# Retention of Enhanced and Induced Superconductivity at Ambient Pressure Through High-Pressure Quenching

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> Doctor of Philosophy in Physics

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### DEDICATION

It has long been a dream of mine to follow in the footsteps of my grandfather and become a physicist. Unfortunately, just as I began my journey, his came to an end, and shortly thereafter, my grandmother followed. I wish they had both made it to this day with me to see what I have accomplished. I know they would have been proud of me, as they always were. So, I would like to dedicate this work to my late grandparents, Nolen, and Edwena Massey, for all the love and support they gave me in the time I had with them. I never would have pursued a Ph.D. in physics without their encouragement.

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#### ABSTRACT

In the past eight years impressively high superconducting critical temperatures  $(T_{cs})$  have been reported in numerous materials. Among these include instances of anomalously high  $T_{cs}$  that approach, and in some contested reports, meet and exceed room temperature (RT), pushing the field to new heights. Unfortunately, achieving such impressive critical temperatures requires ultra-high external pressures, rendering them unviable for commercial use. Therefore, one of the most significant challenges remaining in the field of superconductivity is to retain the high T<sub>c</sub> phases induced by pressure while lowering or removing it completely. We have therefore employed a pressure quenching technique to retain highpressure-induced/-enhanced superconducting phases in Bi, FeSe, and  $Cu_xFe_{1.01-x}Se$  at ambient pressure. Pressure quenching bismuth at 77 K and 4.2 K from pressures up to 26.6 GPa successfully produced metastable superconducting phases with varying  $T_{\rm c}s$  from  $\sim 5\,{\rm K}$  up to a new record of 9K. By changing the pressure quenching parameters, different metastable phases could be targeted, namely Bi-III with a  $T_c$  around 7K and Bi-V with a  $T_c > 8K$ . Temporal stability testing and thermal cycling revealed a lower temperature limit below  $\sim$ 60 K and an upper temperature limit of 120 K - 150 K in metastable bismuth. Pressure quenches performed on FeSe and Cu<sub>x</sub>Fe<sub>1.01-x</sub>Se near the superconducting dome resulted in metastable phases with maximum  $T_{cs}$  of 37 K and 25 K, respectively. Thermal cycling of FeSe and  $Cu_xFe_{1.01-x}Se$  showed a similar lower temperature limit for temperatures up to ~ 120 K and an upper temperature limit around 175 K for  $\text{Cu}_{x}\text{Fe}_{1.01-x}$ Se. Annealing metastable FeSe to room temperature produced  $T_{cs}$  from 15 K - 24 K. Notably, a non-superconducting hexagonal phase retained in FeSe was slowly annealed to room temperature for a few days resulting in a superconducting phase near the dome peak. Lastly, a temporal stability test of metastable Cu<sub>x</sub>Fe<sub>1.01-x</sub>Se was conducted which showed perfect phase stability for 7 days when kept below  $50 \,\mathrm{K}$ . Overall, these results demonstrate the potential this technique has in targeting desirable superconducting phases induced or enhanced by pressure and retaining them in a metastable state at ambient pressure.

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### LIST OF ABBREVIATIONS

bcc body-centered cubic.

cBN cubic boron-nitride.

CCD charge coupled device.

C-H-S carbonaceous sulfur hydride.

DAC diamond anvil cell.

**DAQ** data acquisition.

**EMF** electromotive force.

**FC** field cool(ed,ing).

GL Ginzburg-Landau.

**GPIB** General Purpose Interface Bus.

 $\mathbf{H_{c2}}$  (superconducting) upper critical field.

 $H_{c1}$  (superconducting) lower critical field.

 $\mathbf{H}_{\mathbf{c}}$  (superconducting) critical field.

hcp hexagonal close-packed.

HeNe helium-neon.

**LBCO**  $La_{1.85}Ba_{0.15}CuO_4$ .

LHe liquid helium.

 $\mathbf{LN_2}$  liquid nitrogen.

MPMS Magnetic Property Measurement System.

 $\mathbf{P}_{\mathbf{A}}$  applied pressure.

**PPMS** Physical Property Measurement System.

 ${\bf PTR}\,$  Physikalisch-Technische Reichsanstalt.

**RT** room temperature.

**RTS** room-temperature superconduct(or,ors,ivity), resistance temperatures sensor.

 $\mathbf{T}_{\mathbf{Q}}$  quench(ing) temperature.

 $\mathbf{T_c}$  (superconducting) critical temperature.

**UI** user interface.

**YBCO**  $YBa_2Cu_3O_7$ .

**ZFC** zero-field cool(ed,ing).

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## Chapter 1

# Introduction

Superconductivity is distinguished by its hallmark properties of zero resistance and expulsion of magnetic fields which manifest at the superconducting critical temperature  $(T_c)$ . It is a phenomenon with one of the greatest potentials to revolutionize humanity. From lossless energy transfer and storage, to MRI scans, and maglev transportation, the applications of superconductivity are many.

In the modern era, superconductivity serves many vital needs but is mostly utilized for its unrivaled performance in electromagnets. The narrow market that currently exists for this impressive phenomenon can be accredited to the extreme environment in which it persists.

The majority of superconducting materials exhibit the phenomenon at temperatures that approach absolute zero, accessible only by liquid helium (LHe)[1–17]. In fact, there exist few materials that become superconducting above 77 K, the boiling point of liquid nitrogen (LN<sub>2</sub>)[18–25]. Only a handful of contested reports provide evidence of materials that exhibit superconductivity near room temperature [26–33].

While cryogenic temperatures are typically required for superconductivity, extreme pressure is often used to induce and improve superconductivity. The importance of high pressure can best be understood by looking at the periodic table of elements. While 31 elements are superconductors at ambient pressure, an additional 23 elements are known to become superconducting with the application of high pressure[34]. Furthermore, the highest recorded  $T_cs$  are only achievable with high pressure[24, 25, 27, 28].

Knowing this, it becomes clear that one of the main challenges facing this field is the high pressure required to support high  $T_c$  superconductivity. As it is the ultimate goal of superconductivity research to produce materials that exist in this state at ambient temperature and pressure, it is vital to keep the enhanced  $T_c$  produced with high pressure while lowering or removing the external pressure. Therefore, a method to produce a metastable superconducting phase at ambient would be a route to achieving this goal. This dissertation looks to pressure quenching as a potential pathway to stabilizing such a metastable superconductor at ambient.

The technique of pressure quenching and the phenomenon of superconductivity are built upon decades of research. In this introductory chapter the work that led to the discovery of superconductivity, the details of the phenomenon, and some theoretical and experimental details of superconductors are discussed.

### **1.1** History of Cryogenics

Superconductivity has a rich history which is deeply intertwined with the field of cryogenics. Since cryogenics is indispensable in the study of superconductors, this section is dedicated to the history of its development and the instruments that facilitate lowtemperature science.

