducing the intensity of the ruby fluorescence.

### 3.3.2 Raman Diamond Vibron

Due to difficulties in using the ruby fluorescence technique for measuring pressures above 1 Mbar, we utilized the diamond anvil Raman gauge to determine pressures up to 2 Mbar. This technique depends upon Raman scattering, named after Sir C. V. Raman who, along with K. S. Krishnan, discovered the phenomenon in 1928 [100]. When light of frequency $\nu$ is incident upon a material, most of the light is scattered back elastically with the same energy in the form of Rayleigh scattering. A small fraction of the reflected spectrum ($\sim 10^{-7}$), however, scatters inelastically due to Raman scattering. This light has a frequency $\nu + \nu_0$ (anti-Stokes) or $\nu - \nu_0$ (Stokes), where $\nu_0$ is a vibrational frequency of the molecule upon which the light is incident. Stokes scattering occurs when energy is absorbed by the material,
whereas anti-Stokes scattering occurs when the material loses energy, as seen in Fig. 3.10. Stokes and anti-Stokes scattering are symmetric about the incident wavelength, $\nu$, although

Figure 3.10: Most light incident on a material scatters back elastically in the form of Rayleigh scattering. A small fraction, however, scatters back with a slightly lower (Stokes) or higher (anti-Stokes) energy. This form of inelastic scattering is known as Raman scattering. The dashed lines represent virtual states.

the relative intensity varies with temperature as the populations of the energy levels change.

If the intensities of the Stokes and anti-Stokes lines are given as $I_S$ and $I_A$, respectively, the ratio $I_S/I_A$ will increase with decreasing temperature. For this reason, one can use the relative intensity as a measure of the temperature. The Raman spectrum gives information about vibrational and rotational modes in a material. It can therefore be used to probe the properties of materials to investigate phenomena such as phase transitions and structural transitions.
The first-order Raman spectrum of diamond was first observed by Ramaswamy [101] who noted a single peak at $\nu_0 = 1333.1 \text{ cm}^{-1}$, where $\nu_0$ is the frequency shift due to Raman scattering. This peak is commonly referred to as the diamond vibron. The frequency of this peak increases monotonically with pressure, making it possible to use it as a pressure manometer. The availability of this pressure gauge spurred diamond anvil cell research in the multi-megabar regime, where ruby fluorescence is difficult to measure. Pressures could rather easily be determined in most laboratories, where previously x-ray diffraction measurements at synchrotrons were typically used to determine pressure against the EOS of a known material.

Pressure Dependence

Diamond anvils are usually cut along the [100] crystallographic direction\(^4\) so the discussion in this section will refer to this orientation. In 1985 Hanfland and Syassen [102] focused an Ar-ion laser onto the culet of a diamond anvil cell and studied the Raman spectrum of diamond. By simultaneously measuring pressure in the gasket using ruby fluorescence, they were able to show that the high-frequency edge of the Raman spectrum increased linearly with sample pressure to $\sim 30 \text{ GPa}$. They therefore proposed the use of the high-frequency edge as a possible manometer. Using the diamond vibron to determine the sample pressure provides a significant advantage in that it requires no separate pressure marker that takes up space in the gasket hole and could interfere with measurements of properties of the sample itself.

The use of the Raman spectrum to determine the sample pressure is based on the idea that the normal component of diamond pressure at the culet-sample interface is the same as

\(^4\)To avoid confusion with references, the notation for crystallographic direction will always be in bold face.
the normal component of stress on the sample. Under hydrostatic conditions, therefore, the normal pressure would be the same as the sample pressure. For non-hydrostatic conditions, the normal pressure on the diamond will be almost the same as the sample pressure. The pressure dependence is independent of the shape of the anvils (flat or bevelled) [103] and almost independent of loading conditions [104], making it ideal for determination of multi-megabar pressures.

A calibration to 310 GPa by Akahama et al. [60] gives the pressure in terms of the relative Raman frequency change, $\Delta \nu/\nu_0$ by

$$P(\text{GPa}) \approx K_0 \frac{\Delta \nu}{\nu_0} \left[ 1 + \frac{1}{2} (K'_0 - 1) \frac{\Delta \nu}{\nu_0} \right],$$  \hspace{1cm} (3.5)$$

where $\nu_0 = 1334 \text{ cm}^{-1}$, $K_0 = 547(11) \text{ GPa}$, and $K'_0 = 3.75(20)$. Upon extending the pressure calibration to 410 GPa, however, it was shown that the high frequency Raman edge deviates to higher pressure from Eq. 3.5. Thus a new calibration, given by

$$P(\text{GPa}) = 31413 = 4.157_{20} \omega + 1.429_{12} \times 10^{-3} \omega^2,$$  \hspace{1cm} (3.6)$$

was proposed that is valid for pressures 200–410 GPa [61]. Here, $\omega$ is the frequency shift of the Raman line and the subscripts represent uncertainties to the fit. As measurements performed in the course of this dissertation extended to about 200 GPa, the calibration given in Eq. 3.5 was used.
Raman Measurements in the Laboratory

Raman measurements in the lab were carried out at room temperature using an Ar-ion laser \((\lambda=514 \text{ nm}, \nu=19460 \text{ cm}^{-1})\). A QE65000 spectrometer from Ocean Optics (# H11 grating with 1800 mm\(^{-1}\) groove density) was used to collect Raman spectra. The spectrometer measures spectra between 515 nm and 615 nm with a resolution of \(\sim 0.1 \text{ nm}\). For the Ar-ion laser, this corresponds to a Raman shift from 40 cm\(^{-1}\) to 3190 cm\(^{-1}\). The frequency resolution therefore ranges from \(\sim 4 \text{ cm}^{-1}\) at the low frequency end of the spectrum down to \(\sim 2 \text{ cm}^{-1}\) at the high frequency end of the spectrum. More information on the optical setup used can be found in App. B.

Effect of Diamond Orientation on Raman Spectrum

The diamond vibron, which corresponds to a zone-center optical phonon mode, is triply degenerate [102]. With the application of hydrostatic pressure to the diamond, the Raman mode remains triply degenerate as the Raman frequency, \(\Delta \omega_H\), increases with pressure. Pressure within the diamonds in a diamond anvil cell is not isotropic. Rather, uniaxial pressure perpendicular to the diamond culet is accompanied by stresses and strains in the radial direction. Uniaxial stress parallel to the [100] or [111] direction results in splitting of the vibron into a singlet and doublet mode whereas stress in the [110] direction causes the degenerate mode to split into three singlets [102]. The Raman spectrum therefore gives information about the distribution of stress within the anvil. The singlet and doublet modes have different pressure dependences, which also depend upon the orientation of the diamond. It is therefore important to understand how these factors can affect the calibration of pressure.

Fig. 3.11(a) and (b) show the splitting of the triply degenerate mode of a [111] and [110]
Upon application of pressure, the triply degenerate mode of the diamond anvil splits due to stresses and strains in the anvils. For anvils oriented in the [100] direction, the high frequency edge corresponding to the singlet state can be used to determine pressure [60, 61]. (a) For a [111] anvil, the Raman peak splits into a higher frequency singlet ($\omega_S$) and lower frequency doublet ($\omega_D$) mode. (b) Splitting into three modes, $\omega_1$, $\omega_2$, and $\omega_3$ occurs in a [110] diamond. (c) For each anvil orientation, the mode corresponding to the high frequency edge of the Raman spectrum that would be seen during a pressure measurement is shown. In addition, the position of the triply degenerate mode of the Raman peak under hydrostatic pressure is seen. The black line through the data for the [100] diamond corresponds to the pressure calibration given by Eq. 3.5, while the other lines are guides to the eye. Note that the high frequency mode of the [110] anvil lies between the singlet modes for the [100] and [111] diamond. For a randomly oriented diamond, the high frequency edge would also lie within this range. It is therefore possible that using the [100] pressure calibration for a randomly oriented diamond might overestimate the pressure by up to 10%. Data for [111] anvils, hydrostatic pressure, and for [100] anvils denoted with closed circles comes from [105], while data for [110] anvils and [100] anvils denoted with open squares comes from [106].

The high frequency edge of the Raman spectrum for each anvil is shown along with that for the [100] anvil in Fig. 3.11(c). Just as the [110] high frequency edge falls between that for the [100] and [111] diamond, so too would the high frequency peak for a diamond with a random orientation. Diamonds used for Raman measurements during the course of this dissertation were procured from d’Anvils. These diamonds were cut in a random orientation. Therefore, depending upon orientation of our anvils, it is possible that
Raman measurements of the diamond vibron could have overestimated the pressure by up to 10%.

3.4 AC-Susceptibility

Ac-susceptibility measurements can be used to measure magnetic properties of materials. An ac current is generated in a primary coil surrounding the sample. This current gives rise to a magnetic field which permeates the sample. Any changes in the magnetic properties of the sample lead to a change in this field. By Lenz’s law, this changing field induces a current in a pick-up (secondary) coil which also surrounds the sample. For superconductors, ac-susceptibility measurements utilize the Meissner effect. As the sample is cooled through the superconducting transition, it expels the magnetic flux, resulting in a signal that may be detected by the coil system.

During the course of this research, ac-susceptibility measurements were performed at 1023 Hz. The magnetic field experienced by the sample was typically 0.1 Oe and 3.0 Oe for measurements in the He-gas and DAC systems, respectively. The low applied field ensures that there is no shift or broadening of the superconducting transition. The ac magnetic field was generated using a lock-in amplifier (SR820), which outputs a constant voltage. The induced voltage from the secondary coils is magnified through a low-impedance pre-amplifier (SR554) before being detected by the lock-in amplifier. For each system, an external resistor placed in series with the primary coil ensures that the current varies only very slightly upon cooling.
3.4.1 Coil Systems

The coil form used for ac-susceptibility measurements in the He-gas system can be seen in Fig. 3.12. The holder is made of Vespel, which has no magnetic response. A 16 mm long primary coil is wound about two 4 mm secondary coils. Each coil consists of six layers of 60 \( \mu \)m wire. The sample is positioned at the center on one of the secondary coils. It is possible to place a sample in each coil, thereby allowing two samples to be measured simultaneously. The secondary coils are wound in opposite directions and then balanced to minimize the background temperature dependence of the signal by canceling out the induced voltage from each of the secondary coils. This coil is connected to the electrical feed-through in the He-gas system.

For the DAC system, we use a side-by-side coil system, originally designed by V. G. Tissen. This coil, seen in Fig. 3.13 consists of two identical coils systems, each containing an inner secondary coil and an outer primary coil. Each coil is wound using 60 \( \mu \)m Cu wire. The coils are counterwound and balanced to try and minimize the temperature dependent
Figure 3.13: The side-by-side coil system for the DAC system. The coil on the left is centered about the diamond and sample space, while the coil on the right contains a ‘dummy’ gasket of the same gasket material as that used in the experiment in order to cancel out its ac response.

background from the surrounding material. One of these coils is placed around the diamonds and sample, while the second coil contains a ‘dummy’ gasket (same material as the gasket used for the experiment) to cancel out the signal of the sample gasket.

3.4.2 Signal Size

Ac-susceptibility measurements are important in detecting bulk superconductivity in a sample. For a superconductor, the induced voltage in the pick-up coil is given by

\[ S = \frac{\pi f \alpha HV N}{R(1 - D)} \chi, \]

where the signal size is related to the applied field (frequency \( f \) and magnitude \( H \)), the geometry of the coil (\( N \) turns, radius \( R \), and a geometric factor \( \alpha = 1/\sqrt{1 + (L/R)^2} \), where \( 2L \) is the length of the coil), and on the sample size and shape (volume \( V \) and demagnetization factor \( D \)). For a superconductor, \( \chi = -1 \) in MKS units. The demagnetization factor depends
on the geometry of the sample and its orientation relative to the applied field. For a needle-shaped sample parallel to the magnetic field, \( D \rightarrow 0 \), while for an extremely flat sample perpendicular to the field, \( D \rightarrow 1 \). In between these extremes, \( D = \frac{1}{3} \) for a perfect sphere. For a given volume then, the induced signal increases as the sample is flattened out.

When loading a sample for measurements in the DAC system, it is important to select a sample with the correct dimensions. This is especially important in hydrostatic measurements, where the diamonds and gasket may press on the sample if it is too large, thereby eliminating the hydrostaticity of the measurement. On the other hand, if the sample is too small, the small superconducting signal may be obscured by the background signal or by noise. It is important to note that for a sample with a given cross-section, a thinner sample increases \( D \), thereby enhancing the signal size, while the reduced volume acts to decrease the signal size. It is not immediately clear then, how much the signal would change if the height were halved.

Calculating the demagnetization factor for complex geometries is difficult, but an excellent article by Chen, Brug, and Goldfard gives a table with the demagnetization factors for a sample with a cylindrical geometry parallel to the applied field [107]. The cylinder has a diameter \( d \) and height \( h \). This can be reduced to a single, dimensionless parameter, \( \gamma = h/d \).

For two samples placed in the same coil, the ratio of the signal sizes is given by

\[
\frac{S_A}{S_B} = \frac{V_A(1 - D_B)}{V_B(1 - D_A)},
\]

(3.8)

where the subscripts \( A \) and \( B \) refer to each sample. How much, then, would the signal size vary if the height of the cylinder changes while the diameter remains the same? Using
<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$D$</th>
<th>$\gamma$</th>
<th>$D$</th>
<th>$\gamma$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.9780</td>
<td>0.3</td>
<td>0.6393</td>
<td>3</td>
<td>0.1717</td>
</tr>
<tr>
<td>0.02</td>
<td>0.9576</td>
<td>0.4</td>
<td>0.5766</td>
<td>4</td>
<td>0.1358</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.5260</td>
<td>5</td>
<td>0.1123</td>
</tr>
<tr>
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<td>0.9205</td>
<td>0.7</td>
<td>0.4488</td>
<td>7</td>
<td>0.0834</td>
</tr>
<tr>
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<td>0.9035</td>
<td>1.0</td>
<td>0.3692</td>
<td>10</td>
<td>0.06015</td>
</tr>
<tr>
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<td>0.2860</td>
<td>20</td>
<td>0.03168</td>
</tr>
<tr>
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<td>2.0</td>
<td>0.2339</td>
<td>50</td>
<td>0.01284</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7200</td>
<td>2.5</td>
<td>0.1979</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Superconducting demagnetization factors, $D$, for cylinders with height-to-diameter ratios given by $\gamma$, as given by tables in Ref. [107].

$$V = \pi (d/2)^2 h$$ and the definition of $\gamma$, holding the sample diameter constant gives

$$\frac{S_A}{S_B} = \frac{\gamma_A (1 - D_B)}{\gamma_B (1 - D_A)}.$$  \hspace{1cm} (3.9)

where $D$ is determined for a specific $\gamma$.

For example, if we consider a typical size of a sample in a hydrostatic DAC using 0.3 mm anvils (60 $\mu$m diameter, 18 $\mu$m thickness), $\gamma = 0.3$. Using a thinner 12 $\mu$m thick sample ($\gamma = 0.2$) reduces the possibility of the diamonds pressing directly on the sample at the highest pressures. Thus, in this case a 33% reduction in the sample volume reduces the signal by approximately 14%.

Figure 3.14 shows a plot of the relative signal size $S_A/S_B$ in terms of $\gamma_A$ for various values of $\gamma_B$ between 0.1 and 1.

3.4.3 Magnetic Field in Coil Systems

In order to set the applied field for a measurement, it is important to understand how the current through the primary coil is related to the induced magnetic field. For an infinite
Figure 3.14: Relative signal size between two samples, $A$ and $B$, given by Eq. 3.9. Here, the sample is a cylinder with a height-to-diameter ratio given by $\gamma$. The cylinder diameter is assumed to remain constant as the sample becomes flatter. Curves are shown in terms of $\gamma_A$ for various values of $\gamma_B$ (0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0 from top to bottom). Based on demagnetization factors from [107].
solenoid, the magnetic field at the center of the coil is given by

\[ B = \mu_0 n I, \]  
(3.10)

where \( \mu_0 = 4\pi \times 10^{-4} \text{ G cm/mA} \), \( I \) is the current, and \( n = N/L \) is the number of turns per unit length. For the coils used in the high pressure cells during the course of this research,

![Diagram of a solenoid](image)

Figure 3.15: The dimensions of a finite solenoid, defined above, are used to calculate the axial field of the coil.

it is important, however, to take into account the finite size of the coil. For a finite solenoid, the field along the axis is given by

\[ B(x) = \frac{\mu_0 n I}{2w} \left[ (x + L/2) \ln \frac{\sqrt{(r + w/2)^2 + (x + L/2)^2 + (r + w/2)}}{\sqrt{(r - w/2)^2 + (x + L/2)^2 + (r - w/2)}} - (x - L/2) \ln \frac{\sqrt{(r + w/2)^2 + (x - L/2)^2 + (r + w/2)}}{\sqrt{(r - w/2)^2 + (x - L/2)^2 + (r - w/2)}} \right] \]  
(3.11)

where the dimensions of the coil, \( L, r, \) and \( w \), are defined in Fig. 3.15.
At the center of the coil \((x = 0)\) in the limit \(w \to 0\), this reduces to

\[
B = \mu_0 I n \left[ \frac{L}{\sqrt{d^2 + L^2}} \right] \tag{3.12}
\]

where \(d = 2r\) is the coil diameter.

It is interesting to consider how much the magnetic field varies over the length of the coil. For the He-gas coil, in particular, the sample is not positioned at the center of the primary coil, but rather at the center of one of the two secondary coils, at \(\frac{1}{4}\) and \(\frac{3}{4}\) of the length of the primary coil. For each system the 6-layer primary coil is wound with 60 µm Cu wire, giving a coil width, \(w = 0.360\) mm. The inner radius in each case is 2.1 mm, giving an average radius of 2.28 mm. The only difference in the dimensions of the primary coil, then, is the length – 16.0 mm for the He-gas coil, and 2.0 mm for the DAC coil. Fig. 3.16 shows the strength of the magnetic field inside the coil, determined using Eq. 3.11, in terms of the field determined using Eq. 3.12. As \(w\) is small compared to \(r\) and \(L\), the field at the center of the coil is within 0.1% of the field approximated by Eq. 3.12. Moving out from the center of the coil, the field gradually decreases. In the case of the He-gas system, the field at the center of the secondary coils is 96.2% of the calculated field, varying from 85.6% to 99.3% over the range of the secondary coil. For a large \(\sim 4\) mm sample, then, the field over the sample may vary by more than 10%. On the other hand, for a sample in the diamond anvil cell, as long as the sample is placed within the center 50% of the side-by-side coil, the field will vary by less than 5%.
Figure 3.16: The axial magnetic field of the primary coil used for ac-susceptibility measurements in both the He-gas and the DAC systems is given in terms of the field at the center of the coil in the limit $w \to 0$, given by Equation 3.12, where $d = 2r$ is the coil diameter. The field along the axis at a distance $x$ from the center (given in terms of the total length, $L$, of the coil) decreases gradually, as given by Eq. 3.11. For each coil, the average radius and the width of the primary coil are given by $r = 2.28$ mm and $w = 0.360$ mm, respectively. The lengths of the DAC and He-gas primary coils are $L = 2$ mm and $L = 16$ mm, respectively. For the DAC coil, the field in the center half of the coil (from $x = -L/4$ to $x = L/4$) varies by less than 5%. In the He-gas system, the sample is positioned at the center of one of the secondary coils, whose region is marked by the shaded gray area. The magnetic field across the secondary coil varies from 85.6 % to 99.3% of the maximum field, with the field at the center of the secondary coil 96.2% of the maximum field.
Chapter 4

Alkali Metals

On the periodic table, the first column (excluding hydrogen) is made up of the alkali metals – lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr). Under sufficient pressure it is likely that hydrogen will also become an alkali metal. With only one electron in their outer shell, these elements are extremely reactive.