### 1.1.1 The Development of Thermometry

Thermometry is the fundamental tool of cryogenics and ultimately led to the creation of the field with the discovery of an absolute lowest temperature. In modern times, thermometry is one of numerous relationships between temperature and a measurable property of thermosensitive material. One of the most popular properties used today is resistance. However, the earliest instrument capable of distinguishing changes in temperature utilized the relations of temperature and volume. This was developed sometime between 240 and 200 BCE by Philo of Byzantium[35]. The instrument could register changes in the water level inside an inverted glass tube partially submerged in a vessel of water. Philo noted the water level dropped when brought into the sunlight but rose in the shade. It was then the expansion and contraction of air due to temperature that drove this instrument.

It was not until centuries later that the invention of Philos inspired others to use similar tools to track changes in temperature. Many individuals created a form of thermoscope with conflicting reports on who was first to use it[35, 36]. Notably, Galileo created a thermoscope between 1592 and 1603 that relied on the density of different spirits in sealed glass spheres whereas others utilized the expansion of air in a glass tube[35]. Changes in the density of these liquids due to temperature would cause the glass spheres to sink or rise.



**Figure 1.1:** Some thermometers of the 17th century (I-V). Figure V is based on the original design by Galileo. (Saggi di naturali esperienze fatte nell'Accademia del Cimento [1667; p 8][35])

While these instruments could indicate a change in temperature, they all lacked a scale, making them thermoscopes rather than thermometers. It was not until Santorio Santorio that a true thermometer was created. Santorio Santorio was actively using his open-air thermometer by 1612 which he used to gauge his patients' wellbeing.[35–37].

By 1644 Evangelista Torricelli had created a mercury barometer with Vincenzo Viviani[35, 36, 38]. Torricelli used this barometer to conduct a series of experiments and concluded that air pressure could vary with weather and altitude. This was of great importance to thermometry as it showed that all thermoscopes and thermometers that were open to air would also act as barometers. The discovery in the Torricelli experiments led to the creation of closed thermometers. Torricelli himself quickly produced a closed thermometer as a result of this knowledge. However, it was Ferdinand II de' Medici, Grand Duke of Tuscany, who is thought to have created the first sealed liquid-in-glass thermometer in 1641[35, 36]. Though this thermometer was sealed, it differed in that it used glass balls filled with liquids of different densities unlike conventional sealed liquid thermometer[36]. It was not until 1654 that Ferdinand II created such a liquid thermometer, similar to those used today.

Soon after this development, sealed thermometers became the norm, but the issue of standardization quickly arose. With thermometers created using different methods and reference points it was not possible to compare measurements between them. Ultimately, it was the thermometer produced by Daniel Gabriel Fahrenheit, who drew inspiration from the calibration method of Ole Rømer, that drove the standardization of thermometers[35, 36]. The high quality of Fahrenheit's mercury thermometers led to their widespread adoption[37]. The Fahrenheit calibration used three fixed points, setting the temperature of icy salt water as 0°, ice water as 32°, and "blood heat" as 96°[35, 36]. He also assigned 212° as the boiling point of water, but it was not originally intended as a fixed point. Later, this replaced the temperature of the human body as a fixed point due to the variability in body temperature.

Shortly after the development of the Fahrenheit thermometer Anders Celsius created his own mercury thermometer using a centesimal temperature scale[35, 36]. The Celsius thermometer was calibrated so melting snow was 100° and boiling water was 0°. Shortly after the death of Celsius, in 1744, the temperature scale was inverted to the scale used today.

### 1.1.2 The Absolute Temperature Scale

In the 17th century, when thermometry really began to develop, the concepts of heat and cold had not been well-defined. While many temperature scales were developed, they were typically calibrated to some accessible phase transitions like melting ice or boiling water, or other naturally occurring sources like the human body temperature or the temperature of fire. Due to the very limited access to low temperatures, and lack of understanding of thermodynamics at the time, thinking of temperatures beyond the bounds of what was experienced in nature was a mostly philosophical question. Therefore, the idea of an absolute minimum temperature had yet to appear.

It was not until 1682, when Boyle read a paper on his experiments with frigorific mixtures to the Royal Society, that the idea of an absolute lowest temperature was pushed into the public discourse[39, 40]. In his paper Boyle talked about Primum Frigidum and the nature of cold. The question of what should be taken as the Primum Frigidum, or the ultimate cold, helped drive the search for the lowest temperature.

Two decades later, between 1703 and 1704, Guillaume Amontons discovered that the air pressure in air thermometers changed linearly with temperature between the boiling point of water and room temperature[39–41]. Even when cooled to the freezing point of water the air sealed inside the thermometer displaced a few inches of mercury. From this Amontons surmised that if the "spring of the air" were to be cooled until it disappeared, an absolute coldest temperature would be reached. Extrapolating the relationship between mercury height and temperature, he calculated an absolute lowest temperature of -240 °C. Later, in 1779, Johann Lambert duplicated the work of Amontons with more careful measurements[39, 40]. From his work he determined the lowest temperature obtainable was actually -270 °C, a very good estimation of absolute zero.

It was not until the 19th century that the field of thermodynamics began to emerge with Sadi Carnot's work on the efficiency of a heat engine[42]. In his work Carnot related the heat, work, and temperature of an idealized engine. It was the relating of "quantities of heat, and intervals of temperature" that led Lord Kelvin (William Thomson) to develop his absolute temperature scale[39, 40, 43]. Kelvin wanted to establish a temperature scale that was independent of any substance's physical properties. Rather than creating an arbitrary scale between two reference points, Kelvin hypothesized a temperature scale with absolute zero defined by a single set point. Using the coefficient of expansion for air recorded by Regnault, 0.366, Kelvin determined absolute zero to be -273 °C, just a fraction of a percent different from the true value.

### 1.1.3 Vacuum Pump Technology

Long before the development of thermometry, humankind had a natural interest in low temperature for cooling themselves, beverages, as well as preparing and preserving food[44]. The knowledge and technologies related to cryogenics of the ancient world were very limited, but there was an understanding some of the most fundamental ideas. For example, many ancient peoples were able to harvest ice in the winter and keep it for the summer months by storing it in ice pits. The structures that they built to house ice, such as the Yakhchāls of modern-day Iran, display their understanding of insulation. Basic principles of air pressure and density are also evident in the design of early wind-catchers. These structures provided passive cooling to buildings, particularly in North Africa and the Middle East. This was a very effective method when paired with a basin of water to take advantage of evaporative cooling. Evaporative cooling was even used for producing ice in the ancient world and is the earliest example of this key process in cryogenics. As will soon be discussed, insulation and evaporative cooling are two of the three key concepts in the field of low-temperature physics and are integral to the liquefaction of cryogens. When it comes to cryogenics, these seemingly distinct topics are both connected by one vital instrument: the vacuum pump. Today, the vacuum pump is used to create insulating vacuum barriers for cryogenic containers, such as dewars or thermos flasks. It also significantly enhances the power of evaporative cooling by lowering the vapor pressure of volatile liquids. Therefore, it is important to first introduce the vacuum pump and briefly discuss the history of its development.