At low pressures the alkali metals are considered simple metals, and closely obey the nearly-free electron model. Valence electrons interact only very weakly with the periodic lattice and the Fermi surface is almost spherical. In a metal nearly-free electron theory predicts broadening of bands and a reduction in the size of energy gaps as a material is compressed. As pressure is applied, this broadening of the bands leads to a reduction in the density of states at the Fermi surface, $N(E_F)$. When combined with lattice stiffening, this leads to reduced electron-phonon coupling strength under pressure. According to the BCS theory, then, $T_c$ in simple metals is expected to decrease with pressure based on Eq. 2.16. This is confirmed in simple metals such as Pb, Al, In, and Sn. Among the alkali metals only Li has been found to be superconducting at ambient pressure, albeit at very low temperatures,
with $T_c = 0.4$ mK [108]. By the nearly-free electron model, then, one would not expect any of the other alkali metals to become superconducting under pressure. Under extreme compression, however, the nearly-free electron model breaks down.

Two radii can be used to describe a solid lattice – the radius of the ion core, $R_c$, and the Wigner-Seitz radius, $R_{WS}$, which is determined by the average volume per atom. Under extreme pressures, a solid lattice is compressed to the point that $R_c \sim R_{WS}$, as seen in Fig. 4.1. When this occurs, localized electron orbitals begin to overlap. Unsurprisingly, this can significantly affect the properties of a material. In the alkali metals extreme compression of the lattice at high pressures results in a radical departure from the nearly-free electron model and can lead to novel electronic properties. Calculations by Neaton and Ashcroft on Li and Na, for example, indicate that under pressure, the electronic charge density is
localized in the interstitial regions between the ionic cores [109, 110]. Complex behavior is also evident in the other alkali metals at extreme pressures where the core electrons begin to overlap and a narrowing of bands occurs [111–113]. Confinement of the valence electrons to the interstitial regions leads to the formation of electrides, with the interstitial electrons forming the anions [113–116]. In the heavier alkali metals – K, Rb, and Cs – pressure induces an $s$–$d$ charge transfer [117–119], while Li and Na undergo an $s$–$p$ transfer [111, 120]. These electronic changes are associated with strong electron-phonon coupling that can lead to the appearance of superconductivity [121–123]. At ambient pressure, the alkali metals crystallize in the $bcc$ structure. Under pressure they transform first to an $fcc$ structure and then to more complex, lower symmetry structures [124–126], as shown in Fig. 4.2.

High pressure studies on the first five alkali metals thus far reveal pressure-induced superconductivity only in Li [130–133] and Cs [134]. It is predicted, however, that all of the alkali metals should become superconducting under pressure [110,135,136]. Fr is the most unstable of the first 103 elements, with an extremely short half-life [137]. There is at most one ounce of Fr on Earth at any given time, thereby precluding the possibility of high pressure studies. Early high pressure ac-susceptibility measurements on Na indicated no evidence of superconductivity above 4 K under hydrostatic pressures in the range 6–65 GPa [138,139]. Similarly, no superconductivity has been observed in K above 1.5 K to 94 GPa [99,138,139]. In Rb, no superconductivity has been observed above 50 mK between 13 and 21 GPa [140,141].

During the course of this research, further ac-susceptibility experiments were carried out on Na and K in search of pressure-induced superconductivity. Their properties under pressure are therefore expounded in greater detail below. Characteristics of Li under pressure will be presented briefly in the following chapter.
Figure 4.2: Under pressure, the alkali metals transform from a bcc structure to an fcc structure before undergoing further transitions to more complex phases. Higher pressure phases, with the exception of the incommensurate host-guest (h-g) structure and the dhcp structure, are labelled with Pearson notation. Figure modified from 2004 publication by Ackland and Macleod [125] using Refs. [113, 126–129]. Structures are determined at room temperature, except for Li, which is for $\sim 200$ K.
4.1 Sodium

4.1.1 Previous Results

Sodium has long been considered a quintessential simple metal, first described according to the nearly-free electron model by Wigner and Seitz in the classic articles “On the Constitution of Metallic Sodium” [142, 143]. Under high pressure, however, Na exhibits complex behavior as it departs from the nearly-free electron model as predicted by Neaton and Ashcroft [110]. Under ambient pressure Na crystallizes in the \textit{bcc} structure, partially undergoing a martensitic transition at $\sim 35$ K to a Sm-type, faulted hexagonal $9R$ structure [144–146]. At 65 GPa Na transforms to an \textit{fcc} structure, where it remains stable to 105 GPa [147]. The stability range of these cubic structures is much larger than that of the other alkali metals. Remarkably, the Fermi surface of Na remains almost spherical throughout this pressure regime, with no singularities in the electronic structure near the Fermi level [110,148,149]. Phonon softening in the \textit{fcc} phase may induce structural instabilities leading to the wide array of lower symmetry structures observed at higher pressure [149]. Following a transformation at 105 GPa to a cubic \textit{cI16} structure, which is basically a distorted \textit{bcc} supercell, Na undergoes a series of phase transitions to orthorhombic \textit{oP8} (117 - 125 GPa), to an incommensurate host-guest structure (125–200 GPa), and finally to hexagonal \textit{hP4} ($> 200$ GPa) [113, 127, 150, 151].

These low-symmetry structures exhibit unusually low melting temperatures. X-ray diffraction studies of the melting curve of dense Na to 130 GPa indicate a maximum in the melting curve in the \textit{bcc} phase, followed by a steep decrease of the melting temperature in the \textit{fcc} phase. At 103 GPa near the transition from the \textit{fcc} to \textit{cI16} structure, the study by Gregoryanz et al. [152] shows a melting temperature of 345 K, lower than the ambient pressure melting temperature of 371 K. At 118 GPa the minimum of the melting curve even passes
through room temperature. A later study indicates that Na passes through a myriad of phases near the minimum of the melting curve, with six distinct crystalline phases observed within ±2 GPa of 118 GPa. Some of these complex structures are characterized by a very large number of atoms in the unit cell [127]. This structural diversity seen at high pressure in solid Na is analogous to a series of electronic and structural transitions which simulations show are present in dense liquid Na and which are expected to cause significant changes in physical properties of the liquid above 60 GPa [153].

Sodium’s structural complexity and the behavior of its melting curve are indications that dense Na can no longer be considered a simple metal. A series of inelastic x-ray scattering measurements of the plasmon frequency of Na also indicate a significant departure from the nearly-free electron model [154]. It has been suggested that the stability of the $oP8$ phase can be explained if sodium is a divalent metal at those pressures [155]. Several calculations have predicted that Na might become insulating at high pressure [120,156]. This was recently confirmed by Ma et al., who observed an optically transparent state of Na at 200 GPa [113]. Calculations show that this insulating state arises from electron localization in interstitial regions caused by hybridization of the $3p$ and $3d$ bands due to compression of the lattice.

Calculations indicate that electron-phonon coupling in Na remains quite weak to about 90 GPa, so any superconductivity is predicted to occur above the $fcc$ phase transition (or at least very close to the $fcc$ to $cI16$ transition) with a low critical temperature [136,157].

4.1.2 Experimental Results

Previous hydrostatic measurements on Na performed by S. Deemyad indicated no superconductivity above 4 K for pressures between 6.2 and 58.0 GPa [138,139]. To extend the search
for superconductivity to lower temperatures and to higher pressures, three non-hydrostatic ac-susceptibility measurements were performed in conjunction with W. Bi and J. Hamlin. A CuBe gasket was used to permit measurements to temperatures as low as 1.35 K. High pressures were attained by using 0.18 mm culet anvils bevelled at 7° to 0.35 mm for the first experiment and 0.1 mm culet anvils bevelled at 7.5° to 0.3 mm for the last two experiments. After filling the sample space with a pure Na sample for each experiment, the cell was closed tightly in the glove box to prevent sample oxidation. For all experiments pressure was increased at room temperature, where it was measured using the Raman diamond vibron signal.

For the first experiment the CuBe gasket was pre-indented to about 40 µm, with a 90 µm hole drilled through the center to form the sample space. Ac-susceptibility measurements were performed between 1.35 K and 30 K for pressures of 64, 80, 105, 119, and 135 GPa. No superconducting transition was observed. The sample pressure before and after each cooling run varied by only about 1 GPa, indicating that, in this case, the room temperature pressure measurement is also a good measure of the low temperature pressure. Diamond failure occurred upon trying to increase the pressure above 135 GPa.

The gasket for the second experiment was pre-indented to 32 µm and contained a sample space with a diameter of 50 µm. Note that for this experiment, Pt foil was placed between the diamonds and the backing pieces as it does not become superconducting unless it is a fine powder and because it is slightly softer than the Zr foil that is usually used. Ac-susceptibility was measured at an initial pressure of 104 GPa and again at 113 GPa. No superconducting transition was observed at these pressures. Unfortunately, the experiment ended prematurely when the capillary at the top of the cryostat insert broke off, resulting
in diamond failure as the membrane pressure decreased suddenly.

For the final experiment, the gasket was pre-indentented to 28 µm. Once again the sample space had an initial diameter of 50 µm. Ac-susceptibility measurements were performed between 1.35 and 30 K at 62, 90, 105, 120, 146, and 161 GPa. No superconductivity was discovered. Diamond failure occurred at ∼ 180 GPa (extrapolated from the membrane pressure) as pressure was being measured and before we were able to cool at that pressure. The pressure distribution across the culet was measured at 90 GPa, 120 GPa, and 161 GPa. In each case, the pressure gradient across the sample varied by about 10–20% of the maximum pressure.

4.2 Potassium

4.2.1 Previous Results

Potassium is the lightest of the alkali metals to undergo an s-d transfer under pressure [118, 158], which accounts for much of its complex high pressure behavior. At room temperature K undergoes a number of structural phase transitions under pressure, first from bcc to fcc at 11 GPa and then at ∼ 23 GPa to K-III, an incommensurate host-guest structure [126, 159, 160]. When pressures reach 54 GPa, K takes on an orthorhombic oP8 structure that is stable to 90 GPa before transforming to a tetragonal tI4 structure and subsequently to an orthorhombic oC16 structure at 96 GPa [128]. Several measurements have also indicated stability of a hexagonal hP4 phase between 25 and 35 GPa [161]. Parker et al. [162] reports that the chemical behavior of K is significantly different above ∼ 30 GPa, enabling the formation of compounds with transition metals.¹ Studies of the melting curve indicate that

¹At ambient pressure large differences in size and electronic structure prevent the formation of compounds between the alkali and transition metals, with the notable exception of Au.
the melting temperature passes through a maximum in the bcc phase before passing through a minimum temperature of $\sim 375$ K at the transition from fcc to the lower symmetry incommensurate phase [163].

Previous measurements of K using ac-susceptibility techniques have failed to find any evidence of superconductivity. S. Deemyad [138, 139] conducted hydrostatic measurements above 1.5 K for pressures between 3.6 and 35 GPa and above 4 K for pressures between 4.7 and 43.5 GPa, while M. Debessai [99] performed non-hydrostatic measurements above 1.35 K for pressures between 8 and 94 GPa. However, various theoretical calculations predict pressure-induced superconductivity in potassium above the bcc to fcc transition at temperatures ranging from $\sim 2$–13 K [121, 135, 136, 164]. Very recently Pickard and Needs have predicted ferromagnetism in the stable, low temperature phases of K around 20 GPa [116]. If this is the case, one would expect the ferromagnetism to suppress any superconducting phase.

### 4.2.2 Experimental Results

To search for superconductivity in K, several diamond anvil cell experiments were carried out using ac-susceptibility techniques. Measurements were performed in conjunction with W. Bi and V. Tissen using Ni(Mo 25% wt.) gaskets. The NiMo gaskets were brought to our lab by V. Tissen, who made them in Russia. Per his recommendation, gaskets were pre-indentled to an initial thickness of 40–50 $\mu$m for the first few experiments. A hole with a 260 $\mu$m diameter was drilled through the gasket to form the sample space. For each experiment K (99.98% purity, metal basis) from Alfa Aesar was loaded into the sample space along with several ruby spheres to measure pressure. For hydrostatic measurements this sample had an
initial diameter of about 100–130 $\mu$m and a thickness of about 30 $\mu$m, as seen in Fig. 4.3(a). Potassium is extremely reactive with both air and water, even more so than Li and Na, so after loading the sample in the glove box, the cell was closed quickly to prevent the sample from tarnishing. For the first three attempts, 0.5 mm anvils bevelled at $25^\circ$ to 0.67 mm were used for hydrostatic measurements. Unfortunately, upon applying pressure the gasket closed completely about the sample, thereby precluding the possibility of hydrostatic measurements. We believed that the bevel on the anvils could be hindering sealing of the He pressure medium within the gasket, so later measurements were performed using flat 0.5 mm cuet anvils. High pressures were successfully obtained during three subsequent measurements, which, for clarity, shall henceforth be termed Exp. #4, Exp. #5, and Exp. #6.

For Exp. #4 the NiMo gasket was pre-indentent to 40 $\mu$m. After transferring the cell from the glove box to the cryostat, pressure was applied below the lambda point of LHe. Upon increasing the membrane pressure, the hole shrunk to the size of the sample just as pressure began to increase, and at a sample pressure of 1.5 GPa no transmitted light could be seen. Due to this apparent non-hydrostaticity, we warmed to room temperature. Upon doing so we were able to once more see transmitted light, indicating that the gasket had in fact sealed, as seen in Fig. 4.3(b). The membrane pressure increased slightly upon warming due to a small leak in the needle valve between the capillary and the metal pipe leading to the high pressure helium bottle. Hence, the sample pressure also increased significantly upon warming. Pressure measurements through the metallurgical microscope indicated pressures of 10.3 GPa and 10.8 GPa in two ruby clusters. A pressure measurement in the cryostat before cooling confirmed a pressure of 10.8 GPa. For the remainder of the experiment, the temperature was kept below 160 K to minimize the possibility of He getting into the
diamond. Pressure was increased in the temperature range of 40–60 K. Low temperature ac-susceptibility measurements were performed between 1.35 K and 30 K at 11.2 GPa, 13.0 GPa, 15 GPa (estimated), 19.1 GPa, and 23.8 GPa. These pressures indicate the average pressure, since pressure gradients could be measured across the sample. These pressure gradients steadily increased from about 1–2 GPa at the lowest pressures, to about 4 GPa at 19.1 GPa, and to as high as about 7 GPa at 23.8 GPa. Ruby peaks at the highest pressure were also very broad, indicating non-hydrostaticity. For this reason we released pressure following the measurement at 23.8 GPa. Initial speculation that there might be a piece of ruby on the gasket proved not to be the case, so non-hydrostaticity was most likely caused by the diamond anvils pressing directly on the sample, as transmitted light could be seen through the sample space. No indications of superconductivity or ferromagnetism were found at any of the measured pressures.

For the following experiment (\#5) the gasket was pre-indented to 75 \( \mu \text{m} \) (almost twice as thick as in the previous experiments) to reduce the possibility of the diamonds pressing directly on the sample at high pressure. Upon application of pressure, it seemed that the gasket sealed, as the hole began shrinking and pressure increased very slightly, to about 0.6 GPa. Upon warming above LHe temperatures the hole in the gasket remained open and transmitted light could be seen. We therefore increased the membrane pressure at about 100 K. Upon doing so, however, the hole actually shrank even more, and at only about 1 GPa had completely collapsed about the sample. No transmitted light could be seen. A set of ac-susceptibility measurements were performed at this near-ambient pressure and then the membrane pressure was increased slightly, although no ruby signal could be seen through the cryostat to determine sample pressure. Warming to room temperature after completing
Figure 4.3: (a) For hydrostatic measurements a potassium sample with a diameter of approximately 130 µm is loaded in a 260 µm sample space drilled through a NiMo gasket. Image is taken in the glove box before closing the cell. (b) Image of potassium sample with transmitted light under the metallurgical microscope. The sample is surrounded by dense helium to provide hydrostatic pressure. Under pressure both the hole in the gasket and the sample shrink. Here, the pressure is 11.2 GPa and the sample space has a diameter of about 100 µm. Both images are set to the same scale.
another set of ac-susceptibility measurements between 1.35 and 30 K, we determined the pressure to be about 12.0 GPa, as it ranged from 11–13 GPa across various ruby spheres. No superconducting signal was observed. Observation of the sample space confirmed that the gasket had collapsed around the sample and that the measurement would be non-hydrostatic. For this reason, and because we were interested in obtaining some measurements at lower pressures, we released pressure.

As we were having difficulties successfully completing a hydrostatic measurement, we decided to perform a non-hydrostatic measurement for the final experiment (#6). This offered several advantages. First, as we did not have to worry about a He pressure medium, we were able to completely fill the sample space with K and close the cell more tightly in the glove box. The larger sample size would increase the size of any superconducting signal, making it more likely to be discernible from the background susceptibility. By sealing the cell completely in the glove box, we eliminated the possibility of sample oxidation as the cell was being transferred to the cryostat. Finally, in the previous two measurements, our lowest non-ambient pressure measurement was at about 10 GPa. For this non-hydrostatic measurement we were able to obtain ac-susceptibility measurements at lower pressures. Based on measurements of superconducting Li [130–133], we believed that if K were found to be superconducting, it would most likely be so under both hydrostatic and non-hydrostatic conditions, although the temperature might vary slightly. If superconductivity were detected, we would then go back and try to measure it using a hydrostatic pressure medium.

For this non-hydrostatic measurement the NiMo gasket was pre-indentated to 82 µm. The sample space was almost completely filled with K, so even taking into account the high compressibility\(^2\) of K, we would expect the superconducting signal for full shielding to be

\(^2\)The volume at 10 GPa is about 50% of the ambient pressure volume, reducing to approximately 40% at 20 GPa.
Figure 4.4: Images of potassium in DAC through metallurgical microscope at various pressures. Photographs are all to the same scale and were taken through cross-polarizers. Note at higher pressure the sample started to extrude from the sample space.

as high as 100–200 nV. After initially closing the cell, a pressure of 0.4 GPa was measured through the metallurgical microscope at room temperature and ac-susceptibility measurements were performed upon cooling. We were unable to successfully measure pressure inside the cryostat, so subsequent pressures were also measured at room temperature through the metallurgical microscope. A ruby at the center of the sample space was used to measure pressures of 0.4 GPa, 5.4 GPa, and 10.8 GPa. At 10.8 GPa the pressure gradient across the sample was quite small, with a ruby sphere at the edge of the sample space indicating a pressure of 10.6 GPa. As pressure increased even further, the sample (and ruby) started to extrude from the sample space, as seen in Fig. 4.4. Upon increasing pressure from 10.8 GPa, we successfully measured pressure up to 13.1 GPa. When the membrane pressure was in-
Figure 4.5: Sample vs. membrane pressure for non-hydrostatic measurement on potassium. Pressure was measured at room temperature. The final three pressures were estimated (■) from the membrane pressure by extrapolation of measured (•) sample pressure. Approximate uncertainties for estimated pressures are shown by vertical bars.

...increased one more time, however, the ruby signal could no longer be detected in the original sample area, but rather only farther out on the sample on top of the gasket. This pressure was in fact lower (8.5 GPa and 10.1 GPa for two ruby chips) than that measured previously, indicating the presence of large pressure gradients. Above 10.8 GPa, therefore, pressure at the center of the sample space was extrapolated from a plot of the sample vs. membrane pressure, seen in Fig. 4.5. At each of the six pressures (0.4, 5.4, 10.8, 14±1, 17.5±1.5, and 23 ±2 GPa), ac-susceptibility measurements were performed between 1.35 K and 30 K. No evidence was found for superconductivity or for a ferromagnetic transition. To prevent...
amond failure and because the sample had extruded so much onto the gasket at 23 GPa, pressure was not increased further. Note that for 14 GPa and higher, when the sample was not contained within the sample space, the pressure gradients were likely quite large, which would have made any superconducting transition very broad and therefore more difficult to detect.

In summary, superconductivity was not observed in a series of ac-susceptibility measurements for temperatures between 1.35 K and 30 K at pressures of 0.4, 5.4, 10.8, 11.2, 12.0, 13.0, 14±1, 15 (estimated), 17.5±1.5, 19.1, 23±2, and 23.8 GPa. While both hydrostatic and non-hydrostatic measurements were attempted, we were unable to complete a purely hydrostatic measurement. Even in Exp. #4, the most hydrostatic of the measurements, large pressure gradients could be observed at the highest pressures. These pressure gradients would cause any superconducting signal to be quite broad; along with a small signal size, this could have prevented any superconducting transition from being discernible in the background temperature dependence of the ac-susceptibility measurements. In earlier hydrostatic measurements it is also possible that slight oxidation of the sample may have occurred as the cell was being transferred from the glove box to the cryostat. Predictions of ferromagnetism around 20 GPa [116] were published following our experiments. No indications of a ferromagnetic transition could later be observed in data from our measurements, although it is possible that the transition could occur at a higher temperature than the range we focused on during our search for superconductivity. Further experiments using resistivity techniques and in the synchrotron are vital in the search for superconductivity and for determining potassium’s magnetic state under pressure.
Chapter 5

Li$_{1-x}$Mg$_x$ Alloys

5.1 Theory and Previous Results

Like the other alkali metals described in the previous chapter, Li undergoes a radical departure from the nearly-free electron model under pressure, resulting in a plethora of surprising phenomena. At ambient pressure, bcc Li transforms martensitically at 77 K to a Sm-type, faulted hexagonal 9R structure [144]. Under pressure Li undergoes a number of structural phase transitions, as seen in Fig. 4.2, first to fcc at 6.9 GPa, to rhombohedral hR1 at 39 GPa, and to cubic cI6 at 42 GPa [111]. At even higher pressures, Li subsequently undergoes phase transitions at 55, 69, and 80 GPa to orthorhombic oC88, oC40, and oC24 phases, respectively [129].

The profound departure from the nearly-free electron model is illustrated through a series of calculations by Neaton and Ashcroft [109]. Under extreme compression, the Li ions undergo pairing and electrons are confined to highly distorted interstitial regions between the ion cores. The resulting strong electron-phonon coupling leads to pressure-induced superconductivity and a maximum $T_c$ value near 14 K that is among the highest of the
elements [130–133]. The sudden disappearance of superconductivity above 67 GPa [133] has recently been attributed to the fact that Li undergoes a pressure-induced metal-to-semiconductor transition at 70 GPa, as observed by Matsuoka and Shimizu [165]. Measurements have shown that the melting temperature passes through a minimum near room temperature in the pressure range of about 40–70 GPa [129, 166].

Under ambient conditions the alkaline-earth metal Mg adopts a hcp structure [158], transforming to bcc at 50 GPa [167]. No pressure-induced superconductivity has been found in Mg to 1 Mbar [168]. What happens, then, when divalent Mg is alloyed into monovalent Li? What is the effect of increasing electron concentration? As shown in previous studies, superconductivity in Li$_{0.9}$Mg$_{0.1}$ is suppressed relative to pure Li [169]. As measurements were only conducted to 47 GPa, we wished to extend superconductivity studies of Li$_{0.9}$Mg$_{0.1}$ to higher pressure, in particular to observe whether superconductivity vanishes near 70 GPa when pure Li becomes semiconducting. In addition, we wished to study the evolution of the superconducting phase diagram for increasing concentrations of Mg in the alloy. In furtherance of this, a series of ac-susceptibility measurements were carried out on Li$_{0.9}$Mg$_{0.1}$ and Li$_{0.8}$Mg$_{0.2}$.

5.2 Experimental Results

5.2.1 Sample Preparation

Samples of the Li$_{1-x}$Mg$_x$ alloys were prepared in the laboratory in an argon gas glove box, as both Li and Mg are extremely air sensitive. Mg turnings from Alfa Aesar (99.98%, metal basis) were used, while the Li was cut from rods with a 0.5" diameter (ESPI Metals, 99.99%). Sturdy Ta foil was used to cut the desired amount of Li from the rods, after first removing
the darker, harder oxidized layer on the outside. The melting temperature of Mg (923 K) is much higher than that of Li (454 K), so the melting temperature of the alloy increases with increasing Mg concentration, as seen in Fig. 5.1. To ensure uniform formation of the alloy, it is important that the alloy be mixed at temperatures well above the melting temperature.

![Figure 5.1: Experimental phase diagram for Li(Mg), from Ref. [170]. $x_{Mg}$ is the atomic concentration of Mg in the alloy.](image)

A Fisher Scientific *Isotemp* hot plate in the argon glove box was used to prepare Li$_{1-x}$Mg$_x$ samples for $x = 0.1, 0.2, \text{ and } 0.3$. The temperature on the hot plate can be set to a maximum of 550°C, but the actual temperature on top of the ceramic hot plate is only about 70% of the indicated temperature, as found in 2008 by undergraduate student Hunter Banks. Thus, the maximum temperature that can be obtained is only about 400°C. This was also confirmed by temperature measurements taken during sample preparation. From the phase diagram, the
melting temperatures for an alloy with 10%, 20%, and 30% Mg are approximately 240°C, 300°C, and 380°C, respectively. For higher concentrations of Mg, the hot plate does not reach temperatures sufficient for formation of the alloy.

In order to obtain the correct atomic concentrations for each sample, the fraction of Mg by weight, \( w \), was first calculated using

\[
w = \frac{x \times (24.31 \text{ g/mol})}{(1 - x)(6.941 \text{ g/mol}) + x \times (24.31 \text{ g/mol})},
\]

where 6.941 \( \text{g/mol} \) and 24.31 \( \text{g/mol} \) are the molecular weights of Li and Mg, respectively. The correct amounts of Li and Mg were then carefully measured in the glove box using a Mettler balance (AB54), which has an uncertainty of 0.1 mg. A thermocouple, either ‘Type T’ or ‘Type K’ was placed between the hot plate and a stainless steel crucible to monitor the temperature. The Li was placed on a piece of Ta foil in the crucible and the temperature was slowly increased until the Li had completely melted. The temperature was then further increased until it was higher than the melting point of the alloy. Mg pellets were then gradually added to the Li. Since the temperature was greater than the melting point of the alloy, the Mg dissolved into the Li liquid. A copper rod with Ta foil on the end of it was used to stir the mixture throughout the process. After the Mg pellets had dissolved, the mixture was stirred for approximately 30 minutes to ensure that the alloy was well mixed. Ta foil was used during the process as it does not react with the alloy.

Four samples, subsequently referred to as \( S_1 - S_4 \) were prepared using this method, diagrammed in Fig. 5.2. For \( S_1 \) and \( S_4 \), \( x = 0.1 \), while \( x = 0.2 \) for \( S_2 \). The hot plate temperature did not reach high enough for sample \( S_3 \), with \( x = 0.3 \). At this concentration of Mg, the melting temperature of the alloy is about 380°C. While the Mg pellets did seem
Figure 5.2: $\text{Li}_{1-x}\text{Mg}_x$ samples for $x = 0.1, 0.2$ were prepared in an argon glove box. A stainless steel crucible was placed on a hot plate and the desired amount of Li was placed on a piece of Ta foil within the crucible. The temperature (measured between the hot plate and the crucible using a thermocouple) was increased above the melting point of the alloy so that Mg pellets would dissolve into the Li liquid. To ensure a uniform sample, it was stirred for about 30 minutes with a Cu rod with Ta foil on the end. The hot plate did not reach a temperature sufficiently high enough to produce a uniform $x = 0.3$ sample. However, the higher temperatures and the corresponding higher vapor pressure of Mg make it increasingly difficult to effectively and safely prepare the $\text{Li}_{1-x}\text{Mg}_x$ samples in the glove box using this technique. Therefore, to prepare alloy samples with a higher concentration of Mg, a different method is required.
<table>
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<th></th>
<th>Desired Mass</th>
<th>Measured Mass</th>
<th>Initial Mass</th>
<th>Final Mass</th>
<th>Mass Loss</th>
<th>Max % of Mg lost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li  Mg</td>
<td>Li  Mg  Ta foil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$: $x = 0.1$</td>
<td>360.0  140.0</td>
<td>362  141  432</td>
<td>935</td>
<td>931</td>
<td>4</td>
<td>2.9%</td>
</tr>
<tr>
<td>$S_2$: $x = 0.2$</td>
<td>266.5  233.5</td>
<td>266.8  233.4  591.9</td>
<td>1092.1</td>
<td>1092.5</td>
<td>-0.4</td>
<td>-0.2%</td>
</tr>
<tr>
<td>$S_3$: $x = 0.3$</td>
<td>200.0  300.0</td>
<td>200.3  300.2  464.4</td>
<td>1076.4</td>
<td>1072.9</td>
<td>3.5</td>
<td>1.2%</td>
</tr>
<tr>
<td>$S_4$: $x = 0.1$</td>
<td>360.0  140.0</td>
<td>360.6  140.4  357.0</td>
<td>858.0</td>
<td>856.1</td>
<td>1.9</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

Table 5.1: Masses (in mg) of Li and Mg used for preparation of Li$_{1-x}$Mg$_x$ alloys. The final column indicates the maximum percentage of Mg relative to the total mass of the Mg that could have been lost due to evaporation.

Masses were measured before and after sample preparation to ensure that no sample was lost in the process. The combined mass of the alloy and Ta foil was measured and the final mass was compared to that of the individual components, as seen in Table 5.1. Note that in preparing the first sample, $S_1$, the mass of the Ta foil on the end of the copper rod was not included in the measurement. As a very small amount of the alloy stuck to this foil after stirring the material, this could account for some part of the discrepancy in the mass. It is unclear why the final mass of $S_2$ was slightly larger than the initial mass. It is possible that some of the tape that had been holding the Ta foil in place on the rod was not completely removed before measuring the mass. The discrepancy could also simply be due to uncertainties in the measurements themselves. The scale has an uncertainty of 0.1 mg, but the uncertainty of measurements in the glove box is slightly higher due to slight air flow and vibrations, even when the pressure regulator and pump are turned off. At temperatures near the melting point of the alloy, the vapor pressure of Mg is much higher than that of Li so any sample lost due to evaporation of the liquid was most likely to be Mg. Thus, the mass loss was compared to the initial mass of Mg to determine the maximum percentage of Mg that could have been lost. For each sample, there was less than a 3% variation, which is insignificant in terms of the concentrations that we are studying.
5.2.2 X-ray Diffraction Measurements

Under ambient conditions Li and Mg crystallize in the bcc and hcp structures, respectively. Previous x-ray diffraction studies indicate that, as the Mg concentration in Li$_{1-x}$Mg$_x$ increases, the bcc lattice gradually contracts until $x \sim 0.5$, at which point the lattice parameter starts increasing again [171–174]. At atomic concentrations of Mg greater than about 70%, the lattice transforms to a hcp structure.

After preparing the Li$_{1-x}$Mg$_x$ alloy samples, x-ray diffraction measurements were carried out to confirm phase purity. Ideally, measurements should be performed on a powder sample—however with the soft, malleable Li(Mg) alloys, this is not possible. As the alloy is extremely air sensitive, care had to be taken to prevent oxidation as much as possible while conducting the x-ray diffraction measurements. First, a clean piece of clay was rolled out and placed around the shallow indentation on the x-ray slide. This slide was then transferred to the glove box, where the sample was cut into small pieces and then gently pressed together to randomize the crystalline directions as much as possible. Flattening the sample also helped improve the x-ray pattern by minimizing height variations. One side of the sample was coated with a very thin layer of petroleum jelly and Si powder. The sharp reference peaks from the Si are more well-defined when the Si is only a thin layer at the top rather than mixed through the sample. The flattened alloy was then placed (Si side up) on the sample area of the slide, which was covered with a thin layer of petroleum jelly to prevent the sample from sliding around during the measurement. Two pieces of plastic wrap were then pressed down on top of the clay and wrapped tightly around the slide. This kept the sample isolated as much as possible from the surrounding air, allowing the x-ray measurements to be completed without the entire sample oxidizing. A photograph of a prepared slide (without the plastic
Figure 5.3: As the Li(Mg) alloys are extremely air sensitive, care has to be taken to minimize oxidation during the x-ray diffraction measurements. Here, the sample is shown on the x-ray slide surrounded by a piece of clay. Plastic wrap is then placed tightly around the slide.

The x-ray diffraction measurements were carried out in the Earth and Planetary Sciences department at Washington University using a Rigaku Geigerflex D-MAX/A Diffractometer. Power settings were 35 kV and 35 mA. The system uses Cu-Kα radiation. Scans were performed from 20–70° with a step size of 0.02° and a dwell time of 4 s. In this range, the Si standard has four peaks at 28.420°, 47.306°, 56.172°, and 69.172°. Since the sample was generally not level with the surface of the slide, these peaks were shifted slightly in our measurements. To correct for these height differences, the entire curve was shifted so that the Si standard peaks were correct. X-ray measurements were performed on pure Li and on the $x = 0.1$ and $x = 0.2$ alloys, as seen in Fig. 5.4. For this range of angles, three peaks should be seen from the bcc lattice of the Li(Mg) alloy. Using the notation (hkl), these peaks correspond to the (110), (200), and (211) planes. X-ray scattering occurs when

$$n\lambda = 2d\sin(\theta)$$  \hspace{1cm} (5.2)
Figure 5.4: X-ray diffraction peaks for Li$_{1-x}$Mg$_x$ alloys ($x = 0, 0.1$, and $0.2$), along with lattice parameters. Peak positions from the silicon standard are indicated at the bottom by red lines. Approximate positions of the three $bcc$ peaks corresponding to the (110), (200), and (211) planes are also shown. Note that the relative intensities of these peaks differs between measurements. This occurs because of texture in the samples – the crystals in the may have a preferred orientation, which is not the case when powder x-ray diffraction measurements are performed. This texture could explain the absence of the (200) peak in pure Li. Finally, the small peak visible alongside the Si peak for one of the Li$_{0.9}$Mg$_{0.1}$ samples ($a = 3.503$ Å) could arise from Si powder on the opposite side of the sample or from a slight impurity.
Figure 5.5: Lattice parameters of \( bcc \) \( \text{Li}_{1-x}\text{Mg}_x \) alloys. When compared to previously published lattice parameters (●) [171–174], the lattice parameters determined for our samples (◆) using x-ray diffraction measurements are consistent with increasing Mg concentration.

where, in this case, \( \lambda = 1.5406\text{Å} \) for the Cu-K\( \alpha \) radiation. For a \( bcc \) lattice, the interplanar separation, \( d \), is given simply by

\[
d = \frac{a}{\sqrt{h^2 + k^2 + l^2}},
\]

where \( a \) is the lattice parameter and \( h, k, \) and \( l \) are the indices of the plane. Combining these equations allows one to calculate the lattice parameter of the samples from the x-ray diffraction data. The results, compared against those of previous publications, are seen in Fig. 5.5.
While our lattice parameters are generally somewhat larger than those determined by other groups, the lattice parameter does decrease continuously as the Mg concentration is increased, so the phase purity of our samples can be verified. No Li or Mg oxides (LiO, Li₂O, Li₂, MgO, Mg₂, Mg₄) could be detected in any of the measurements.

5.2.3 Ac-susceptibility Measurements

Ac-susceptibility measurements were performed above \(~ 4.5\) K on samples of Li₀.₉Mg₀.₁ and Li₀.₈Mg₀.₂ under hydrostatic pressure. Unless otherwise stated, all experiments were performed using 0.3 mm culet anvils and a gold-coated Re gasket, pre-indentied to an initial thickness of \(~ 40\) µm. Samples were loaded in the glove box, and the cell was then quickly transferred to the cryostat. Hydrostatic pressure was initially applied below the lambda point of LHe.

Li(Mg 10%)

As superconductivity in Li₀.₉Mg₀.₁ had already been measured between 30 and 47 GPa [169], our goal was to measure superconductivity at a few pressures in this range to verify that our sample was behaving as expected, and then to extend the high pressure measurements above 50 GPa. In particular, we were interested in whether superconductivity in the alloy would be suppressed at the pressure that Li undergoes a transition to a semiconducting state [165]. With this goal in mind, several experiments were carried out under hydrostatic pressure using 0.3 mm culet anvils. For each experiment, a sample with a diameter \(~ 80\) µm was loaded into the sample space of a gasket pre-indentied to \(~ 40\) µm. For five of our nine attempts, the sample space unfortunately did not seal at low temperature upon application of pressure, so no hydrostatic measurements could be performed. For the remaining four
Figure 5.6: (a) A superconducting transition is observed at 33.0, 40.7, and 44.2 GPa. At each pressure, $T_c$ is determined from the midpoint after making a background subtraction. (b) $T_c$ for Li$_{0.9}$Mg$_{0.1}$ determined during the course of these measurements is compared to previous measurements on Li and on Li$_{0.9}$Mg$_{0.1}$ by Deemyad et al. [133] and Hamlin et al. [169]. Measurements of $T_c$ are consistent with those measured earlier for the alloy, although the average pressure dependence is slightly lower – 0.22 K/GPa vs. 0.34 K/GPa.