Figure 1.2: The water manometer built by Gasparo Berti as described by Emmanuel Maignan. The main glass body and reservoir of this manometer appear in many of the early open-air thermometer designs.[38, 45]

The concept of a vacuum had existed since ancient times, but it was not until 1631 that the first experiments to create a vacuum were proposed [45]. A decade later Gasparo Berti became the first to produce a vacuum and attempt to prove its existence. He used a large water barometer with a bell suspended inside an emptied glass sphere at the top of a long glass neck[38, 45]. However, when the bell was rung inside the vacuum it could be heard, likely due to the connections made to the sphere to support the bell.

A few years later, in 1644, Vincenzio Viviani repeated this experiment with a mercury barometer created by himself and Torricelli[38, 45]. It was the experiments of Torricelli and Viviani which convinced most people that a vacuum had been created in the space above the liquid mercury. Around the same time, Otto von Guericke began experimenting with pumps which relied on a simple piston and the power of two men. This pump was used to remove water from a wooden barrel and later air from a copper sphere[45, 46]. In this way, Guericke became the first to create a vacuum pump. His most famous experiment showcased the power of vacuum in 1654, the so-called Magdeburg experiment[46]. Two metal hemispheres were connected and evacuated using Guericke's pumping method and then attached with ropes to two teams of fifteen horses. Despite their efforts, the hemispheres could not be separated until the valve was opened.

Guericke's experiments were first reported in 1657 by Kaspar Schott in his "Mechanica Hydralica-Pneumatica" which made it to Robert Boyle shortly thereafter[38, 46]. Boyle designed his own vacuum pump which was built by Robert Hooke between 1658 and 1659. The new pump was much more elegant than the Guericke pump and used a rack and pinion hand crank. By placing a mercury manometer in a bell-jar and evacuating it, Boyle was able to make the first measurement of subatmospheric pressure, measuring 1/4 inch of Hg.



In the 200 years following the creation of Guericke's solid-piston vacuum pump, improvements

**Figure 1.3:** Illustrations of Guericke's solid-piston design used to pump a wooden barrel (top) and a copper sphere (bottom).[45]

to the design were made with the ultimate pressure decreasing one order of magnitude by 1851[45]. Notably, in 1709 Francis Hauksbee greatly improved a two cylinder pump design[46]. This type of pump remained in use into the nineteenth century.

1855 saw an important development in vacuum pump technology as Heinrich Geissler designed and build a mercury piston pump at the behest of Julius Plücker[45, 46]. This design was greatly improved by August Töpler in 1862. By raising and lowering the mercury level, gas was removed from the vacuum line in these liquid piston pumps.



Figure 1.4: Gaede's rotary mercury pump.[45]

Following Geissler and Töpler, Hermann Sprengel created his own version of the mercury pump in 1865[45, 46]. His design used a head of mercury to trap gas between drops of the liquid. Over time, the gas pockets trapped would grow smaller as the pressure inside the volume decreased. The Sprengel pump was used through the end of the nineteenth century, particularly in producing incandescent lamps. By 1894 pressures as low as  $3x10^{-6}$  Torr could be reached with a Sprengel type mercury pump[45].

The beginning of the 20th century saw the development of much of the vacuum pump technology used in the modern era[45, 46]. The rotary mercury pump was developed in 1905 by W. Kaufmann, but it was Wolfgang Gaede who ensured its popularity with the version he produced at the end of the same year[46]. This pump was extremely popular in the lamp and vacuum-tube industries as they were motor driven, unlike the manually operated Sprengel pumps, and could reach pressures in the  $\mu$ Torr range.

Gaede went on to cement himself as arguably the most important figure in the history of vacuum pump technology. After his popular rotary pump, he produced the earliest version of two of the most widely used vacuum pumps in the field of cryogenics to date[45, 46]. In 1907 he created a rotary oil pump with strong similarity to Prince Rupert's water-bolt. Later, in 1912 he created the first type of molecular-drag vacuum pump, albeit unpopular at the time due to the difficulty of manufacturing and expense.

The popularity of the molecular-drag pump was also undercut by the creation of the mercury vapor stream pump which had no moving parts and a high efficiency. This vacuum pump was created independently by both Gaede and Irving Langmuir between 1915 and 1916[45, 46]. In 1928, Cecil Burch replaced the mercury with oils he developed, featuring a low vapor pressure. It is this oil vapor diffusion pump which is still used to this day. Though this type of vacuum pump is typically used for producing high vacuum rather than for cryogenics applications, it is a testament to Wolfgang Gaede's contribution to the field of vacuum technology.





Figure 1.5: The rotary oil pump Gaede designed (top) and Prince Rupert's water-bolt (bottom) from around 1650.[45]

The molecular-drag pump saw improvements in the 1920's by Fernand Holweck and Manne Seigbahn. However, due to the high precision needed for closely spaced stators and rotors that operate at high speed, the molecular-drag pump was not widely adopted until the 1970s. The modern version of this pump is the turbomolecular pump which combines the molecular-drag pump with a turbo pump. It is widely used in the field of cryogenics for achieving high vacuum, particularly for vacuum insulation.

A final vacuum pump worth mentioning is the scroll pump which was originally designed in 1905 by Léon Creux[47]. Much like the molecular-drag pump, the scroll pump required more precision than was possible at the time. It was not until 1975 that scroll pumps were made viable through the patented design of Neils Young and John McCullough. By the 1990s the scroll pump was widely produced, mostly for use in refrigerators. Despite this, the first paper on the applications of the scroll pump was for shipboard helium liquefier systems. Scroll pumps are commonly used in helium liquifies today due to their "dry", or liquidless nature.

### **1.1.4** The Development of Cryogenics

Attention now turns to the history of cold itself. From simply storing ice, to creating ice with evaporative cooling, to chemical cooling, and finally using thermodynamics and the physical properties of gases to come within 1 degree of absolute cold, this section will highlight many of the most important developments leading up to 1908.

Early steps toward low temperature were taken in the beginning of the 16th century, nearly a century before the nascence of thermometry[44]. In 1525 Marcus Antonius Zimara created an early frigorific mixture of snow and saltpeter, or ammonium nitrate. He described this mixture as an effective cooling medium. Later, in 1550 Blasius Villafranca discovered that the freezing temperature of an aqueous solution could also be lowered by adding potassium nitrate. About a century later in the 1660s, Robert Boyle created freezing mixtures of numerous salts, ultimately concluding that ammonium chloride was the superior salt. Several frigorific mixtures could reach temperatures well below the freezing point of seawater as reported by Richard Walker in 1788[48].