Experiments, hydrostatic pressure was successfully applied. For the first of these experiments, ac-susceptibility measurements were initially performed at 23.1 GPa to serve as a reference for background subtractions. Pressure was subsequently increased to 33.0, 40.7, and 44.2 GPa. A small ($\sim 10$ nV) superconducting transition was seen at each of these pressures, in good agreement with previously published results, as seen in Fig. 5.6. To protect the diamonds, we had decided to maintain the temperature below 180 K for the duration of the experiment. At 44.2 GPa and 170 K, however, diamond failure occurred, thereby preventing us from measuring the superconducting transition at higher pressures. We resolved to maintain the temperature below 150 K for subsequent experiments.

For the next set of measurements, ac-susceptibility measurements were made at an initial pressure of 21 GPa after the gasket had sealed. While transmitted light could be seen, the
ruby signal was quite small and already broadened at the lowest pressure. When the pressure was increased in 5 GPa steps to 35 GPa, the ruby signal became progressively smaller and was eventually lost completely. Using the membrane pressure, the pressure was increased to \( \sim 40 \) GPa in the hope that the ruby signal would reappear. As it did not, we believe that the ruby may have gotten buried within the sample. Even at 35 and 40 GPa, the expected superconducting transition was not observed. The sample may have oxidized while moving the cell from the glove box to the sample space, or non-hydrostatic conditions could have resulted in an extremely broad superconducting transition that could not be distinguished from the background. Due to the lack of a transition and our inability to determine the sample pressure, we released pressure.

For the final two experiments (performed following numerous unsuccessful measurements for which the gasket did not seal for hydrostatic measurements) we decided to use a W-Re gasket rather than Re, which we had used previously. We thought that using this material for the gasket might make it more likely to seal at low temperature. In both cases the gasket sealed so that the sample space contained hydrostatic helium around the sample, and pressure was subsequently increased to 35–40 GPa in the temperature range 30–60 K to conduct ac-susceptibility measurements in the search for superconductivity. Temperature was maintained below 100 K for the duration of the experiment. Unfortunately, during both experiments, the gasket failed in the temperature range 25–35 K, causing the pressure to decrease instantaneously when one of the diamonds broke as a result. When we took apart the cell, the gasket had broken into several pieces, with large cracks also evident. It seems that the W-Re gaskets were too brittle at the low temperatures where we increased pressure, and broke rather than deforming to support the diamonds.
Li(Mg 20%)

As seen in Fig. 5.6(b), when a 10% atomic concentration of Mg is alloyed with pure Li, superconductivity is suppressed somewhat. The pressure at which superconductivity first emerges above 5 K increases from 20 GPa in Li to 30 GPa in Li\textsubscript{0.9}Mg\textsubscript{0.1}. In addition, the initial pressure dependence of the alloy is much lower. By increasing the Mg concentration to $x = 0.2$, then, one expects superconductivity to be suppressed even further, perhaps appearing above 40 GPa with an even lower pressure dependence, $dT_c/dP$. With this in mind, several experiments were carried out on Li\textsubscript{0.8}Mg\textsubscript{0.2} to search for pressure-induced superconductivity.

During the first two measurement attempts, the gasket did not seal upon initial application of pressure and the gasket completely collapsed around the sample. More success was had during the following experiment, in which a sample with a diameter of $\sim 70 \, \mu$m and a thickness of $\sim 70 \, \mu$m was loaded into a 150 $\mu$m diameter sample space. While initially applying pressure at LHe temperatures, the sample space diameter decreased from 150 $\mu$m to $\sim 85 \, \mu$m. A series of ac-susceptibility measurements were performed at 17.2, 26.2, 33.3, 36.9, 42.1, 45.9, 52.7, and 55.9 GPa. No superconducting transition was observed at any of these pressures. Diamond failure occurred at 40 K after increasing the pressure to 59.8 GPa. The temperature was kept below 150 K for the duration of the experiment and pressure was increased in the temperature range 30–80 K. At 17.2 and 26.2 GPa, pressure was purely hydrostatic, while at 33.0 GPa, the high-pressure tail of the ruby signal began to broaden, indicating the onset of a degree of non-hydrostaticity. At the three highest pressures, a pressure gradient of at least 2–5 GPa could be measured. As transmitted light was still visible and the peak of the largest ruby signal was still quite sharp, this most likely indicates that
the gasket thickness had decreased to the point that diamonds started to press directly on
the sample and several of the ruby pieces. Note that during this series of measurements,
the membrane pressure was leaking through the capillary connection inside the cryostat.
Therefore, the membrane and sample pressure both noticeably decreased when the system
was left to warm for several hours. For instance, after making measurements at 52.7 GPa,
the membrane pressure decreased by almost 8 bars in 14 hours (even with the temperature
increasing from 30 K to 150 K), and the sample pressure decreased by \( \sim 5 \) GPa. When the
cell was taken apart following the experiment, several cracks were visible in the Re gasket.
It is possible that the pressure cycling could have contributed to the gasket and diamond
failure just below 60 GPa.

For the final experiment, 0.5 mm culet anvils were used. While the highest attainable
pressure with these anvils is lower than that with the 0.3 mm culet anvils, we decided that the
larger sample size would make it more likely to observe a superconducting signal if it existed.
A 260 \( \mu m \) hole was drilled through the center of a Re gasket that was pre-indent to 80 \( \mu m \).
A sample with a diameter \( \sim 130 \mu m \) and a thickness of \( \sim 30 \mu m \) was loaded into the sample
space. When initially applying pressure, the sample space diameter decreased by about 10%.
Upon warming, the sample space shrunk further to \( \sim 200 \mu m \) at 70 K and to \( \sim 150 \mu m \)
at room temperature, as seen in a series of photographs in Fig. 5.7. Hydrostaticity was
maintained throughout the experiment, as evidenced by sharp ruby peaks and the visibility
of transmitted light. After a pressure of 11.0 GPa had been measured at room temperature,
the cell was kept below 160 K to protect the diamonds. Pressure was increased above
11.0 GPa in the temperature range 100–150 K. No superconducting transition was observed
above 4.5 K for 11.0, 17.9, 26.1, 30.3, 33.7, 37.7, and 41.5 GPa. Diamond failure occurred
Figure 5.7: Li$_{0.8}$Mg$_{0.2}$. (a) The sample is loaded into the sample space of a gold-coated Re gasket. Hydrostatic pressure was maintained throughout the experiment, and transmitted light could be seen. Upon increasing pressure, the sample space shrinks, from an initial diameter of (a) 250 µm to (c) $\sim$ 200 µm at 70 K (d) 85 µm at room temperature at 11 GPa. Several ruby spheres may also be seen clearly at room temperature through the metallurgical microscope. The size of the sample space subsequently remained the same upon cooling (e) and throughout the remainder of the experiment.

at 115 K after increasing the pressure to 45.4 GPa.

**Summary**

For the 10% alloy, Li$_{0.9}$Mg$_{0.1}$, we have not yet managed to extend the pressure range across which superconductivity has been studied. Further measurements are planned to reach higher pressure. For Li$_{0.8}$Mg$_{0.2}$ no superconductivity has been observed above 4.5 K for pressures between 11.0 and 52.7 GPa, indicating that the increased Mg concentration significantly suppresses superconductivity present in Li and Li$_{0.9}$Mg$_{0.1}$. Studies should be extended to higher pressure and could also be performed with CuBe to determine whether the material is superconducting at lower temperatures. For both alloy concentrations, the most successful measurements have been performed when the pressure is increased at $\sim$ 100 K and the temperature is kept below 150 K for the entire experiment. For the 0.3 mm culet anvils, in particular, it is critical that the sample be the correct size – if the sample is too
large the diamonds and gasket will press directly on the sample, leading to non-hydrostatic conditions, while if the sample is too small, any superconducting transition may not be observed through the background. W-Re gaskets should not be used as they are too brittle at these low temperatures.
Chapter 6

Benzene

6.1 Theory

Since the discovery of superconductivity about 100 years ago, the dream of finding a room temperature superconductor has remained elusive. Currently the highest known $T_c$ value is only about half of room temperature – 138 K at ambient pressure [12] and about 160 K under pressure [13]. In 1968 Neal Ashcroft suggested that solid metallic hydrogen might be superconducting. Assuming BCS-like superconductivity, the low mass of hydrogen would enhance the critical temperature (see Eq. 2.3), possibly leading to a $T_c$ value near room temperature [19]. Under ambient pressure hydrogen is an electrical insulator. However, under sufficient pressure it is expected to become metallic. Static pressure measurements at low temperatures have shown no evidence of metallic hydrogen at 300+ GPa [62, 63, 175]. Recently, Eremets and Troyan reported that hydrogen became metallic at about 260-270 GPa at room temperature [176]. These results have not yet been substantiated by other groups, however, and considerable controversy exists regarding whether hydrogen has indeed been metallized [177–180].
In any case, hydrogen does not become metallic until at least 260 GPa. One possible way to reduce the metallization pressure is through chemical pre-compression, similar to the technique employed to first discover superconductivity above liquid nitrogen temperatures through substitution of Y for La to form YBCO [11]. The idea is that the combination of hydrogen with other elements may effectively compress the hydrogen, yielding an electronic structure that favors metallization at lower pressures. Neil Ashcroft has proposed that covalent hydrides such as CH₄, SiH₄, GeH₄, and PbH₄ and ternary, complex hydrides such as LiBH₄ and LiAlH₄ may serve as possible alternatives to metallic hydrogen [181–183].

Under sufficient pressure, all materials are expected to eventually become metallic. A simple method for predicting the onset of metallization was proposed by Goldhammer [184] and Herzfeld [185] before the theory of band structures in solids was even developed. By the Clausius-Mossotti relation,

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha}{3V} N_A = \frac{R}{V},
\]

where \(n\) is the index of refraction, \(\epsilon\) is the relative permittivity, \(\alpha\) is the molecular polarizability, \(V\) is the molar volume, \(N_A\) is Avagadro’s number, and \(R \equiv \left(\frac{4}{3}\pi\alpha\right) N_A\) is the molar refractivity. When the electrons are no longer bound, \(\epsilon \to \infty\), indicating that the material is a metal. When this occurs, \(R/V \to 1\). Thus, by the Goldhammer-Herzfeld criterion, a material is insulating for \(R/V < 1\) and metallic for \(R/V \geq 1\). Another way to think about this is to approximate each atom as a conducting sphere – then \(R = \frac{4}{3}\pi\alpha N_A\) is a measure of the volume occupied by a mole of conducting spheres. Electrons are free to move about the material when \(R/V \geq 1\) since the conducting spheres overlap. The material is therefore metallic. Application of pressure reduces the molar volume, so metallization occurs when a
critical volume $V_c = R$ is obtained. In this way, it is possible to make a simple prediction of metallization pressure. For more details, and for evidence of the accuracy of this remarkably simple criterion with regard to predicting metallic character, refer to Refs. [76, 186].

While the metallic character of materials may be assessed in various ways, one of the simplest techniques involves using the optical transparency to detect band gap transitions from a wide gap to metallic character. Insulators and semiconductors are characterized by a band gap between valence and conduction bands. Photons with energies higher than the band gap are absorbed, while photons with lower energies may pass through the material. As the band gap is reduced through the visible range from $\sim 3.1$ eV (400 nm) to $\sim 1.8$ eV (700 nm), the higher energy blue photons will be absorbed first, causing the material to appear yellow. As the band gap decreases further, lower energy photons will be absorbed, causing the sample to progressively turn from orange to dark orange to red. Eventually, the sample will appear black when the entire visible spectrum is absorbed by the material. This does not, however, necessarily indicate metallic character, as a band gap $\lesssim 1.8$ eV may still exist. For materials with a direct gap, the band gap energy is seen as a sharp edge in the transmission spectrum. Thermal broadening of the edge in indirect band gap materials makes it more difficult to determine the exact band gap energy. This technique has been utilized in high pressure measurements on LiBH$_4$ and LiAlH$_4$ to 53 and 42 GPa, respectively [76]. At the highest pressures observed, neither of these materials is metallic, although a reduction of the band gap is observed in LiAlH$_4$ at 37 GPa when the sample begins to turn orange. Similarly, measurements on hydrogen have reported darkening of the sample at pressures near 300 GPa [62, 175].

One hydrogen-rich compound that deserves consideration is benzene – C$_6$H$_6$. In a recent
6.1 Bond structure of benzene (C$_6$H$_6$) under ambient conditions. The hexagonal ring consists of six carbon atoms with alternating single and double bonds. A hydrogen atom is bound to each carbon atom.

6.2 Previous Studies

Benzene was first isolated in 1833 by Michael Faraday and is today considered a hallmark of organic chemistry. As the simplest of the aromatic hydrocarbons, it consists of a hexagon of alternating single and double bonds between carbon atoms, as seen in Fig. 6.1. Each carbon atom is bonded to a single hydrogen atom. Under ambient conditions, benzene is a liquid with a freezing point of 279 K and a boiling point of 353 K. Upon freezing or with modest pressure application of 0.07 GPa at room temperature, benzene crystallizes into
an orthorhombic \textit{P}bca structure with four molecules per unit cell [188, 189]. Phase I has
been well studied, and results include measurements of the lattice and internal vibrational
modes using Raman spectroscopy [190–196]. For the \textit{P}bca structure, 12 Raman-active lattice
modes are predicted [191, 192], several of which have been observed experimentally. Benzene
also has ten Raman active vibration bands [193] that correspond to the internal vibrational
modes. For each of these modes, either four or eight Raman active components are expected,
depending on symmetry. Under pressure these Raman lines shift to higher frequency. Bands
may also be resolved into components due to larger splitting. This is seen in various studies
of the pressure-dependence of the internal vibrational modes of crystalline benzene to about
30 GPa [193–196]. Phase changes may be indicated by changes in the slope of the pressure
dependences.

Crystalline benzene under pressure was first studied by Bridgman [197]. Since then, it
has been studied experimentally to about 30 GPa, resulting in two main phase diagrams for
solid benzene. In 1988 Thiéry and Léger studied benzene at room temperature to 25 GPa
using Raman spectroscopy and x-ray diffraction [193]. They suggest the presence of an inter-
mediate phase I’ based on discontinuities in lattice constants. At slightly higher pressures,
benzene transforms to phase II (\textit{P}4_3\textit{2}_1\textit{2}) between 1.4 GPa and 4 GPa and to a monoclinic
phase III (\textit{P}2_1/c) with two molecules per unit cell. Upon further application of pressure
above 11 GPa, phase III’, which is a slight modification of phase III, persists until 24 GPa.
Benzene IV is stable at higher pressures. More recently, Ciabini \textit{et al.} [198, 199] developed
another phase diagram based on infrared spectroscopy and x-ray diffraction. Their mea-
surements indicate fewer phases, with a transformation from phase I to phase II (\textit{P}2_1/c)
at $\sim$ 1.5 GPa which is stable to about 20–25 GPa. At higher pressures, a chemical re-
action between the benzene units occurs. Note that phase II proposed by Ciabini et al.
is the same as phase III referred to by Thiéry and Léger. This transition to the mono-
clinic ($P2_1/c$) structure is consistent with measurements by Piermarini et al. and Katrusiak
et al. [200, 201]. Earlier measurements by Ciabini et al. [196] had indicated a transition
between benzene phases II and III at 4.8 GPa and between phases III and III' at 11.2 GPa,
using the same notation as Thiéry and Léger. It is possible that the apparent inconsistencies
between these two phase diagrams may be the result of technological improvements [187].
It is well known that the phase transitions of benzene at room temperature are extremely
sluggish – annealing benzene at temperatures of at least 370 K ensures the completion of
the phase transition [192, 198]. Intermediate phases reported in earlier measurements could
be due to the metastability of phase I upon pressurization at room temperature.

Theoretically, Raiteri proposed several high pressure phases of benzene based on a crystal
structure prediction method – phases I ($Pbca$), II ($P4_32_12$), and III ($P2_1/c$) were reproduced
utilizing a metadynamics method [202]. Very recently, Wen, Hoffman, and Ashcroft con-
ducted a theoretical study of benzene to 300 GPa in which they calculated enthalpy as a
function of pressure [187]. Structure optimization reproduced these same three phases at
lower pressures. Enthalpy calculations indicate that phase III transforms to phase V ($P2_1$)
above 40 GPa before undergoing a spontaneous chemical reaction at 80 GPa to a polymeric
phase ‘polymer I’. However, it turns out that phase V is dynamically unstable, and polymer
I is more stable at all pressures. On the other hand, molecular phase III remains dynamically
stable to about 190 GPa, with a pressure-induced chemical transformation occurring only at
∼ 200 GPa. At this point, phase III transforms to ‘polymer II’. In fact, Wen et al. found that
saturated, four-coordinate C-H phases are more stable at all pressures than phases containing
discrete benzene molecules. However, significant barriers to polymerization most likely prevent spontaneous conversion to these polymeric phases. Calculations indicate that the band gap vanishes at $\sim 180 \text{ GPa}$. Thus, it is possible that metallic benzene may exist in the narrow pressure range 180–200 GPa. Let us consider the Goldhammer-Herzfeld criterion for metalization. Benzene has an average polarizability $\alpha = 67.55 \text{ bohr}^3 = 1.001 \times 10^{-23} \text{ cm}^{-1}$ [187] and a molar volume of $89.12 \text{ cm}^{-1}/\text{mol}$ under ambient conditions. Substituting this into the Goldhammer-Herzfeld criterion yields $4\pi \alpha N_A/3V = R/V = 0.283$ at ambient pressure. Then one expects metallization for $R/V = 1$ when the material has been compressed by a factor of $\sim 3.5$. This is in fairly good agreement with calculations by Wen et al. that the band gap of benzene shrinks to zero at 180 GPa when the relative compression is about 3.3. The group speculated that in this narrow pressure regime, benzene could be a phase coherent Kekulé metal and serve as a possible basis of high-temperature superconductivity [187, 203].

### 6.3 My Results

Three high pressure experiments (subsequently referred to as M1, M2, and M3) were conducted on high purity benzene to determine whether it becomes metallic as predicted by [187]. Each experiment was performed using 0.1 mm culet anvils bevelled at a 7.5° angle to 0.3 mm. A 250 $\mu$m thick Re gasket, pre-indented to a thickness of 20–25 $\mu$m was employed. A hole with diameter $\sim 50 \mu$m (54 $\mu$m for M1 and M3, 43 $\mu$m for M2), was drilled through the center of the gasket. Experiments were set up with the side-by-side coil system so that ac-susceptibility measurements could be performed to probe for superconductivity in the case that metallization of benzene was observed.