As discussed, evaporative cooling was used by many in the ancient world. As early as 400 BC evaporative cooling was used to make ice in Egypt and India[44]. However, it was not until 1755 that William Cullen revealed the true power of evaporative cooling. Using a vacuum pump to lower the vapor pressure of diethyl ether, Cullen greatly decreased the temperature of the liquid and condensed a small amount of ice from air. Similarly, Benjamin Franklin and John Hadley cooled a thermometer from 65 °F to 7 °F in 1758 by wetting the bulb with ether and evaporating it with bellows.

At the end of the 18th century, it was discovered that both temperature and pressure could be used to liquify gases. The first pure gas to be liquified was sulfur dioxide and was carried out by Gaspar Monge and Clouet between 1783 and 1784[49]. This was accomplished by passing the gas through a U-tube submerged in a frigorific mixture of ice and salt. In 1799 Martin van Marum and Adriaan Paets van Troostwijk compressed ammonia at room temperature to see if it would follow Boyle's Law. They found the pressure stopped increasing at 7 atm and further compression led to the liquefaction of ammonium gas[50].

Beginning in 1810 John Leslie investigated vacuum refrigeration, and by 1823 he became the first to freeze water through direct evaporative cooling[44]. His method utilized an air pump and sulfuric acid to rapidly remove water vapor from a bell-jar and cool the bowl of water within. In the same year Micheal Faraday happened to liquify chlorine gas as he was observing the decomposition of a compound. This led him to liquify numerous gases which had been attempted previously[41].

By mid-century, all but a handful of gases had been liquified. Those that remained became known as permanent gases and included oxygen, nitrogen, and hydrogen. Even Natterer, who had constructed a compressor capable of producing pressures up to nearly 3000 atm, was unable to condense air[41]. It was not until the experiments of Thomas Andrews, from 1861 to 1869, that the reason so many had failed became apparent.

In Andrews' experiments he studied Boyle's Law for  $CO_2$  along different isotherms. He found that at temperatures below 31 °C the P-V diagram would reach a plateau region where further reduction in volume condensed the gas. However, above 31 °C the gas and liquid phases could no longer be distinguished, instead forming a supercritical fluid. At even higher temperatures, above the critical temperature, this supercritical fluid began to conform to Boyle's Law[41].

Following Andrews' discovery, Johannes van der Waals was able to provide an interpretation in 1872. His modified equation for real gases considered the size of the gas molecules and their attractive forces. Very importantly, the two constants in his real gas equation could be determined for a given gas and used to predict the critical temperature[41].

Shortly thereafter, in 1877, Louis Cailletet and Raoul Pictet succeeded in condensing small amounts of oxygen independent of each other, finally dispelling the myth of permanent gases[41]. Cailletet first compressed oxygen to 300 atm and cooled it with sulfur dioxide. Releasing the pressure, he was able to produce a mist of liquid oxygen as the gas cooled by doing work on the atmosphere. This is now known as the Siemens cycle after



Figure 1.6: Isothermal measurements of  $CO_2$  conducted by Thomas Andrews. The regions where the P(V) curves become flat indicate attempts to increase the pressure, leading to volume reduction as gas is condensed into a liquid. Once this flat region no longer appears, it signals that the critical temperature for gas liquefaction has been reached. [51]

Carl Siemens who patented a cooling engine using this method twenty years prior in 1857. Pictet, on the other hand, succeeded in using a cascade method: he used three refrigeration cycles, first with sulfur dioxide, then carbon dioxide, and finally oxygen. Like Cailletet he was only able to produce intermittent streams of liquid oxygen which quickly evaporated.

It was not until 1883 that oxygen and nitrogen were properly liquefied with a visible meniscus[41]. Szygmunt von Wroblewski and Karol Olszewski conquered these permanent



**Figure 1.7:** System used by Wroblewski and Olszewski. By releasing the high-pressure gas into a low-pressure tube partially submerged in boiling ethylene, they successfully condensed oxygen. [51]

gases with two modifications to Cailletet's procedure. The first modification was releasing the compressed gas into a sealed glass tube submerged in liquid ethylene. The second and vital modification was using a vacuum pump to reduce the pressure above the ethylene to 25 mmHg. This reduced the cold bath to about 143 K. Cailletet had previously made another attempt to liquefy oxygen in 1882 using ethylene to cool the gas but was unsuccessful. It was later found that oxygen has a critical temperature of 155 K making his failure obvious as the boiling point of liquid ethylene is 169 K. With oxygen and nitrogen conquered only hydrogen and the newly discovered helium remained to be liquified.

In the following years attempts were made to liquify hydrogen to no avail. More disheartening was the fact that Wroblewski had meticulously calculated the critical temperature of hydrogen to be 30 K, putting it out of reach using the cascade method[41]. Fortunately, a discovery in 1852 by James Joule and Lord Kelvin would provide the solution that allowed the temperature gap to be overcome.

Previously, scientists had exploited the atmosphere to do work against gases under pressure, allowing them to cool substantially. Joule and Kelvin designed an experiment to study the adiabatic expansion of gas in an isolated system. In their experiment, gas was compressed in a tube and forced through a porous plug at a constant pressure. The gas then seeped into a low pressure volume where it expanded adiabaticlly[41]. Since no energy could enter or leave their system Joule and Kelvin expected to see no change in temperature. This isenthalpic process is described by the following equations:

$$H_1 = U_1 + P_1 V_1$$

$$H_2 = U_2 + P_2 V_2$$

$$H_1 = H_2 \implies \Delta U = P_1 V_1 - P_2 V_2$$
(1.1)

For an ideal gas it was assumed that the compression work done to push the gas through the plug would exactly equal the expansion work done in the low-pressure half of the tube. However, to their surprise they found the gases would slightly cool or warm after expanding. In particular, they found that all gases could be cooled through expansion at sufficiently low temperatures. This change in temperature could only be attributed to some change in internal energy and was not understood until the work of Andrews and van der Waals. The discrepancy in the PV work came from the interactions of the molecules described in the van der Waals equation shown below. Warming was due to the effect of their volume represented by "b" and cooling was due to the attraction between them represented by "a". In other words, the work done to overcome what would later be called the van der Waals attractive force could be used to extract kinetic energy from the gas. The Joule-Thomson effect was then the third and final key concept of cryogenics needed to liquefy the remaining gases.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{1.2}$$

The final tool which enabled liquefaction of the remaining gases is also the most essential part of any modern lab that handles cryogenics. This is none other than the famous double walled glass vacuum flask created by James Dewar between 1892 and 1893[41]. Dewar's vacuum flask was very effective at storing liquefied gases due to the exceptional insulation of the silvered glass walls and evacuated space between them. The original design of his flask is still used today and is commonly referred to as a dewar.