As benzene is a liquid, loading it requires a different technique than for solid samples.
Using a syringe, a large droplet is placed on top of the gasket, as seen in Fig. 6.2. A thin needle or wire (in this case 15 µm Cu wire) is lowered into the hole in the gasket. Any air pockets in the sample will attach themselves to the wire and traverse up the wire, thereby freeing the sample space of any air bubbles. These air pockets must be removed immediately after placing the droplet on the gasket, before closing and tightening the cell to apply slight pressure to the sample. Benzene has a high vapor pressure, so sample loading must be performed quickly. This prevents the benzene from completely evaporating, trapping liquid benzene in the sample space. Successful sample loadings were typically completed in about one minute. Due to the fact that the sample was liquid, I found it vital that the entire gasket (not just the culet and pre-indentated area) was extremely clean before loading the sample. Otherwise, any dirt on the surface of the gasket would be drawn into the sample space by the liquid as it evaporated. The entire procedure was performed inside the fume hood due to benzene’s carcinogenic properties and high flammability. After loading the benzene,
Figure 6.3: Benzene in the cell is imaged using transmitted light at ambient pressure. On the left, an air bubble can be seen in the sample space. Assuming a spherical bubble, the volume of air is about 5% of the sample space volume and would collapse immediately when pressure is applied, but the sample was reloaded to avoid worrying about impurities. In the center, the benzene is in three smaller droplets with air between the regions and several small air bubbles. On the right, the benzene is uniform with no air bubbles, indicating successful loading.

The sample was checked with both transmitted and reflected light using the metallurgical microscope to ensure that no bubbles were present. Fig. 6.3 shows several photographs of benzene at ambient pressure using transmitted light.

In the first experiment, a 99.8% purity benzene sample acquired from Dr. Sophia Hayes’ lab in the chemistry department was used, while subsequent experiments utilized a 99.9% purity sample of benzene from Alfa Aesar. Raman spectra were taken at the center of the sample at each pressure, and the high frequency edge of the diamond vibron was used for pressure determination. Note that the d’Anvils diamonds used were cut along a random orientation. Therefore, depending on the orientation of the diamonds, it is possible that Raman measurements could have overestimated the pressure by up to 10% (see Sec. 3.3.2). At the lowest pressures, to about 20 GPa, no clear high frequency edge was seen in the diamond vibron peak. Rather, pressure increase could be seen through broadening of the high frequency side of the diamond vibron peak. This broadening was used to determine pressure in order to prevent significant overestimation of pressure.
Figure 6.4: Sample vs. membrane pressure for benzene measurements. In each case a Re gasket and diamonds with a 0.1 mm culet bevelled from 0.3 mm at 7.5° were used. In the first and third measurement, the final pressure (open symbol) was estimated using the membrane pressure as diamond failure occurred before pressure could be measured.

Fig. 6.4 shows a plot of sample vs. membrane pressure for each of the three experiments. Upon tightly closing the cell for each measurement, a pressure of 5–10 GPa was present at the sample, even with no membrane pressure, so the sample would be solidified. The initial gradual pressure increase was followed by a sharp increase in the sample pressure. At higher pressure the sample vs. membrane pressure leveled out slightly. Pressures of 195 and 213 GPa were obtained for M1 and M3, respectively. This is the highest pressure attained to date in our lab! These final pressures were estimated using the membrane pressure, as diamond failure occurred before the pressure measurement could be completed. For M2,
elongation of the gasket hole was observed upon pressure increase, and the hole shifted away from the center of the gasket. This is indicative of impending gasket failure. We therefore halted the experiment at 54 GPa and slowly released pressure in order to save the diamonds.

In the first experiment diamond failure occurred immediately upon focusing the laser on the diamond culet to perform the pressure measurement. This could be due to heating and strains induced in the diamond by the high laser power. Power output of the laser was 30 mW, although this would be lower at the diamond culet as the beam intensity would be reduced slightly by the mirrors and lenses in the optical path. In order to minimize possible heating effects on the diamond, the laser power was reduced for subsequent measurements by a factor of \( \sim 10 \) using neutral density filters. To compensate for the reduced laser intensity, exposure times for measurements of the Raman spectra were significantly increased. In order to determine the pressure distribution across the sample, at several pressures the laser spot was focused at various distances from the center of the culet. Measurements indicated that while there was a 20-30% drop-off in pressure from the edge of the sample to the edge of the 100 \( \mu \text{m} \) culet, and another drop-off to the edge of the 300 \( \mu \text{m} \) bevelled culet, the pressure across the sample was almost constant, at higher pressures varying by less than 5%, as seen in Fig. 6.5.

### 6.3.1 Raman Spectroscopy

While measuring the diamond vibron to determine pressure, several Raman peaks from internal vibrational modes of benzene were also observed at low pressures, as seen in Fig. 6.6. A linear background subtraction was made and the position of the peaks determined with a resolution \( \pm 5 \text{ cm}^{-1} \). Due to the small sample size of the benzene, it is not surprising
that these peaks have much lower intensity than the diamond vibron – even the highest intensity Raman peak of benzene is weaker by a factor of about 40. As pressure was increased, these lines gradually disappeared, so we were unable to study the pressure dependence of the Raman spectra to the highest pressures. The disappearance of the Raman lines from benzene is likely due to a combination of decreasing intensity of the Raman peaks from benzene and increased diamond fluorescence. A peak in the Raman spectrum seen at $\sim 750 \text{ cm}^{-1}$ does not correspond to any known benzene line. This line, which persists to high pressure can also be seen in Raman spectra of pressure measurements taken at the diamond table, clearly
Figure 6.6: Raman spectrum of benzene at various pressures. Exposure times for each spectrum are identical, although intensity units are arbitrary. After making a linear background subtraction, spectra have been shifted vertically for clarity of viewing. At $\sim 1350 \text{ cm}^{-1}$, the lower portion of the peak from the diamond vibron is visible. Locations of ambient pressure vibrational bands, based on Thiéry and Léger [193] are indicated by labelled dotted vertical lines. Observed vibrational modes of benzene are indicated by short vertical lines below each spectrum. Pressure increase can be observed through the shift of the high frequency edge of the vibron. At the lowest pressure, seven benzene peaks are visible. The peak at $\sim 750 \text{ cm}^{-1}$, which is indicated by downward arrows and which persists to high pressures, does not correspond to any vibrational mode of benzene, and is in fact also visible in Raman measurements of the pressure at the table of the diamond. Upon increasing pressure, the benzene peaks gradually weaken, until only one peak is visible at 43.9 GPa. Above that pressure, no more Raman peaks are visible from the benzene.
Figure 6.7: Pressure dependence of several Raman peaks of benzene to 20 GPa. For each internal vibrational band of benzene, at most only one peak can be seen. However, good agreement is seen between peak position in the current measurements at 6.3, 12.7, and 18.1 GPa and those found by Thiéry and Léger [193] at 0, 1.4, 2.7, 4.9, and 11.0 GPa. As expected these peaks shift to higher frequency upon increasing pressure.

indicating that it does not correspond to benzene or any sample impurity. Possibly it is related to reflections of the laser inside the cell.

At the lowest pressure, seven peaks from benzene were observed, corresponding to various vibrational bands. In fact, previous studies have shown that each of these bands is actually represented by a combination of several peaks. In our case, only a single peak is resolved at each frequency. Thus, in each case, either only the strongest of the bands is seen or only a single band can be resolved. A comparison of these peaks and their pressure dependence with those found by Thiéry and Léger [193] shows good agreement, as seen in Fig. 6.7. As expected, the peaks shift to higher frequency upon application of pressure. At the lowest
Frequency (cm$^{-1}$) & Vibrational Mode & \\
6.3 GPa & 12.7 GPa & 18.1 GPa & 43.9 GPa & \\
--- & --- & --- & --- & \\
605 & 616 & – & – & $\nu_6$ ($e_{2g}$) \ in-plane C-C-C bond angle bending & \\
856 & 861 & – & – & $\nu_{10}$ ($e_{1g}$) \ angle C-H bending & \\
1004 & 1060 & 1073 & 1113 & $\nu_1$ ($a_{1g}$) \ ring breathing mode & \\
1185 & 1206 & 1212 & – & $\nu_9$ ($e_{2g}$) \ C-H in-plane bending & \\
1596 & 1637 & 1649 & – & $\nu_8$ ($e_{2g}$) \ resonance with $\nu_1 + \nu_6$ \ ? & \\
3100 & – & – & – & $\nu_7$ ($e_{2g}$) \ C-H stretching mode & \\
3150 & – & – & – & $\nu_2$ ($a_{2g}$) \ symmetric C-H in-phase stretching & \\

Table 6.1: Raman lines of benzene were observed at low pressures. These lines have tentatively been assigned vibrational modes based on the publication by Thiéry and Léger [193].

pressure, six peaks to benzene are visible. The position of these peaks as a function of pressure can be seen in Table 6.1 alongside the vibrational modes that are tentatively assigned to these peaks based on their intensities and on analysis performed by Thiéry and Léger. Bands are labelled according to a numbering convention developed for benzene in 1934 [204].

The most intense peaks, in order of decreasing intensity, are expected to correspond to peaks in the $\nu_1$, $\nu_9$, and $\nu_2$ bands. It is not surprising, then, that the $\nu_1$ and $\nu_9$ peaks are among the last to disappear. Despite the intensity of $\nu_2$, it cannot be seen at higher pressures. Since this peak was already near the edge of the spectral range at 6.3 GPa, it is possible that, along with $\nu_7$, it shifted outside the measurement range with application of pressure.

### 6.3.2 Optical Transparency

In order to search for possible metallicity of benzene at high pressures and to observe any reduction in the band gap, white light was transmitted through the sample. At each pressure, photographs were taken through the metallurgical microscope using a Nikon 5000 Coolpix digital camera set for a range of exposure times. In addition, the sample was carefully
observed visually for signs of reduction of the band gap. Unfortunately, I was unable to measure the band gap edge using the spectrometer, perhaps due to the low intensity of the white light that could be transmitted through the sample for optical measurement.

Despite using the same camera settings including exposure time for photographs, the sample color was not consistent from one photograph to the next. However, it is still clear from the photographs that benzene remains transparent to the highest pressures, as can be seen in Fig. 6.8. Changes in the color of the sample were also observed by the naked eye. No change in the color was seen upon each incremental increase of pressure, but the sample was clearly a darker yellow/light orange color at the highest pressure compared to the initial color at ambient pressure. Darkening of the sample is an indication that the band gap was indeed narrowing. However, the sample never became opaque. Therefore, our measurements indicate that benzene remains insulating to 213 GPa, and does not become metallic in the narrow pressure regime 180–200 GPa as predicted by Wen et al. [187]. Note that these predictions were made based on calculations performed at absolute zero, so it is possible that benzene might become metallic at still higher pressures. Structural transformations in benzene have also been shown to be quite sluggish at room temperature, where our measurements were carried out. It is therefore possible that the structural transformations predicted by Wen et al. occur at higher pressures or upon thermal activation. In order to test this, future experimental measurements should be carried out to determine the high pressure structure and to precisely measure the band gap.
Figure 6.8: Images of benzene at various pressures using transmitted light (smaller photographs) and a combination of transmitted and reflected light (larger photographs). All images are set to the same scale with the same approximate orientation. Pressures indicated in parentheses were estimated from the membrane pressure. The red circle in the photograph at the top left indicates the original size of the sample space. Although camera exposure time is $\frac{1}{2}$ second for each image, the color of transmitted light seen in the photographs is not consistent from one image to the next. However, it is clear that even at the highest pressure, the sample is still transparent to some visible light and is therefore not metallic. Visual observation with the naked eye showed no clear change in the color upon each incremental increase of pressure, but the sample was a dark yellow/orange at the completion of the experiment compared to almost white at the beginning. This clearly indicates a reduction in the band gap. Slight deformation of the sample space may be seen under pressure. In addition, some structure is visible at higher pressure. This is especially noticeable in comparing the image at 7 GPa with the two images at 16 GPa, taken a day apart. In the second of these images, the structural features in the sample are less visible. Benzene transitions are notoriously sluggish at room temperature, so this is a good indication that the passage of time enabled the sample to homogenize slightly.
Chapter 7

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

7.1 High-$T_c$ Cuprate Superconductors

In 1986 J. G. Bednorz and K. A. Müller, researchers at the IBM Research Laboratory in Zurich, detected superconductivity at about 30 K in the ceramic material Ba$_x$La$_{5-x}$Cu$_5$O$_{5(3-y)}$ (LBCO) [9], setting a new record for the highest $T_c$ value for any known superconductor. Previously, this record had been held at $T_c = 23.2$ K by Nb$_3$Ge [205]. Their breakthrough discovery earned Bednorz and Müller the 1987 Nobel Prize in Physics. Upon application of pressure, Chu et al. showed that $T_c$ increases rapidly to about 40 K at a pressure of 13 kbar [10]. By replacing La with the smaller Y element, researchers were able to induce chemical pressure. Astoundingly, $T_c$ for (Y$_{1-x}$Ba$_x$)$_2$CuO$_{4-\delta}$ reaches an onset $T_c = 93$ K, with the resistance falling to zero at 80 K [11]. The appearance of high-temperature superconductivity in this material, now commonly referred to as YBCO, represented a vital breakthrough in studies of superconductivity, as the technological and psychological barrier signified by the boiling point of liquid nitrogen at 77 K was surpassed for the first time. A flurry of research followed this discovery, and many other high temperature cuprate superconductors
Figure 7.1: Each unit cell of cuprate superconductors consists of $m$ layers of CuO$_2$ planes between block layers (thick and white). In the three-layered compound, the CuO$_2$ planes are topologically inequivalent, distinguished above by thin gray and white layers. The set of CuO$_2$ layers sandwiched between the block layers may be referred to as a planar group. Figure from Ref. [206].

have since been found. Today, the highest known $T_c$ at ambient pressure is 138 K in the Tl-doped Hg-1223 cuprate [12], while under pressure $T_c$ reaches about 160 K [13].

The cuprate superconductors are unconventional in that they can not be described by BCS theory. In more than 25 years since their discovery, the microscopic mechanism responsible for superconductivity in these materials has not been clearly identified. The cuprates are characterized by a layered structure with CuO$_2$ planes sandwiched between oxide block layers, as seen in Fig. 7.1. The compounds are often referred to in terms of the number of CuO$_2$ layers, $m$, in the unit cell. As the number of layers increases from one to three, the maximum $T_c$ of each superconductor ($T_{c_{\text{max}}}$) also increases. The layered structure makes the cuprates quasi two-dimensional and results in highly anisotropic properties, as evidenced in uniaxial pressure dependences and electrical conductivity. The parent compounds are antiferromagnetic Mott insulators. Doping (either electrons or, more commonly, holes) in the CuO$_2$ planes suppresses the antiferromagnetism, allowing superconductivity to emerge. As doping levels increase, $T_c$ follows an inverted parabolic shape, reaching a maximum $T_{c_{\text{max}}}$ at optimal doping, $n_{\text{opt}}$. This parabolic dependence can be described in terms of the hole
carrier concentration \( n \) per Cu cation in the CuO\(_2\) sheet by the canonical equation

\[
T_c(n) = T_c^{\text{max}} [1 - \beta (n - n_{\text{opt}})^2],
\]

where \( \beta = 82.6 \) and \( n_{\text{opt}} \approx 0.16 \) \[207, 208\]. For \( n < n_{\text{opt}} \), the sample is referred to as underdoped, while \( n > n_{\text{opt}} \) for overdoped samples. Fig. 7.2 shows a typical phase diagram for the cuprate materials.

Application of pressure is known to increase doping levels. It is, therefore, not surprising that the pressure-dependence of \( T_c \) for most cuprate superconductors also follows an inverted bell-shaped curve \[206\]. Pressure dependences for several cuprate superconductors may be seen in Fig. 7.3 \[210\].
Figure 7.3: Pressure dependence is shown for various cuprate superconductors. In most cases, $T_c$ increases initially with pressure, reaching a maximum pressure as it follows a bell-shaped curve. Figure taken from [210].
If only $n$ is pressure dependent, as predicted by the simple charge-transfer model, one would expect that $dT_c/dP = 0$ at optimal doping, as $T_c$ is already maximized. However, this is not the case, as experiments show that $dT_c/dP > 0$ at optimal doping. There exists an intrinsic pressure dependence, so the total pressure dependence is best described by [211]

$$\frac{dT_c}{dP} = \left( \frac{dT_c}{dn} \right) \left( \frac{dn}{dP} \right) + \left( \frac{dT_c}{dP} \right)^{int}. \quad (7.2)$$

For optimally doped cuprates with $T_c \geq 90$ K, the intrinsic pressure dependence is about $+1$ to $+2$ K/GPa [77].

Most high temperature superconductors contain oxygen defects, the concentration and relative positions of which can greatly influence the normal and superconducting properties of the cuprates. These defects are quite mobile, even at room temperature, leading to a phenomenon known as oxygen ordering. In Y-123, for example, $T_c$ may be changed by quenching the sample in liquid nitrogen [212]. Pressure can also induce oxygen ordering effects [213–216]. In Tl-2201, for example, $T_c$ decreases upon initial application of pressure at room temperature. Upon releasing pressure at low temperature, however, $T_c$ decreases further! Annealing the sample at progressively higher temperatures gradually increases $T_c$ until it finally returns to its initial value [217]. Effects of oxygen ordering may be minimized by carrying out the entire experiment at low temperature so that the oxygen defects are frozen in place, or by determining pressure dependences on optimally doped samples, where $T_c$ is maximized and pressure-induced charge transfer from oxygen ordering should have no effect.

The high structural complexity of these cuprate superconductors has hindered efforts to develop a microscopic model of superconductivity in these layered materials. In addition
to an intrinsic pressure dependence, application of pressure can induce oxygen ordering, change doping levels, and alter the structure of the material. The use of different pressure media can also affect pressure dependences due to the presence or absence of shear stresses [218]. For reviews of pressure effects in high-$T_c$ cuprates, refer to several review articles [20, 21, 206, 210, 219–221]. The diversity of high pressure results is a testament to the importance of determining the intrinsic pressure dependence in order to develop a model of the superconducting mechanism and understand how $T_c$ can be further enhanced.

7.2 Previous Studies

Among the cuprate superconductors, the one-, two-, and three-layered Hg compounds, HgBa$_2$Ca$_{m-1}$Cu$_m$O$_{2m+2+\delta}$, commonly referred to as Hg-12(m-1)m, $T_c$ ranges from 94 K in Hg-1201 [222] to 134 K in Hg-1223 [223]. Hydrostatic pressure studies on optimally doped, polycrystalline Hg-1201 show an initial pressure dependence $dT_c/dP = + 1.75$ K/GPa [224]. Incredibly, Hg-1221 and Hg-1223 also show the same initial hydrostatic pressure dependence despite their markedly different ambient pressure $T_c$ values [225]. Even to higher pressure (up to 45 GPa), studies show that these materials have very similar pressure dependences, with $T_c(P) - T_c(P = 0)$ being almost identical in each case [13]. Near 30 GPa $T_c$ for Hg-1223 material reaches about 160 K, currently the highest $T_c$ among all known superconductors.

In a quest to understand the superconducting mechanism in the high-$T_c$ cuprates and to further enhance $T_c$, it is important to try and understand how $T_c$ depends on various parameters. In addition to altering the carrier concentration, applied pressure can change the area, separation, and flatness of the CuO$_2$ planes in cuprate superconductors. One way to extract information regarding which of these parameters is responsible for increasing $T_c$
is to determine uniaxial pressure derivatives, \( dT_c/dP_i \). Experiments on two optimally doped cuprates with orthorhombic structure, La\(_{2-x}\)Sr\(_x\)CuO\(_4\) (La-214) [226] and Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) (Bi-2212) [227] revealed a negative pressure dependence \( dT_c/dP_c \) which is larger in magnitude than the positive pressure dependences \( dT_c/dP_a \) and \( dT_c/dP_b \). However, experiments on optimally doped YBa\(_2\)Cu\(_3\)O\(_{6.95}\) [228, 229] indicate that \( dT_c/dP_c \) is almost negligible, with \( dT_c/dP_a \) and \( dT_c/dP_b \) having opposite signs, but being almost identical in magnitude. In-depth hydrostatic and uniaxial pressure studies on the one-, two-, and three-layered Hg compounds can help us to understand these seemingly contradictory results. With their simpler tetragonal structure, these compounds only have two partial pressure derivatives that need to be considered, \( dT_c/dP_a \) and \( dT_c/dP_c \).

### 7.3 Experimental Results

Recently, high quality single crystals of Hg-1201 have become available [230, 231], enabling uniaxial pressure studies. In the course of this research, I carried out hydrostatic He-gas measurements on a (nearly) optimally doped, single crystalline Hg-1201 (0.7 mg). Crystals were received from Neven Bari\’si\’c in Stuttgart. These measurements were performed in conjunction with thermal expansion and specific heat measurements made by collaborators in Karlsruhe to determine uniaxial pressure dependences [232]. The ambient pressure superconducting transition was first measured using ac-susceptibility, giving \( T_c = 94.85 \) K at the midpoint (see Fig. 7.4). After applying pressure at room temperature to 0.76 (0.69) GPa, pressure was subsequently released at 170 K to 0.45 (0.42) GPa and to 0.21 (0.21) GPa at 105 K. Numbers in parentheses correspond to sample pressure at the transition temperature. Finally, pressure was completely released at 140 K. At each pressure, the superconducting
transition was measured several times to ensure reproducibility within 20 mK. Note that for two of the measurements (0.69 GPa and 0.42 GPa), a connection existed between the primary coil and ground, resulting in a phase change of 19°. The phase change in these two measurements was corrected for using the lock-in-amplifier, and upon reduction in the pressure to 0.21 GPa, the connection from the primary coil to ground disappeared. Size and phase of the superconducting transition returned to the same values present during the initial ambient pressure measurement. Fig. 7.4 shows the real part of ac-susceptibility measurements at each pressure. The signal was converted to emu/cm³ in terms of $4\pi\chi$ using the density 7.0 g/cm³. Results are consistent with full shielding. No correction has been made for the demagnetization factor. The transition remains sharp even under pressure, with the 10%-90% transition width $\Delta T_c \approx 0.3$ K.

At ambient pressure $T_c$ was determined using the transition midpoint, while $T_c$ under pressure was determined using the shift of the entire superconducting transition. After initial pressure application and cooling, temperatures were kept below 170 K throughout the remainder of the experiment. Upon releasing to ambient pressure, $T_c$ returns to its original value, thereby indicating that $T_c(P)$ is a reversible function of pressure, regardless of the temperature at which pressure is changed – i.e., no pressure-induced oxygen ordering effects were observed. A linear least-squared fit to the data yields $dT_c/dP = +1.48(5)$ K/GPa. A better fit is obtained with the quadratic fit, $T_c(K) = 94.85 + 1.21(8)P + 0.49(13)P^2$, where $P$ is the pressure in GPa. Fig. 7.5 shows a plot of $T_c(P)$ for the sample, along with both the linear and quadratic fits to the data.

Using jumps in thermal expansion coefficients ($\Delta\alpha_i$) and molar specific heats ($\Delta C_p$) at $T_c$ measured by collaborators (details may be found in Hardy et al. [232]), partial pressure
Figure 7.4: Ac-susceptibility for Hg-1201 is seen at various hydrostatic pressures. Ambient pressure $T_c$ is determined using the midpoint of the transition, while $T_c$ under pressure is determined with respect to this midpoint using the shift of the superconducting curve. No demagnetization factor has been taken into account.
Figure 7.5: $T_c$ versus pressure for single-crystalline Hg-1201 under hydrostatic pressure from ac-susceptibility data. Numbers give order of measurements. $T_c(P)$ is a reversible function of pressure. Data is fitted by both a linear least-squares fit (dashed red line) and by a quadratic function (solid black line).
derivatives can be determined using the Ehrenfest relation

\[
\frac{dT_c}{dP_i} = \frac{\Delta \alpha_i V_m T_c}{\Delta C_p},
\]

where \(V_m\) is the molar volume. Doing so indicates that the partial pressure derivatives are highly anisotropic, yielding \(dT_c/dP_a = +2.3(2)\) K/GPa and \(dT_c/dP_c = -3.6(3)\) K/GPa. For tetragonal structures, the total pressure derivative is given by \(dT_c/dP = 2dT_c/dP_a + dT_c/dP_c = 1.0(7)\) K/GPa. This is in good agreement with the initial pressure dependence \(dT_c/dP = +1.21(8)\) K/GPa from hydrostatic He-gas measurements.

For nearly optimally doped Hg-1201, then, it is clear that \(dT_c/dP_c\) is negative and larger in magnitude than the positive derivative \(dT_c/dP_a\). \(T_{c_{\text{max}}}^c\) can be enhanced either by reducing the area of the CuO\(_2\) planes or by increasing their planar separation, i.e., by increasing the \(c/a\) ratio of the lattice constants. Appreciable cancellation in the partial pressure derivatives leads to a total hydrostatic pressure dependence \(dT_c/dP\) which is much smaller in magnitude than either of the partial pressure derivatives. As seen in Fig. 7.6, these results are similar to those observed in optimally doped La-214 [226], Bi-2212 [227], and Hg-1223 [233], suggesting that this behavior is intrinsic to the cuprate superconductors, and that Y-123 [228, 229] is anomalous.

What structural features, then, are responsible for increasing \(T_c\) when the \(c\)-axis expands or the area of the CuO\(_2\) planes is compressed? Hydrostatic and partial pressure derivatives in the one-, two-, and three-layer Hg compounds are remarkably similar [225] despite the large difference in ambient pressure \(T_c\) values at optimal doping (94 K, 127 K, and 133 K, respectively) [222, 223, 225]. This suggests that the separation \textit{between} the CuO\(_2\) planar groups, rather than the separation of the CuO\(_2\) planes \textit{within} a group is responsible for the
increase in $T_c$ (refer to Fig. 7.1). In addition, Jorgensen et al. has shown that $T_c$ in the two-layer cuprates is correlated with the Cu-O apical bond distance and with the closely related in-plane buckling angle [234]. Our results agree qualitatively with this finding if we assume that the Cu-O apical bond distance increases with the length of the c-axis. This has indeed been shown to be the case in hydrostatic high-pressure neutron diffraction studies on Hg-1201 and Hg-1223 [235].

Measurement results conclusively show that the partial pressure derivatives are highly anisotropic. $T_c$ can be enhanced by increasing the $c/a$ ratio. As this agrees with earlier findings for La-214 and Bi-2212, results suggest that this behavior is intrinsic to the cuprates.
Any microscopic theory later developed for the high-$T_c$ cuprates needs to be able to predict this pressure dependence. These findings, then, will hopefully help to narrow down the vast number of proposed superconducting mechanisms in these materials.
Chapter 8

\[ \text{LnFePO (Ln = La, Pr, Nd)} \]

8.1 Iron-based Superconductors

A new class of iron-based superconductors first emerged in 2006 with the observation of superconductivity near 4 K in LaFePO \cite{236}. It was the discovery two years later of superconductivity at 26 K in the isostructural compound LaFeAsO$_{1-x}$F$_x$ \cite{14}, however, that spurred a flurry of research. Substitution of La with other lanthanides leads to an enhancement of superconductivity, with $T_c$ reaching as high as 55 K in SmFeAsO$_{1-x}$F$_x$ \cite{15,237}. In just a few short years, the number of compounds belonging to this new class of superconducting materials has expanded rapidly. The high transition temperatures, second only to the cuprate superconductors, that are observed in these compounds are surprising, as one would expect the presence of ferromagnetic iron to suppress superconductivity.

The “parent” compound of the iron-based superconductors exhibits an antiferromagnetic phase. Suppression of this phase through chemical doping or through application of high pressure leads to the emergence of a superconducting dome-shaped region, as seen in Fig. 8.1 \cite{79}. Like the cuprate superconductors, the iron-based superconductors are characterized by a
layered structure. An iron pnictide or iron chalcogenide layer is responsible for superconductivity. Compounds are grouped into various families based on their structures. Five tetragonal structures, shown in Fig. 8.2, are known to support superconductivity in the iron-based materials. The maximum ambient pressure $T_c$ value for each of these structures is 14 K in 11-type [238], 18 K in 111-type [239], 38 K in 122-type [240], 55 K in 1111-type [15, 237], and 37 K in 32522-type [241]. As a result of systematic studies, various models have been proposed that relate $T_c$ to the anion height of the Fe layer [242] and to the Fe-As-Fe bond angle [243].

Complex electronic and magnetic behavior is evident in the iron-based superconductors, which exhibit non-BCS characteristics. The superconducting state is, therefore, believed to be unconventional, and debate exists regarding the nature of the superconducting mechanism, and whether or not it is the same as for the cuprate superconductors. High pressure
Figure 8.2: Five layered tetragonal structures are known to support superconductivity in the iron-based materials. Crystal structures of these five families – 11-type, 111-type, 122-type, 1111-type, and 32522-type – are shown above. Below each structure is listed one of the compounds belonging to each family. Common among each family is an iron pnictide or iron chalcogenide layer responsible for superconductivity. Figure taken from Ref. [50].
studies are vital for furthering our understanding of this class of materials. Pursuant to this goal, a series of high pressure measurements have been carried out on $LnFePO$ ($Ln = \text{La–Nd, Sm, Gd}$). For more information regarding the iron-based superconductors, the reader is referred to several extensive review articles encompassing studies of structural, transport, magnetic, and optical properties [50, 78, 244–246].

8.2 Previous Studies

Among the iron-based superconductors, the rare-earth transition metal phosphide oxides $LnFePO$ ($Ln = \text{La–Nd, Sm, Gd}$) have not been studied as extensively due to their low superconducting transition temperatures. These compounds were first synthesized and characterized in 1995 and were found to crystallize in a ZrCuSiAs-type structure, a tetragonal structure containing two formula units in the primitive cell [247]. It was not until more than a decade later, however, that superconductivity was discovered in LaFePO near 4 K [236] using both resistivity and susceptibility measurements. Superconductivity was also subsequently observed in SmFePO at $\sim 3$ K [248], in PrFePO and NdFePO at 3.2 K and 3.1 K, respectively [249], and in GdFePO at about 6.1 K [250]. CeFePO, on the other hand, remains non-superconducting to 400 mK [251]. Like the other iron-based superconductors, the LnFePO compounds are layered, consisting of alternating layers of lanthanide oxide ($Ln^{3+}O^{2-}$) and iron phosphorus ($Fe^{2+}P^{3-}$) [236, 247, 252].

Following the discovery of superconductivity in LaFePO, attention turned to the study of the effect of pressure on the transition temperature. Two independent sets of measurements indicated that $T_c$ initially increased with pressure before passing through a maximum. The detailed pressure dependences, however, differed greatly, as seen in Fig. 8.3. Non-
Figure 8.3: Previously published measurements of LaFePO under pressure show $T_c$ initially increasing and passing through a maximum before subsequently decreasing. Measurements by Hamlin et al. [253] show that $T_c$ of a non-crystalline sample initially increases at about $+0.5 \text{ K/GPa}$, reaching a maximum temperature at 5.4 GPa. Horizontal error bars indicate the pressure gradient. For measurements by Igawa et al. [254] on a polycrystalline sample, $T_c$ initially increases much more rapidly ($+4.0 \text{ K/GPa}$), passing through a maximum at 0.8 GPa. For each measurement the legend lists the type of pressure cell, the pressure medium, and whether $T_c$ was determined from the onset temperature of resistivity (black, $\rho$) or magnetization (red, $M$) measurements. Lines are guides to the eye.
hydrostatic resistivity measurements performed by Hamlin et al. in a mechanically loaded DAC to 20.4 GPa showed an initial pressure increase at a rate $dT_c/dP = +0.5 \text{ K/GPa}$, with $T_c(P)$ passing through a maximum at $P_{\text{max}} = 5.4 \text{ GPa}$ [253]. Note that as no pressure medium was used, the single crystal would have been crushed in the DAC as soon as pressure was applied, resulting in a non-crystalline sample. A series of resistivity measurements performed by Igawa et al. on polycrystalline LaFePO using Fluorinert FC70/FC77 pressure medium, on the other hand, indicated a much steeper initial pressure dependence given by $dT_c/dP = +4.0 \text{ K/GPa}$. $T_c(P)$ also passed through a maximum at 0.8 GPa. Above this pressure $T_c$ gradually declined up to 12 GPa [254]. The marked difference in the pressure dependence $T_c(P)$ for these experiments is likely indicative of differences in the pressure environment; shear stresses exerted on the LaFePO sample during the non-hydrostatic DAC measurements are likely much larger than in those experiments performed in the Fluorinert pressure medium. Differences are consistent with earlier reviews pointing out the sensitivity of magnetic, structural, and superconducting properties of the iron-based materials to shear stress [48, 50, 78, 79, 255–257]. In collaboration with Dr. James Hamlin at the University of California, San Diego (UCSD), we therefore decided to determine the intrinsic superconducting pressure dependence of $LnFePO$ ($Ln = \text{La, Pr, Nd}$) using single crystals and the most hydrostatic pressure medium – dense He. Based on previous studies, one might expect $T_c$ to initially increase even more rapidly under purely hydrostatic pressure. Our subsequent findings led to a comprehensive study of $dT_c/dP$ of single-crystalline and polycrystalline LaFePO using various pressure media.
8.3 Experimental Results

All samples for measurements were obtained from UCSD. Single crystals were grown using a flux growth technique [249], while polycrystalline samples were prepared using the method reported in [248]. Samples referred to as annealed were heated to 700°C for 24 hours under flowing O2 [249]. Masses of the LaFePO single crystals used in hydrostatic ac-susceptibility measurements were measured at UCSD prior to being sent to us, while masses of the PrFePO and NdFePO single crystals were measured using a microbalance at Washington University.

8.3.1 Hydrostatic Pressure on LaFePO, PrFePO, and NdFePO

Hydrostatic ac-susceptibility measurements were carried out using the He-gas system. Transition temperatures for each sample were low, so the Janis cryostat was used to obtain the lowest possible temperatures and to ensure accurate temperature control. Due to the small size of the single crystals, we were careful to ensure that the crystals remained centered within one of the secondary coils and could not slide around.

To remove any background susceptibility resulting from the surrounding materials, an ambient pressure susceptibility measurement with no sample present was made from 2 K to 13 K. This background measurement showed a small transition (≈ 2 nV) that most likely originated from a small amount of lead solder used to secure the coil to the electrical feed-through. The background measurement was separated into two components – the susceptibility from the surrounding cell (assumed to be pressure-independent) and the pressure-dependent lead transition, which shifted to lower temperatures at a rate of $-38.6 \text{ mK/kbar}$ [258]. In addition, several of the measurements showed a small superconducting transition at low temperature from the indium coating on the CuBe gaskets used to seal the high pressure cell.
$$T_c(P) = 3.40 - 0.3812P + 0.0122P^2$$ was used [259].

Lattice parameters of each of the compounds [247] can be seen in Table 8.1 and were used to calculate the volume of the tetragonal cell ($V = a^2c$). Using the atomic masses of the elements comprising the compounds and the fact that these unit cells contain two formula units, the density of each compound was determined using $ho = \frac{2M}{N_AV}$, where $M$ is the atomic mass, $N_A$ is Avogadro’s number, and $V$ is the volume of the unit cell. Using the density, the hydrostatic ac-susceptibility signals could be put in terms of $4\pi\chi$. Any demagnetization effects stemming from the shape of each sample were not taken into account. In each case, the signal is consistent with full shielding.

### Table 8.1: Lattice parameters and volume of $LnFePO$ ($Ln = La, Pr, Nd$) compounds [247], along with atomic masses, $M$, and calculated densities, $\rho$.

<table>
<thead>
<tr>
<th>$LnFePO$</th>
<th>$a$ (pm)</th>
<th>$c$ (pm)</th>
<th>$V$ ($nm^3$)</th>
<th>$M$ (amu)</th>
<th>$\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFePO</td>
<td>395.70(9)</td>
<td>850.7(4)</td>
<td>0.1332</td>
<td>241.728</td>
<td>6.027</td>
</tr>
<tr>
<td>PrFePO</td>
<td>391.13(6)</td>
<td>834.5(2)</td>
<td>0.1277</td>
<td>243.728</td>
<td>6.339</td>
</tr>
<tr>
<td>NdFePO</td>
<td>389.95(5)</td>
<td>830.2(3)</td>
<td>0.1262</td>
<td>247.058</td>
<td>6.502</td>
</tr>
</tbody>
</table>

Initially, the ambient pressure superconducting transition of an O$_2$-annealed, single crystal sample of LaFePO (0.0228 mg) was measured. Superconductivity was confirmed, with $T_c = 6.71$ K determined using the transition midpoint. Pressure was then applied to 0.91 GPa at room temperature. After measuring the transition, pressure was subsequently released.
to 0.58 GPa, to 0.27 GPa, and to ambient pressure at 78 K, 70 K, and 40 K, respectively. Pressure decreased slightly with temperature, resulting in high pressure measurements at the transitions corresponding to 0.76 GPa, 0.52 GPa, and 0.24 GPa. To our surprise, the O$_2$-annealed LaFePO sample showed a negative dependence of $T_c$ on pressure. This was in stark contrast to the positive pressure dependences seen previously [253, 254]. To confirm our findings, 0.90 GPa was applied at room temperature, corresponding to 0.745 GPa at the transition. Afterward, pressure was released to ambient at 68 K. The resulting pressure dependence remained the same, with $dT_c/dP = -2.46(7)$ K/GPa, where $T_c$ at each pressure was determined using the midpoint.