Although Joule and Kelvin had proven it was possible to cool gases by throttling, it was not until 1895 that this idea found its use in a liquefaction process. At this time, both William Hampson and Carl von Linde independently patented gas liquefiers making use of the Joule-Thomson effect[41]. They modified the Siemens cooling process so that the gas would expand through a throttling plug rather than doing PV work. Both were able to successfully construct and



Figure 1.8: Illustration of the Linde-Hampson cycle. Gas is compressed at (P) and passes through a heat exchanger (K). Cooled, high-pressure gas then passes through a second heat exchanger (G) before it is throttled at the Joule-Thomson valve (E). Gas enters the low-pressure liquefaction chamber where it cools due to work through van der Waals attraction. Gas that cools enough to liquify is collected in chamber (F) while the boil-off forms a countercurrent cooling gas at (G). The warm low-pressure gas is then compressed again at (P) where the cycle repeats.[51]
utilize their air liquefiers shortly after filling their patents.

It was not long before Dewar put this liquefaction method to effect in combination with his vacuum flask. On May 10th 1898 Dewar became the first to liquify hydrogen gas utilizing the full arsenal of technologies that had been created in the pursuit of cold[41]. Using a hydrogen gas manometer, he later determined the boiling point of hydrogen to be 20 K. In his final major victory in the race to absolute zero Dewar used two of his vacuum flasks to solidify hydrogen around 14 K. The outer flask provided insulation to the liquid air held inside which cooled a second vacuum flask to about 80 K. It was this inner flask that held the condensed hydrogen allowing Dewar to solidify it by evaporative cooling using a vacuum pump.

### 1.1.5 Helium and "Supraconductivity"

With hydrogen liquified the only gas that remained was the recently discovered helium. It is this precious resource that has come to define the field of low-temperature physics and has facilitated the study of superconductivity for over a century.

Helium was first found August 18th, 1868 when Pierre Janssen noted a discrepancy in the sun's emission spectrum[41, 51]. Initially, he thought a bright yellow line from the sun was due to sodium. He later concluded it must belong to a new element that had yet to be observed on earth. Similarly, Joseph Lockyer noticed this new emission line, submitting his finding at the same time as Janssen. So rare is terrestrial helium that it was not until 1882 that its presence on Earth was confirmed. It was Luigi Palmieri who detected the same bright yellow line from helium while analyzing materials from a recent eruption of Mount Vesuvius. Then, in 1895 Sir William Ramsey became the first to isolate helium. He accomplished this by dissolving cleveite, a uranium containing material, with mineral acids and subsequently used sulfuric acid to remove oxygen and nitrogen gas. Like the others, Ramsey observed the bright yellow emission line from the sun, which he later sent to Lockyer for confirmation.

Almost immediately, scientists who were lucky enough to get their hands on helium tried to liquify the gas. In fact, by the time Dewar succeeded in liquifying hydrogen there had already been a few attempts at the newly discovered gas[41]. Dewar himself thought that he had managed to liquify helium alongside hydrogen, but soon found out helium would not be easily conquered.

The main contenders for the liquefaction of helium at the time were Dewar, Olszewski, and Heike Kamerlingh Onnes. By 1904 Dewar had calculated the critical temperature of helium to be around 6 K. At first, this was disputed by both Olszewski and Onnes with claims of a critical temperature near 1 K, but a later experiment by Onnes in 1907 concluded the critical temperature should lie between 5 and 6 K, restoring hopes of liquifying helium[41]. Ultimately, it was Onnes who would succeed, in no small part due to his access to abundant amounts of helium and the strong cryogenics infrastructure he developed at Leiden University. Taking advantage of evaporative cooling, counter-current heat exchange, Joule-Thomson throttling, the insulation of Dewar's vacuum flask, and the air and hydrogen liquefaction plants at Leiden, Onnes managed to liquify helium on July 10th, 1908, putting an end to the cryogenics race.

With the incredible facilities Onnes had established at Leiden he was positioned to lead the new field of low-temperature physics. Soon, he began investigating the properties of materials within a few Kelvins of absolute zero. Of particular interest was the electronic



**Figure 1.9:** An illustration of the system that Kamerlingh Onnes used to liquify helium.  $P_1$  recycles warm helium and compresses it to be forced through the Joule-Thomson valve shown as an X above the helium space. As the gas traveled to the liquefaction chamber it was cooled by countercurrent heat exchange at the exchangers  $S_1$  and  $S_3$ . The heat exchanger at  $S_2$  provided cooling by boiling off liquid  $H_2$  using a vacuum pump  $P_2$ . Multiple silvered vacuum flasks filled with other cryogens like liquid air insulated the helium vessel from ambient temperatures.[51]

behavior of pure metals at low temperatures. At the time there were several theories concerning the movement of electrons near absolute zero. Proposed theories included a gradual drop to zero resistance by Drude, an infinite resistance due to motionless electrons by Lord Kelvin, and a minimum non-zero resistance that would continue to 0 K by Matthiessen[52]. These theories are illustrated in Figure 1.10 above.



**Figure 1.10:** Diagram showing early prevailing theories of metallic behavior. The high-temperature region in black shows the expected linear response described by Ohms Law. The red curve which goes to zero resistance near absolute zero was supported by Nernst. The blue curve shows the theory both Dewar and Onnes supported where electrons would become frozen in place at absolute zero resulting in an infinite resistance. The green curve shows true metallic behavior at low temperatures where the resistance plateaus at a non-zero value due to impurities and lattice distortions.

Onnes began his investigation with platinum by noting that the samples varied in resistance at low temperature, but overall showed the same behavior. From this he concluded that the variation was due to the purity of the samples he measured. Soon he switched to gold as it could be made with a higher purity than other metals. Onnes' investigation of gold quickly confirmed his impurity hypothesis. Still unsatisfied with the metal purity, he turned to mercury as it could easily be distilled to high purity.

On April 8th, 1911, Onnes discovered what he would come to call supraconductivity. As he cooled mercury to 4.2 K a narrow and abrupt drop to zero resistance occurred. It would take Onnes a few more years to recognize superconductivity as a new phenomenon apart from the metallic behavior he had been studying. With more sensitive equipment and his confirmation of this phenomenon in tin and lead, it slowly became clear that superconductivity was something new entirely.

# **1.2** History of Superconductivity

Following the discovery of superconductivity by Onnes, interest began to grow around the new phenomenon. The main challenge facing newcomers was liquid helium as it was the only way to reach temperatures below 14 K. In fact, Onnes had a monopoly on liquid helium from 1908, when he first liquefied the gas, until 1923 as Leiden University was the only place in the world with a helium liquefier[53, 54]. In 1919 John McLennan requested assistance from Onnes to establish a cryogenics lab at the University and provided guidance[54]. By 1921 McLennan had succeeded in liquifying hydrogen, and on January 10th, 1923 the facility at Toronto produced its first liter of liquid helium, finally ending the monopoly. Researchers at University of Toronto would go on to investigate the physics of liquid helium.