After measuring $T_c$ of the annealed sample, the pressure dependence of an unannealed LaFePO single crystal was also measured to test whether annealing the sample in oxygen could have any effect on the pressure dependence of $T_c$. The transition of a single crystal (mass = 0.0870 mg) was measured at ambient pressure, giving $T_c = 6.56$ K, which is slightly lower than that of the annealed LaFePO crystal. At room temperature, 0.88 GPa was applied to the sample, which decreased to 0.73 GPa at the transition. Pressure was then released at 79 K to 0.43 GPa (0.38 GPa at low temperature) and finally to ambient pressure at 42 K. The transition was measured once more at ambient pressure upon cooling from room temperature to confirm that no oxygen ordering effects were present. Under pressure, $T_c$ was determined from the shift of the entire superconducting curve. Once again, $T_c$ decreases with pressure, with $dT_c/dP = -3.24(6)$ K/GPa, which is steeper than the pressure dependence for the annealed LaFePO sample. At each pressure, $T_c$ of the unannealed sample is below that of the annealed sample, which is consistent with earlier findings that O$_2$-annealing of the LnFePO compounds enhances their superconducting properties [249]. Ac-susceptibility measurements
for both the annealed and unannealed LaFePO samples may be seen in Fig. 8.4.

**PrFePO**

Next, ac-susceptibility measurements were performed on annealed PrFePO. As the crystals were small, the measurement was made on seven single crystals (combined mass = 0.0775 mg) simultaneously. All of the crystals were centered within the secondary coil. At ambient pressure, PrFePO becomes superconducting at a lower temperature than either LaFePO crystal, with $T_c = 3.97$ K, determined using the midpoint of the transition. Pressure was increased to 0.89 GPa at room temperature, decreasing to 0.74 GPa at the transition. After measuring the superconducting transition, pressure was released at 100 K to 0.42 GPa (0.36 GPa at the transition) and to ambient pressure at 43 K. $T_c$ under pressure was determined using the shift from ambient pressure. As was the case for the LaFePO samples, the transition temperature decreased with increasing pressure, as seen in Fig. 8.5(a), yielding $dT_c/dP = -1.70(7)$ K/GPa.

Prior to conducting any measurements on the LnFePO compounds in the He-gas system, a hydrostatic diamond anvil cell measurement was carried out on O$_2$-annealed, single crystalline PrFePO using 0.5 mm anvils. Several measurements were attempted. A Re gasket (initial thickness 260 µm) was used during the first run, while a CuBe gasket (initial thickness 300 µm) was used for subsequent runs. In each case, the gasket was pre-indent to a thickness of $\sim 50$ µm, and a 260 µm hole was drilled through the center to serve as the sample space. The gasket was gold-coated to ensure that the gasket sealed at low temperature upon application of pressure to ensure hydrostatic pressure. In the first run, no transition could be seen above $\sim 4.5$ K, so no pressure was applied. During the second run (referred to as Run #2), a superconducting transition ($\sim 50$ nV) was observed. The transi-
Figure 8.4: Hydrostatic ac-susceptibility measurements of (a) annealed and (b) unannealed single-crystalline LaFePO. For the annealed and unannealed samples, $T_c$ was determined using the transition midpoint and the shift of the superconducting transition under pressure, respectively. For both samples, $T_c$ clearly decreases with application of hydrostatic pressure. Numbers indicate the order of measurements.
Figure 8.5: Ac-susceptibility measurements performed under hydrostatic pressure of annealed single-crystalline (a) PrFePO and (b) NdFePO samples. Numbers indicate the order of measurements. Values of $T_c$ under pressure were determined using (a) the midpoint, or (b), the shift of the entire superconducting transition relative to the transition midpoint at ambient pressure.
Figure 8.6: The ambient pressure ac-susceptibility of annealed, single-crystalline PrFePO in the diamond anvil cell system is shown. With application of an increasing external field, the onset of the transition shifts to lower temperatures, thereby confirming that the transition corresponds to superconductivity. Curves have been shifted vertically for ease of viewing. The inset, which combines a susceptibility measurement above 3.7 K with one below 4 K shows the entire ambient pressure superconducting transition at 0 Oe. $T_c$ was determined using the onset. Upon application of pressure to 1.8 GPa, no transition was visible above 1.45 K, the lowest temperature measured. This is consistent with later findings from He-gas measurements that $T_c$ of single-crystalline PrFePO decreases under hydrostatic pressure.

The superconducting transition temperature was determined using the onset temperature ($T_c \sim 4.34$ K) since the LHe effects and the sharp increase in the low temperature susceptibility made it impossible to accurately determine the transition midpoint. Superconductivity was confirmed by applying an external magnetic field at 50, 100, 250, and 500 Oe. At each field, susceptibility above 3.7 K was measured using the slow cooling technique described in 3.1.2. As can be seen in Fig. 8.6, the superconducting transition temperature decreased with increasing external field.

After confirming superconductivity, hydrostatic pressure was applied at $\sim 1.7$ K. After
the gasket sealed, the sample space pressure measured 1.8 GPa using ruby fluorescence. Based on previous publications \cite{253,254}, it was believed that $T_c$ of PrFePO would increase under pressure. As no transition could be seen at 1.8 GPa of pressure, it was thought that the transition might have broadened and/or shrunk in size upon application of pressure, becoming lost in the background signal. No further pressure was applied. However, lack of a transition above 1.45 K is actually consistent with the PrFePO pressure dependence later determined by measurements in the He-gas system. Given $dT_c/dP = -1.70(7)$ K/GPa, at 1.8 GPa, $T_c \sim 1.3$ K, below the lowest measured temperature. While further pressure was not applied, our findings support the decrease in $T_c$ of single-crystalline PrFePO under hydrostatic pressure.

\textbf{NdFePO}

A final hydrostatic experiment in the He-gas system was carried out on O$_2$-annealed, single-crystalline NdFePO. These crystals were the smallest of the $Ln$FePO crystals, so the combined signal of five single crystals with a total mass of 0.0182 mg was measured. At ambient pressure $T_c = 3.81$ K. A pressure of 0.91 GPa was applied at room temperature, allowing the transition to be measured at 0.76 GPa. Pressure was then released at 90 K to 0.42 GPa (0.38 GPa at the transition) and to ambient pressure around 45 K. At each pressure, $T_c$ was determined using the midpoint. As expected from measurements on LaFePO and PrFePO, $T_c$ once again decreased with pressure, seen in Fig. 8.5(b). Note that $dT_c/dP$ is slightly steeper than for PrFePO, with $dT_c/dP = -1.94(2)$ K/GPa.
Summary

Ac-susceptibility measurements in the He-gas system on single-crystalline $LnFePO$ ($Ln = \text{La, Pr, Nd}$) clearly indicate that $T_c$ decreases under hydrostatic pressure. Resistivity measurements carried out in the He-gas system by Dr. Neda Foroozani on annealed, single-crystalline LaFePO and on unannealed, polycrystalline LaFePO also indicate a decrease in $T_c$ with pressure [260]. It is, therefore, clear that superconductivity in both single-crystalline and polycrystalline $LnFePO$ compounds exhibits a negative pressure dependence under hydrostatic pressure, regardless of whether or not the sample has been annealed in oxygen.

As expected, resistivity and ac-susceptibility measurements both show a negative pressure dependence. Fig. 8.7 shows a plot of $T_c$ vs. $P$ under hydrostatic pressure for each material.

Moving along the lanthanide series from La $\rightarrow$ Ce $\rightarrow$ Pr $\rightarrow$ Nd $\rightarrow$ Sm $\rightarrow$ Gd, the ionic radius of these elements becomes progressively smaller. As a result of this lanthanide contraction, replacement of La in the $LnFePO$ ($Ln = \text{La} - \text{Nd, Sm, Gd}$) compounds is the equivalent of chemical pressure, leading to decreases in both the $a$ and $c$ lattice parameters. As seen earlier in Table 8.1, the unit cell volumes for LaFePO, PrFePO, and NdFePO progressively decrease from 0.1322 to 0.1277 to 0.1262 nm$^3$, respectively. In light of the fact that $T_c$ decreases under hydrostatic pressure, is it possible that the decreasing values of $T_c$ at ambient pressure for annealed single crystals of LaFePO (6.71 K), PrFePO (3.97 K), and NdFePO (3.81 K) are simply a result of lanthanide contraction, i.e., chemical pressure? Ideally, one would determine the uniaxial pressure dependences to test this hypothesis. No uniaxial studies are available, however, so we consider whether lattice contraction along the $a$ and $c$ directions under pressure is similar to that under chemical pressure. The linear compressibility along each axis is given by $\kappa_a = 2.74 \times 10^{-3}$ GPa$^{-1}$ and $\kappa_c = 4.95 \times 10^{-3}$ GPa$^{-1}$ [254],
Figure 8.7: An overview plot of hydrostatic pressure dependences $dT_c/dP$ for various $LnFePO$ compounds is shown. Unless otherwise noted on the plot, samples are annealed single crystals. $T_c$ for susceptibility measurements is determined using the midpoint of the transition, while $T_c$ for resistivity measurements is determined by the temperature at which the resistance falls to zero. The key in the upper right hand corner gives the pressure dependence $dT_c/dP$ for each material, which in each case indicates that $T_c$ decreases under hydrostatic pressure. Resistivity measurements were carried out by Dr. Neda Foroozani.
so the lattice is more compressible along the $c$-axis, by a factor of $\kappa_c/\kappa_a \sim 1.8$. Comparing lattice parameters for $LnFePO$ compounds, $c$ decreases about 1.65 and 1.66 times faster under chemical pressure than $a$ for PrFePO and NdFePO, respectively. Since the relative change in lattice parameters varies by less than 10% under applied and chemical pressure, it is possible to compare the unit cell volumes in each case. Under hydrostatic pressure, $dT_c/dP = -2.46(7)$ K/GPa for LaFePO. Then at $\sim 1.1$ GPa and $\sim 1.2$ GPa, $T_c(P)$ of LaFePO would be the same as the ambient pressure $T_c$ values for PrFePO and NdFePO, respectively. Using the linear compressibilities, we calculate the volume compressibility for the tetragonal cell as $\kappa_v = 2\kappa_a + \kappa_c = 10.4 \times 10^{-3}$ GPa$^{-1}$. Using this value of $\kappa_v$, the pressure required to reduce the unit cell volume of LaFePO to that of PrFePO and NdFePO would be 4.4 and 5.8 GPa, respectively. These pressures are four to five times higher than those required to reduce the value of $T_c$ for LaFePO to that of PrFePO or NdFePO. It seems clear, then, that the differences in $T_c$ between these three compounds cannot be accounted for by lanthanide contraction alone. This conclusion is supported by a first-principles electronic structure calculation by Vildosola et al. [261], who point out that the detailed band structure and Fermi surface of LaFePO depend very sensitively on small changes in both the interatomic distances and the bond angles within the iron-pnictogen subunit.

8.3.2 Non-hydrostatic Pressure

The negative pressure dependences seen in He-gas measurements on the $LnFePO$ compounds are in stark contrast to previously published high pressure measurements that indicate an initial increase in $T_c$ under pressure, as can be seen in Fig. 8.3 [253, 254]. What, then, is the cause of this difference? The high pressure measurements by Hamlin et al. were performed
in a diamond anvil cell with no pressure medium [253]. Under these circumstances, the single crystals originally placed in the sample space were crushed, yielding a non-crystalline sample. The first high pressure data point in these measurements is at 5.4 GPa, which is significantly higher than the 0.8 GPa where Igawa et al. found a maximum in $T_c$ [254]. Those measurements were conducted on polycrystalline LaFePO in a piston cylinder cell using a Fluorinert FC70/FC77 pressure medium. $T_c$ decreased under pressure in all hydrostatic measurements conducted in the He-gas system, regardless of whether or not the sample was single-crystalline or polycrystalline and whether or not it had been annealed. It seems clear, then, that the pressure dependence must strongly depend on the pressure medium used and on stresses in the sample. In a bid to observe an initial increase in $T_c$ and to reproduce the measurement conditions of Hamlin et al. [253], a series of ac-susceptibility measurements were carried out in the DAC to relatively low pressures ($\sim 1.2$ GPa), in the pressure regime where Igawa et al. found a maximum in $T_c$. No pressure medium was used, so the sample was squeezed directly between the diamonds, leading to extremely non-hydrostatic pressure conditions.

Several DAC measurements were carried out with 0.9 mm anvils, which enable pressures up to about 10-15 GPa to be reached. In each case, a CuBe gasket (with an initial thickness of 400 $\mu$m) was used to ensure that the susceptibility could be measured to temperatures as low as 1.6 K. After pre-indentation a 450 $\mu$m hole was drilled through the center of each gasket. Gaskets were pre-indented to thicknesses between 150 and 160 $\mu$m. For each experiment the sample space was almost completely filled with polycrystalline LaFePO.

Using our optical system, ruby fluorescence can be used to determine the pressure to about 0.2 GPa. As a pressure regime to only several GPa was of the most interest, various
other pressure manometers were considered in order to allow more accurate determination of the pressure. At ambient pressure indium, tin, and lead superconduct at 3.40 K, 3.73 K, and 7.20 K, respectively. Each of these elements has a well-known pressure dependence which may be used to determine the pressure. Based on earlier hydrostatic measurements, $T_c$ of LaFePO was expected to be at $\sim$ 5–6 K. Since indium and tin superconduct at lower temperatures, they would need to be placed at the edge of the sample to ensure that they were not completely shielded. As no pressure medium was used, these pressure manometers, if located at the edge, would underestimate the sample pressure due to pressure gradients in the sample space. For the first experiment, therefore, a small lead sample ($\sim$ 125 $\mu$m diameter, 40 $\mu$m thickness) was placed on top of the annealed sample at the center. Several ruby spheres were also placed in the sample space to serve as additional pressure manometers. Upon measuring the ac-susceptibility signal, only the superconducting transition from lead could be observed. To prevent possible shielding, lead was not placed in the cell for subsequent measurements. For the second experiment an unannealed sample was placed in the sample space. Pressure was applied at about 40–50 K, and temperature was kept below 60 K for the duration of the experiment. Using the normal ac-susceptibility field of 3.0 Oe we observed the onset of a very broad superconducting transition near 5 K. To increase the sharpness of the transition, we decreased the field, measuring the transition at 0.3, 0.1, and 0.03 Oe, as seen in the inset of Fig. 8.8(a). Subsequent measurements were performed at 0.1 Oe to optimize sharpness while still maintaining a good signal-to-noise ratio, since the size of the signal scales with the size of the field. Even with the lower field, the superconducting transition observed at ambient pressure remained quite broad. As we increased the pressure to 0.2 GPa, 0.5 GPa, 0.7 GPa, and 0.9 GPa, the size of the transition was seen to decrease, most likely
Figure 8.8: Ac-susceptibility measurements were performed in the DAC with no pressure medium. (a) Raw data shows a Curie-type increase in the susceptibility at low temperature due to the surrounding cell. Measurements were not performed at the usual 3 Oe, as the ambient pressure transition became noticeably sharper as the field decreased (see top inset). The lower signal-to-noise ratio for the 0.03 Oe measurement negated any benefits arising from the slight increase in the sharpness of the transition between 0.1 Oe and 0.03 Oe. Hence, all measurements were conducted at 0.1 Oe. The ac-susceptibility scale is proportional to the field, so measurements shown in the inset have been scaled to allow comparison with the measurement at 0.1 Oe. (b) A background subtraction performed at each pressure reduced the low temperature increase in the susceptibility. $T_c$ was determined by the onset of superconductivity, as shown in the inset.
due to the sample being broken up into smaller pieces as it was crushed between the anvils. At 1.1 GPa the superconducting transition could no longer be observed. Upon releasing pressure back to 0 GPa, only a very small superconducting transition could be observed. At low temperatures a strong Curie-type temperature dependence could be observed. A background subtraction was made using a measurement with no superconducting transition. Although the background measurement was performed using the same anvils and the same type of gasket, conditions in the cell still varied slightly, so the background measurement was scaled to 60% so that the susceptibility above the transition would be horizontal. The effect of this background subtraction can be seen in Fig. 8.8(b). As we were unable to observe the entire superconducting transition, $T_c$ at each pressure was determined using the onset. The resulting pressure dependence may be seen in Fig. 8.9. $T_c$ initially increases with pressure, passing through a maximum at $\sim 0.5$ GPa. Although this maximum pressure is much lower than the 5.4 GPa observed in earlier experiments [253], the most important thing to note is that an initial positive pressure derivative $dT_c/dP$ is obtained for a strongly non-hydrostatic measurement of LaFePO.

Several more experiments were conducted with an annealed polycrystalline sample of LaFePO, as it was expected to have a higher $T_c$ value and we hoped that this would allow us to measure pressure dependence without worrying about the steep low-temperature increase of the susceptibility. Unfortunately, no superconducting transition was observed above 3.5 K in any of these measurements. It is possible that these annealed polycrystalline samples were not superconducting, an idea supported by various studies indicating that superconductivity in LaFePO is very sensitive to oxygen defects [262].
Figure 8.9: Pressure dependence of the superconducting transition temperature for a non-hydrostatic measurement of unannealed, polycrystalline LaFePO. The measurement was performed using ac-susceptibility techniques in the DAC. $T_c$ (determined by the onset of the transition) is seen to increase initially, passing through a maximum at 0.5 GPa. The curved line is a guide to the eye.

8.4 Conclusions

Our understanding of a given material is complete only when we can account for changes in its properties due to variation of parameters such as temperature, magnetic field, doping level, and pressure. The last of these two parameters are not always clearly defined. Chemical doping may introduce lattice defects and strains and may not be homogeneous over the lattice. In this sense, pressure is a relatively “clean” parameter in that properties may be varied across the entire sample. However, not all pressures are created equal! Ideally, pressure would be either completely uniaxial or purely hydrostatic (exerted by a fluid). These conditions can not always be realized, however, over a wide pressure and temperature range. Uniaxial pressures above $\sim 0.1$ GPa are likely to damage the sample, while all fluids eventually solidify, either upon cooling or upon application of sufficient pressure. Solid pressure media will exert shear stresses on a sample. The hydrostaticity of a pressure medium can depend not only upon its properties at ambient conditions, but upon the temperature at
which pressure is applied and the rates of cooling and warming. It should also be noted that
each high pressure cell has its own characteristic behavior – one piston-cylinder cell with a
Fluorinert pressure medium may not have the same pressure/temperature characteristics as
another piston-cylinder cell containing the same sample and the same pressure medium.