#### **1.2.1** Meissner-Ochsenfeld Effect

The third group to enter the low-temperature space was that led by Walther Meissner. From 1923 to 1925, he collaborated with the Linde Company to install equipment for helium liquefaction at Physikalisch-Technische Reichsanstalt (PTR) in Brunswick, Germany, employing the same methods used at Leiden[55, 56]. The facility at PTR produced its first batch of liquid helium on March 7th, 1925. Not long after, Meissner discovered superconductivity in tantalum in 1928, followed by thorium, titanium, niobium, and vanadium[11, 56]. In 1929, he also discovered superconductivity in CuS, the second superconducting compound, a few days after the discovery of superconductivity in  $Au_{0.96}Bi_{0.04}$ [57, 58]. This began the search for superconductivity in other compounds.

While working with his student Robert Ochsenfeld in 1933, Meissner discovered the hallmark property of superconductivity, which now bears their names. The two observed the complete expulsion of magnetic flux from cylinders of lead and tin in the presence of a small applied field (less than  $H_c$ ) as the temperature was cooled below the superconducting  $T_c$ [59]. It is this expulsion of the magnetic field that is unique to superconductivity and acts as the smoking-gun for confirming superconductivity in new materials.

It cannot be understated how important the Meissner-Ochsenfeld effect is in confirming the presence of superconductivity. Zero resistance is not a unique property of superconductivity as it could also be observed in a perfect conductor. Even the sudden drop observed in superconductors is not unique as an insulator-to-metal transition can easily be mistaken as a sign of superconductivity.

Detecting the Meissner-Ochsenfeld effect also comes with some challenges. Superconductors exhibit superdiamagnetism which prevents magnetic fields from penetrating the material. As such the magnetization response will be directly proportional to the applied magnetic field:

$$B = H + 4\pi M$$

$$B \to 0 \Rightarrow H = -4\pi M$$
(1.3)

The shielding is the result of the induced supercurrent from Lenz's law which acts to cancel the applied magnetic field. Superdiamagnetism is also a property of a perfect conductor as



**Figure 1.11:** Figure showing the difference in the behavior of a perfect conductor (a) and a superconductor (b) in the presence of an applied magnetic field. In Figures (a) and (b) the left side shows the zero-field cooled sequence while the right side shows the field cooled sequence.

it is the byproduct of zero-resistance. For this reason, the measurement sequence of zerofield cooling (ZFC) and particularly field cooling (FC) are important tools for confirming the presence of the Meissner-Ochsenfeld effect.

Figure 1.11 shows how a perfect conductor (1.11a) and a superconductor (1.11b) respond in the presence of an applied magnetic field and help illustrate the ZFC and FC sequences. In the ZFC measurement, the sample is first cooled to low temperature where the zero resistance state exists. When a magnetic field is applied, both the perfect conductor and the superconductor respond as superdiamagnets and prevent the penetration of the magnetic field. As they are warmed up in the presence of the applied field a near perfect diamagnetic response should remain  $(-4\pi\chi)$  up to a temperature at which the supercurrent begins to dampen due to resistance. This manifests as a sharp decrease in the diamagnetic response. In the FC measurement a magnetic field is applied at high temperature in the resistive/normal state and then cooled. As the temperature falls below the superconducting  $T_c$ , the field is abruptly expelled as it becomes superdiamagnetic. In the case of the perfect conductor, it too will become superdiamagnetic and repel magnetic field lines from penetrating the sample. However, unlike the superconductor it will also trap the flux lines that were penetrating it before it entered the resistanceless state. When the applied field is then removed, as shown in Figure 1.11a, the trapped flux will cause a supercurrent to persist in the sample.

#### 1.2.2 The London Brothers

The discovery by Meissner and Ochsenfeld that the magnetic field inside a superconductor becomes zero provided a fundamental phenomenon upon which to build a theoretical explanation. In 1935 Fritz and Heinz London developed a set of equations that could be used to explain the phenomena observed in superconductors[60]. The London equations, as they are known, are shown below in Equations 1.4 and 1.5:

$$\frac{\partial \vec{\mathbf{j}}}{\partial t} = \frac{n_s e^2}{m} \vec{\mathbf{E}}$$
(1.4)

$$\nabla \times \vec{\mathbf{j}} = -\frac{n_s e^2}{m} \vec{\mathbf{B}}$$
(1.5)

where  $\vec{j}$  is the supercurrent,  $n_s$  is the number density of superconducting electrons, e is the fundamental charge of an electron, m is mass, and  $\vec{E}$  and  $\vec{B}$  are the electric and magnetic fields[61].

The London equations are phenomenological rather than being derived from first principles. To arrive at the first London equation, it can be assumed that superconducting electrons move as free particles under the influence of a uniform electric field. The force acting on these free electrons are readily described by Drude's model:

$$\frac{\partial}{\partial t} \langle \vec{\mathbf{p}}(t) \rangle = q \left( \vec{\mathbf{E}} + \frac{\langle \vec{\mathbf{p}}(t) \rangle}{m} \times B \right) - \frac{\langle \vec{\mathbf{p}}(t) \rangle}{\tau}$$
(1.6)

where the first two terms are the Lorentz force, and the third term is due to the scattering of electrons. In the case of a superconductor Equation 1.6 can be simplified to:

$$\frac{\partial}{\partial t} \langle \vec{\mathbf{p}}(t) \rangle = q \vec{\mathbf{E}} \tag{1.7}$$

as there is no magnetic field to consider nor is there scattering in a resistanceless state. Next, the supercurrent can be written as:

$$\vec{\mathbf{j}} = -n_s e \vec{\mathbf{v}} \tag{1.8}$$

Taking the derivative of Equation 1.8 and rearranging Equation 1.7 gives:

$$\frac{\partial \vec{\mathbf{j}}}{\partial t} = -n_s e \frac{\partial \vec{\mathbf{v}}}{\partial t} \tag{1.9}$$

$$\frac{\partial \vec{\mathbf{v}}}{\partial t} = \frac{-e\vec{\mathbf{E}}}{m} \tag{1.10}$$

which when combined yield the first London equation shown in 1.4.

From the first London equation the second equation can be derived. This is accomplished by taking the curl of both sides of Equation 1.4:

$$\nabla \times \frac{\partial \vec{\mathbf{j}}}{\partial t} = \frac{n_s e^2}{m} \nabla \times \vec{\mathbf{E}}$$
(1.11)

Using Maxwell's equation for the curl of E yields:

$$\nabla \times \vec{\mathbf{E}} = -\frac{\partial \vec{\mathbf{B}}}{\partial t} \Rightarrow \frac{\partial}{\partial t} \left( \nabla \times \vec{\mathbf{j}} \right) = \frac{n_s e^2}{m} \left( -\frac{\partial \vec{\mathbf{B}}}{\partial t} \right)$$
(1.12)

Integrating both sides with respect to time results in Equation 1.5 after considering the Meissner-Ochsenfeld effect requires the field inside to be 0 at t = 0.

Probably the most important result of the London equations is its ability to model the Meissner effect in superconductors. Using the second London equation and Maxwell's equation for Ampère's law it can be shown that the magnetic field falls off exponentially as it penetrates the superconductor. Assuming the contribution from the time dependent electric field is negligible inside the superconductor the Maxwell equation is:

$$\nabla \times \vec{\mathbf{B}} = \mu_0 \left( \vec{\mathbf{j}} + \epsilon_0 \frac{\partial \vec{\mathbf{E}}}{\partial t} \right) \cong \mu_0 \vec{\mathbf{j}}$$
(1.13)

The second London equation can therefore be written as:

$$\nabla \times \vec{\mathbf{j}} = \frac{1}{\mu_0} \nabla \times \left( \nabla \times \vec{\mathbf{B}} \right) = -\frac{n_s e^2}{m} \vec{\mathbf{B}}$$
(1.14)

Using the vector identity for the curl of curl shown in Equation 1.15 and combining it with Equation 1.14:

$$\nabla \times \left( \nabla \times \vec{\mathbf{A}} \right) = \nabla \left( \nabla \cdot \vec{\mathbf{A}} \right) - \nabla^2 \vec{\mathbf{A}}$$
(1.15)

$$\nabla \left( \nabla \cdot \vec{\mathbf{B}} \right) - \nabla^2 \vec{\mathbf{B}} = -\mu_0 \frac{n_s e^2}{m} \vec{\mathbf{B}}$$
(1.16)

Since the divergence of the magnetic field is always zero Equation 1.16 simplifies to:

$$\nabla^2 \vec{\mathbf{B}} = \mu_0 \frac{n_s e^2}{m} \vec{\mathbf{B}}$$
(1.17)

Solving this equation in the 1-dimensional case is rather straight forward and perfectly illustrates the Meissner-Ochsenfeld effect.

First, consider a semi-infinite slab of superconducting material as illustrated in Figure 1.12. Here the field outside the superconducting region is  $B_0[62]$ . Then, the field inside the superconductor can be solved for by rewriting Equation 1.17:

$$\frac{d^2B}{dx^2} = \mu_0 \frac{n_s e^2}{m} B \tag{1.18}$$

This simple ordinary differential equation has a solution of the form:

$$B = C_1 e^{-x/\lambda} + C_2 e^{x/\lambda} \tag{1.19}$$

$$\lambda = \sqrt{\frac{m}{\mu_0 n_s e^2}} \tag{1.20}$$

where  $\lambda$  is a parameter with units of length called the penetration depth. Imposing boundary conditions it becomes clear that  $C_2 = 0$  since the field must go to zero as it moves further into the superconducting region. This is the observation of Meissner and Ochsenfeld. Combined with the boundary condition that  $B = B_0$  at x = 0, Equation 1.19 simplifies to:

$$B = B_0 e^{-x/\lambda} \tag{1.21}$$



**Figure 1.12:** This figure illustrates the semi-infinite superconducting slab where the left half is in vacuum and the right half is a superconductor. Note the two vertical axes y and B used in the figure. The x-y axes are used to describe the physical shape of the superconductor while the x-B axes are used to show the magnetic field strength as a function of penetration depth.

Equation 1.21 gives a good mathematical representation of the magnetic field which shows an exponential decay within the superconductor. The penetration length  $\lambda$ , shown in Equation 1.20, gives an idea of how far into the superconductor the field can effectively penetrate. This is presented in Figure 1.12 where the red line shows the strength of the magnetic field as a function of penetration depth.

Note that the penetration depth depends on the number density of superconducting electrons which is, in turn, a function of temperature. In the two-fluids model, the total number of electrons,  $n, n = n_s + n_n$  where  $n_s$  is the number density of superconducting electrons and,  $n_n$  is the number density of the normal state electrons. As  $T \to 0$ , the electrons move into the superconducting state so that  $n = n_s$ . Conversely, as  $T \to T_c$ , the electrons move into the normal state so that  $n = n_n$ . Physically, this means that the penetration depth is minimized at T = 0K and goes to infinity (destruction of superconductivity) as  $T \to T_c$  as is obvious from Equation 1.20. Gorter and Casimir found that the number density of superconducting electrons was well-fitted by assuming[61, 63]:

$$n_s = n \left[ 1 - \left(\frac{T}{T_c}\right)^4 \right] \tag{1.22}$$

Incorporating this into Equation 1.20 provides an equation to describe the penetration depth as a function of temperature and superconducting  $T_c$ :

$$\lambda_L(T) = \frac{\lambda_L(0)}{\left[1 - \left(\frac{T}{T_c}\right)^4\right]} \tag{1.23}$$

#### **1.2.3** Type I & Type II Superconductors

Shortly after development of the phenomenological London equations, a group at the Ukrainian Physical-Technical Institute, Kharkov led by Lev Shubnikov discovered that the properties of superconductors were not as straight forward as initially thought. It had been long reported that the transition into the superconducting state was typically accompanied by a sharp drop to zero resistance below the  $T_c$  and the expulsion of all magnetic flux from within the material. However, there existed some anomalous superconductors where the  $T_c$  had a broad transition to zero resistance [64].

Initially, Wander Johannes de Haas and Josina Maria Casimir-Jonker had measured the magnetization of superconducting alloys of  $Bi_5Tl_3$  and  $Pb_{35}Tl_{65}$ , finding that there were actually two critical fields (H<sub>c</sub>) in the transition from the superconducting to normal state[65, 66]. They attributed this anomalous behavior to inhomogeneous samples. Later, Shubnikov's group followed up on their work by investigating the  $H_c$  of carefully prepared PbTl samples. After annealing the samples for a long time, x-ray diffraction confirmed that there was no inhomogeneity unlike what de Haas and Casimir-Jonker had described. None-the-less, they too observed two critical fields. Above the first critical field,  $H_{c1}$ , the magnetic flux within the material increased with applied field while still retaining its resistanceless property[64, 67, 68]. Only once the applied field exceeded a second, much higher critical field,  $H_{c2}$ , would the superconducting state be destroyed. This work indicated that there was a second kind of superconductor which behaved like a typical superconductor below  $H_{c1}$ , but allowed magnetic flux penetration between  $H_{c1}$  and  $H_{c2}$ . It was not until much later, after he was arrested and later executed, that the work of Shubnikov et al. was recognized by the wider scientific community as the discovery of what is now called type II superconductivity[66].