Studies of the iron-based superconductors under pressure have been carried out using
a variety of pressure media (or, in some cases, no pressure medium at all). The layered
iron-based superconductors are extremely sensitive to strain. It is, therefore, not entirely
surprising that high-pressure measurements of different groups often give conflicting results
for the same compound. For measurements performed over the course of this thesis work,
a negative pressure dependence \( dT_c/dP \) was obtained for all hydrostatic measurements of
\( LnFePO \) (\( Ln = \text{La, Pr, Nd} \)) in the He-gas system. Piston-cylinder measurements performed
at UCSD by Dr. James Hamlin on a single-crystalline LaFePO sample in a Fluorinert FC70
pressure medium also showed a decrease in \( T_c \) under pressure [260]. Only when extremely
non-hydrostatic pressures were applied by crushing an unannealed, polycrystalline sample
between two opposing anvils was an initial \( \text{increase} \) in \( T_c \) observed! The wide range of
pressure dependences that have been observed in LaFePO is summarized in Fig. 8.10.

It is clear, then, that stress in these iron-based superconductors can obscure their intrinsic
pressure dependences and muddy the waters in our quest to enhance \( T_c \) and to further our
understanding of this class of superconductors. Effects of strain may be minimized by using
dense He, the most hydrostatic pressure medium. If this is not possible, then studies with
different pressure media will reveal whether a pressure-dependent property is sensitive to
strain. Whenever possible hydrostatic measurements should be performed on high-quality
single-crystalline samples. In layered materials such as the iron-based superconductors, the
Figure 8.10: The superconducting transition temperature of LaFePO exhibits a wide array of pressure dependences for measurements performed in different types of pressure cells. $T_c$ is only seen to initially increase and pass through a maximum for measurements by Igawa et al. [254] and for extremely non-hydrostatic measurements in the DAC system.
elastic properties are significantly anisotropic. Even for a hydrostatic pressure medium, the anisotropic response of every crystallite in a polycrystalline sample can lead to varying strain fields across grain boundaries.

Previous studies of various iron-based superconductors support the idea that these materials are highly sensitive to strain. In BaFe$_2$As$_2$ Duncan et al. [263] showed that an increasing component of uniaxial pressure favors the appearance of superconductivity, and may even be required to induce superconductivity. Zheng et al. [264] demonstrated that superconducting precursors form above the bulk thermodynamic transition due to strains within a CaFe$_2$As$_2$ sample. High pressure studies of the 122-compounds by Alireza et al. [265] showed that CaFe$_2$As$_2$, SrFe$_2$As$_2$, and BaFe$_2$As$_2$ single crystals become superconducting near 0.3, 3, and 3 GPa, respectively, when Daphne Oil or Fluorinert is used as a pressure medium. A later study by Yu et al. [266] of a single crystal sample of CaFe$_2$As$_2$ in He-gas, however, found no evidence for superconductivity to 0.7 GPa! Finally, Kirschenbaum et al. [267] showed that well-annealed single crystals of SrFe$_2$As$_2$ do not superconduct at ambient pressure, whereas unannealed crystals and crystals subjected to severe deformation actually exhibit superconductivity near 21 GPa. Along with the results found from our measurements of the LnFePO compounds these findings confirm the high sensitivity to strain of the iron-based superconductors and point towards the importance of carrying out systematic hydrostatic and uniaxial pressure measurements on these compounds.
Chapter 9

Summary

• At high pressure the alkali metals Li, Na, K, Rb, and Cs deviate strongly from the nearly-free electron model, leading to complex behavior. Pressure-induced superconductivity is predicted to occur in all of the alkali metals, but thus far superconductivity has only been observed in Li and Cs. With this in mind, a search for superconductivity has been performed in Na and K using ac-susceptibility techniques. In Na no superconductivity was observed between 1.35 K and 30 K during three sets of non-hydrostatic pressures at 62, 64, 80, 90, 104, 105, 113, 119, 120, 135, 146, and 161 GPa. For K superconductivity was not detected between 1.35 K and 30 K in a series of measurements at pressures of 0.4, 5.4, 10.8, 11.2, 12.0, 13.0, 14±1, 15 (estimated), 17.5±1.5, 19.1, 23±2, and 23.8 GPa.

• Previous studies of Li$_{0.9}$Mg$_{0.1}$ showed that alloying divalent Mg into monovalent Li suppresses superconductivity relative to pure Li. A series of ac-susceptibility measurements were performed on Li$_{0.9}$Mg$_{0.1}$ at hydrostatic pressure in the hope of extending the superconducting phase diagram to higher pressure. Measurements of $T_c$ of the alloy
are consistent with earlier results, but we have been unable to reach higher pressure, so further measurements are required. In addition, we performed ac-susceptibility measurements on Li$_{0.8}$Mg$_{0.2}$ to determine the effect of increasing electron concentration on superconductivity. Results indicate that the superconducting state is suppressed even further, as no superconducting transition was observed above 4.5 K for hydrostatic pressures between 11.0 and 55.9 GPa.

• In the quest to metallize hydrogen and to discover a room temperature superconductor, hydrogen-rich compounds are of particular interest as they might become metallic at lower pressures and exhibit superconductivity at relatively high temperatures. Among these, benzene (C$_6$H$_6$) has been predicted to become metallic in a narrow pressure regime between 180 and 200 GPa. A series of room temperature optical measurements were therefore performed on benzene to search for metallization. Results show that benzene remains optically transparent to visible light and hence insulating to 213 GPa.

• In order to determine the mechanism responsible for superconductivity in the cuprate and iron-based superconductors, to test theoretical models, and to find higher values of $T_c$, it is important to understand how the lattice parameters affect $T_c$. Hydrostatic measurements were therefore carried out on HgBa$_2$CuO$_{4+\delta}$ to 0.69 GPa in the He-gas system in conjunction with uniaxial pressure measurements performed by another group. Results indicate that $T_c$ in the cuprates can be enhanced either by reducing the area of the CuO$_2$ planes or by increasing their planar separation, i.e., by increasing the $c/a$ ratio of the tetragonal lattice.

• Hydrostatic measurements have been performed on the iron-based superconductors $LnFePO$ ($Ln = $ La, Pr, Nd). The negative pressure dependence seen in these measure-
ments is in stark contrast to the previously reported results that show $T_c$ of LaFePO increasing initially before passing through a maximum. To explore the effects of non-hydrostaticity, a non-hydrostatic DAC measurement to 0.9 GPa was performed. Under these conditions, $T_c$ increased initially, passing through a maximum at 0.5 GPa. These results suggest that layered iron-based superconductors are extremely sensitive to strains within the sample. The superconducting pressure dependence, therefore, depends strongly on the pressure medium in which the material is studied – in fact, strains induced by non-hydrostatic pressure may even enhance superconductivity. It is vital, therefore, that systematic hydrostatic and uniaxial pressure studies be carried out to further our understanding of these materials.
Appendix A

GdAgMg

The equiatomic ternary intermetallic compounds \(RT\text{Mg} \ (R=\text{Gd, Eu}; \ T=\text{Ag, Au})\) have recently attracted interest, spurring measurements on their magnetic, transport, and thermodynamic properties [268–271]. Among these compounds, the hydrostatic pressure dependence of the magnetic ordering temperature of GdAgMg was studied during the course of this research. Gd is trivalent in this compound [269], so the seven \(4f\) electrons in the outer shell have an angular momentum \(J = L + S = 0 + \frac{7}{2} = \frac{7}{2}\), thereby contributing to a strong local magnetic moment. Magnetic ordering occurs due to Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions. GdAgMg has been found to be ferromagnetic with a Curie temperature, \(T_C = 39.5\) K [271, 272]. At ambient pressure, the magnetic ordering temperature of these four intermetallic compounds increases with decreasing molar volume [272]. One therefore expects that \(T_C\) might be similarly enhanced by the application of pressure. However, combined specific heat and thermal expansion measurements find an initial pressure dependence, \(dT_C^{te}/dP = -35\) K/GPa for GdAgMg. At this rate \(T_C\) could be driven to 0 K with the application of 1–2 GPa, possibly leading to a pressure-induced quantum phase
transition [272].

In order to measure the pressure dependence of the ordering temperature and compare it to that obtained from thermal expansion measurements, I carried out high-precision hydrostatic measurements on GdAgMg in the He-gas system. A polycrystalline sample (14.28 mg) was obtained via the Universität zu Köln [269,270,273], where collaborators also carried out thermal expansion measurements. After measuring the transition at ambient pressure, a pressure of 0.76 GPa was applied at room temperature. At the transition this pressure had reduced to 0.66 GPa. Pressure was subsequently released to 0.31 GPa at 150 K (0.28 GPa at the transition) and 0.14 GPa at 50 K. At each pressure, the measurement was repeated several times to ensure reproducibility to ∼ 20 mK. The transition became broader with increasing pressure, as can be seen in Fig. A.1. At ambient pressure $T_C = 39.7$ K, which agrees well with the published Curie temperature of 39.5 K [272]. $T_C$ decreases rapidly with pressure at a rate $dT_{hyd}^C/dP = -5.1(1)$ K/GPa, seen in Fig. A.2. This magnitude is much smaller than the $dT_{te}^C/dP = -35$ K/GPa predicted by thermal expansion measurements. Note that these measurements had assumed that the sample was isotropic. Subsequent measurements of the linear expansion coefficient in three mutually orthogonal directions yield a smaller value $dT_{te}^C/dP = -12$ K/GPa, which is significantly closer to that which I measured under hydrostatic pressure. Thus, the polycrystalline sample measured was not isotropic, but rather strongly textured. A comparison of thermal expansion measurements and hydrostatic measurements for this compound and other RTMg compounds studied in our lab by Hunter Banks has been published [274].

Given $dT_{hyd}^C/dP = -5.1(1)$ K/GPa for GdAgMg, it is possible that magnetic ordering might be suppressed under a moderate pressure of 8 GPa. To test this, four hydrostatic...
Figure A.1: Ac-susceptibility of ferromagnetic GdAgMg under hydrostatic pressure is shown. Integers give the order of measurements. Curves other than ambient pressure are shifted vertically for clarity. Vertical arrows mark the Curie Temperature, $T_C$, defined by the temperature where the slope is steepest.
measurements were attempted in the DAC system using 0.5 mm anvils with a CuBe gasket for the first three experiments and a Re gasket for the last experiment. In each case that gasket was pre-indent to a thickness $\sim 80 \mu m$ and a 260 $\mu m$ hole was drilled through the center using the EDM. The gasket was sputtered with a thin layer of gold to allow it to seal about the hydrostatic pressure medium. For ac-susceptibility measurements of a ferromagnetic Curie temperature, $S(nV) \sim V/(1 + D)$ where $S$ is the signal size and $V$ is the sample volume. The demagnetization factor $D$ depends on sample shape in the same way as for a superconductor, as described in Sec. 3.4.2. $D$ should be minimized in order to maximize the signal. The geometry of the hole in the gasket favors a large flat sample, corresponding to a larger demagnetization factor. To enhance the signal size, therefore, several smaller pieces of sample (each with a small demagnetization factor) were placed in the cell, as seen in Fig. A.3. Ruby spheres were placed in the cell for pressure measurements.

Figure A.2: Pressure dependence of the magnetic ordering temperature of GdAgMg under hydrostatic pressure. $\frac{dT_C}{dP} = -5.1(1)$ K/GPa. Straight line is a least-squares fit to the data. Integers give the order of measurements.
In the first measurement, no ferromagnetic transition was visible from the GdAgMg, although in subsequent attempts, a small transition could be seen at ambient pressure near 40 K. Neither experiment was successful, however, under application of pressure. In one case, the gasket did not seal, so the hole collapsed about the sample. In the other measurement, the hole became elongated with the application of pressure, rather than shrinking uniformly. The resulting gasket hole was an ellipsoid with approximate dimensions 365 µm by 133 µm. The gasket had not yet sealed, so the membrane pressure was slowly released without continuing the experiment, as pressure distributions and strains in this situation could lead to catastrophic diamond failure. The final measurement, performed in conjunction with Wenli Bi, shows a transition near 40 K. Hydrostatic pressure of 2 GPa was successfully applied. However, the ferromagnetic transition could no longer be detected under pressure. Most likely it became broader with pressure (as was seen in the He-gas measurements) and be-
came lost in the background susceptibility. To confirm the temperature dependence above 1 GPa and determine whether the transition is indeed completely suppressed by moderate pressures of about 8 GPa, hydrostatic measurements with a lower background susceptibility are required.
Appendix B

Optical Setup for DAC

The ability to perform accurate optical measurements in the DAC is vital for determining sample pressure. In addition, optical viewing of the sample space can give important information regarding the state of the sample, gasket, and diamonds under pressure. Three lasers were utilized during the course of this research. A blue He-Cd laser ($\lambda = 441.6$ nm) was used to measure ruby fluorescence. When this laser stopped functioning, it was replaced by a diode laser (Coherent, CUBE laser) with a similar wavelength, ($\lambda = 445$ nm). It has a maximum output of 40 mW. An Ar-ion laser outputs up to 150 mW of power at $\lambda = 488$ nm and 514 nm. This laser can be used for ruby fluorescence measurements to about 50–70 GPa.

For diamond vibron measurements using Raman, this laser (in particular the 514 nm line) must be used as the spectrometer is designed to measure the Raman frequency shift for this laser.

A series of optics set up in conjunction with a metallurgical microscope allows the user to measure the sample pressure at room temperature using ruby fluorescence or the diamond vibron Raman technique. Photographs of the sample space can also be taken using reflected
or transmitted light. *In situ* ruby fluorescence measurements may also be made in the cryostat and images of transmitted light through the sample space may be taken. Unfortunately, we have not yet managed to perform Raman measurements for a sample in the cryostat. Detailed schematics of both optical setups may be found in James Hamlin and Mathiewos Debessai’s theses [76, 99].
Appendix C

LabVIEW Measurement Program

Ac-susceptibility and electrical resistivity measurements for both the He-gas and DAC high pressure systems utilize LabVIEW, a graphical programming language. The programs are designed to be user friendly while still enabling a wide choice of measurement parameters and measurement devices to be used, depending on requirements of the measurement. The original ac-susceptibility program was developed by Mathiewos Debessai [99]. This program could also be used for ac-resistivity measurements, but the selection of measurement devices and settings did not allow for dc-resistivity measurements. During the course of my research, I designed an additional LabVIEW program specifically for this purpose and added options for increased user control from the front panel.

The resistivity program allows dc-resistivity of up to two samples to be measured simultaneously, either in series or using two separate currents. Three voltmeters can be used for resistivity measurements – the Prema 6000, Keithley 2000, or Keithley 182. The user is able to change the integration time for the Prema directly on the front panel. This is especially useful when switching back and forth between using the Prema for temperature and resis-
tivity measurements. When a larger integration time is used, the time between subsequent measurement points is longer. For temperature measurements, using a 0.1 s integration time is usually sufficient. However, for resistivity measurements, a longer integration time is required to allow accurate measurement of sample resistances.

Current polarities are switched using a National Instruments (NI) device, USB-525. Previously, current polarity could only be switched for the thermometers in the He-gas system. This functionality has now been added to the DAC system and for resistivity currents. The addition of a second NI device now allows switching of up to four independent currents for each program. A delay time is used whenever current polarity is switched in order to allow time for the voltage on the measurement device to stabilize before LabVIEW records the voltage. This delay time can now be set depending on measurement requirements, with the only caveat being that it needs to be at least as long as the device integration time to ensure an accurate measurement. For more details on using the LabVIEW program for measurements, see the manual [275].
Appendix D

Refurbishment of Cold Head for Closed-Cycle System

In August 2008, the two-stage cold head from the closed-cycle system was sent to Cool Pair Plus for refurbishment. The seals were replaced to optimize performance. The cooling power was measured before and after refurbishment to determine whether the system had improved, allowing lower temperatures to be reached. To do so, a stainless steel tube insert normally used for measurements in the high magnetic field cryostat was placed in the cryostat sample chamber. A carbon glass resistor attached to the bottom of the insert was used to measure the temperature. Measurement conditions, including the pressure of the He-gas in the sample space, were repeated for measurements before and after refurbishment to ensure that an accurate comparison could be made. At the lowest temperature, helium gas was added to the sample space and then pumped out using a forepump. Repeating this procedure several times allowed lower temperatures to be reached. Above $\sim 15$ K, the cooling rates were very similar. However, before refurbishment, the temperature reached only about
\( \sim 9.5 \text{ K}, \) oscillating between 10 K and 12 K for several hours, as seen in Fig. D.1. After

![Figure D.1: Temperatures in the closed-cycle cryostat, measured using a carbon glass resistor, reached lower values after having the cold head refurbished. Temperatures initially reached only about 10-12 K, but after refurbishment the temperature decreased below 6.5 K. Above \( \sim 15 \text{ K}, \) the cooling power was about the same, as seen in the inset.](image)

refurbishment, the temperature in the cryostat decreased below 6.5 K. As the temperature was still decreasing slowly, it is possible that even lower temperatures may have been reached after waiting for a longer period of time.

Note that the insert to which the carbon glass resistor was attached was much lighter than the normal cryostat insert used during high pressure measurements – the load was significantly smaller than the normal load consisting of the high pressure cell, capillary, and
wiring. With a smaller load, the system may be expected to cool more quickly and to a slightly lower temperature, as less mass has to be cooled. The most effective way to test the cooling power of the cold head would be to not attach any load.

While the cold head was being refurbished, we replaced the adsorber in the compressor unit, as it has a finite life and should be replaced after 26,000 hours of operation. The adsorber is basically a charcoal filter that removes oil vapor from the helium gas before it passes to the cold head.

In addition to measuring the temperature and replacing the adsorber, the supply and return pressures on the compressor were also noted to ensure that they fell within expected values. The compressor supplies clean, compressed gas to the cold head. The supply pressure, then, corresponds to the high pressure gas that travels to the cold head, while the lower return pressure corresponds to the gas pressure as it returns to the compressor after having been used for cooling. According to the compressor operating manual, the low pressure gauge should initially fall to 50 psig\(^1\), while the high pressure should reach 330 psig. These values will fluctuate as the helium gas travels to and from the compressor to the cold head. At the lowest operating temperature of the cold head, the low and high pressure values will be about 100 psig and 300 psig, respectively. These values, however, can vary with the heat load attached to the cryostat. Table D.1 shows the return \((P_R)\) and supply \((P_S)\) pressures noted during cooling before and after the cold head had been refurbished. Note that the return pressure values listed correspond to the maximum rather than minimum pressure on the return pressure gauge as it oscillated between cycles. This accounts in part for the large discrepancy with the ideal values given in the manual.

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\(^1\)psig is a gauge pressure, given relative to the local pressure
Table D.1: Return ($P_R$) and supply ($P_S$) pressures on the compressor before ($b$) and after ($a$) the cold head had been refurbished. Afterward, the pressures were higher, which could indicate that a slight over-pressure might have existed in the cold head prior to refurbishment.
Bibliography


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