One of the questions that arose regarding superconductivity was why the Meissner-Ochsenfeld effect manifested at all. An experiment by Rex Pontius in 1937 confirmed that very fine wires of lead, on the order of the penetration depth, could support significantly higher magnetic fields than the bulk material[41]. This led researchers to conclude that there must be some kind of surface energy that produces a continuous superconducting domain. This explained why the prediction that thin superconducting wires should have a larger threshold field was correct, yet bulk superconductors were not observed to split into fine lines of superconducting and normal state in high fields. The positive surface energy between the superconducting and normal states ensured the energy is minimized when the interface surface is minimized.

The idea of surface energy prompted new investigations into the theoretical description of superconductivity in the 1950s. Vitalii Ginzburg and Lev Landau developed a



**Figure 1.13:** Illustrations of the diamagnetic response of type I and II superconductors. For a type I (a) the blue region represents the superconducting region while the gray represents the normal state. The sharp boundary shows the abrupt transition to the normal state at  $H_c$ . In a type II (b), the colored regions once again represent superconducting and normal states. However, there are now three distinct regions separated by two dotted lines corresponding to  $H_{c1}$  and  $H_{c2}$ . Below  $H_{c1}$  the superconductor acts like a type I, preventing any field penetration. In the region between  $H_{c1}$  and  $H_{c2}$ , there is a mixed state of normal and superconducting regions in the form of flux vortices. Above  $H_{c2}$  all superconductivity is destroyed.

generalization of the London equations using Landau's theory of second-order phase transitions[61, 69]. This allowed for the treatment of inhomogeneous superconducting densities through the order parameter  $\Psi(r)$ . In the case of superconductivity,  $\Psi(r)$  represents the superconducting wavefunction where it is zero above the T<sub>c</sub> and nonzero below T<sub>c</sub>. More physically, the quantity  $|\Psi(r)|^2$  gives the superconducting electron density  $n_s(r)$ . This new theoretical model was very successful in accounting for behaviors of superconductivity.

Around the same time, Alfred Brian Pippard investigated the interface of superconducting and normal state developing a non-local generalization of the London equations[70, 71]. This gave rise to a new length parameter called the coherence length  $\xi$ . In Ginzburg-Landau (GL) theory,  $\xi$  is defined as the length from the boundary between the superconducting and normal states over which the superconducting order parameter diminishes to zero[61]. Physically, this provides a representation of the density of superconducting electrons as a function of distance from the boundary. Another way to describe the coherence length is the length for which superconducting electrons and normal electrons cannot be distinguished[41]. In very clean crystals, such as pure metals, the mean free path of a normal electron is long. Likewise, the coherence length is longer in a clean crystal. In alloys and dirty crystals, the mean free path is much shorter and thus the coherence length is short as well.

The two parameters,  $\lambda$  and  $\xi$ , provided some interesting insights into superconductivity. Initially, Ginzburg and Landau had solved the solution of superconductivity in the limit of short penetration depths as that is what had been observed experimentally. In this region they calculated a positive surface energy matching experimental observations. Ginzburg and Landau also determined that the surface energy would cross over when the ratio  $\kappa = \frac{\lambda}{\xi}$ , later known as the Ginzburg-Landau parameter, was equal to  $\frac{1}{\sqrt{2}}$ [66]. However, they were not interested in the region beyond as it corresponded to a negative surface energy and didn't appear to represent superconductors at the time.

Following the works of Ginzburg and Landau, Alexei Abrikosov began to investigate the limit of  $\kappa > \frac{1}{\sqrt{2}}$ . In 1952, he published his derivations of GL theory in the limit of large  $\kappa$ [66, 72]. The new properties of superconductivity in this limit led to its labeling as type II superconductivity. In the next year, Abrikosov derived the now well-known vortex lattice of type II superconductivity. However, it was not until after 1955, when Richard Feynman published his work on vortices in superfluid helium, that Abrikosov could convince Landau of his vortex lattice theory[66]. Abrikosov's famous paper, that would come to define the modern understanding of type II superconductors, was finally published in 1957[73].

Even so, the difference in type I and type II superconductors described by Shubnikov and Abrikosov was not widely recognized outside the USSR[66]. It was not until the 1960's that this idea began to gain traction in the rest of the world. Finally, in 1964 superconducting vortices of the type II were directly observed via neutron diffraction by Cribier et al., putting an end to all doubt[74].

Figure 1.14 helps illustrate the differences between type I and II superconductors. The one dimensional solution for the magnetic field penetration near the normal-superconductor boundary presented in this figure is found in Equation 1.21. To understand the solution for the superconducting electron density presented in this figure the GL equation must first be solved.

Finding the solution for the superconducting order parameter via GL theory is useful in understanding the coherence length. Below is the time-independent GL equation:

$$\alpha(T)\Psi + \beta(T) \left|\Psi\right|^2 \Psi + \frac{1}{2m^*} \left(-i\hbar\nabla - \frac{e^*}{c}\vec{\mathbf{A}}\right)^2 \Psi = 0$$
(1.24)

where  $\alpha < 0$  and  $\beta > 0$  are phenomenological parameters,  $\Psi$  is the superconducting order parameter,  $m^*$  is the effective mass,  $e^*$  is the effective charge, and  $\vec{\mathbf{A}}$  is the magnetic vector potential. Solving for the order parameter in one dimension with no magnetic field is rather straight forward. Under these conditions Equation 1.24 simplifies to:

$$-\frac{\hbar^2}{2m^*}\frac{d^2}{dx^2}\Psi - |\alpha|\Psi + \beta|\Psi|^2\Psi = 0$$
(1.25)



**Figure 1.14:** These figures help illustrate the difference between type I (left) and II (right) superconductors. In each figure the Y-axis separates the normal and superconducting regions to the left and right respectively. Figures (a) and (b) show the relationship between the penetration depth and coherence length by plotting the 1D solution for the magnetic field (red) alongside the superconducting electron density (blue) near the boundary. Note the difference in how deeply the field penetrates the region of superconducting electrons. Figures (c) and (d) represent the energy associated with the penetrating field and the energy from the condensed super-electrons. Adding these contributions together yields (e) and (f) which show the surface energy of the type I and type II superconductors respectively.

where  $\alpha$  is now positive. Through a suitable substitution Equation 1.25 can be further simplified:

$$-\frac{\hbar^2}{2m^*|\alpha|}\frac{d^2}{dx^2}f - f + f^3 = 0 \quad \text{where} \quad \Psi = \sqrt{\frac{|\alpha|}{\beta}}f \tag{1.26}$$

From the ODE in Equation 1.26 comes the definition of the coherence length. By solving Equation 1.26 it is possible to see the form of the superconducting order parameter.

$$\Psi = \sqrt{\frac{|\alpha|}{\beta}} \tanh\left(\frac{x}{\xi\sqrt{2}}\right) \quad \text{where} \quad \xi = \frac{\hbar}{\sqrt{2m^* |\alpha|}} \tag{1.27}$$

It is now easy to understand how the coherence length defines the distance over which the order parameter falls to zero near the normal-superconducting boundary. The superelectron density,  $n_s$ , can be derived directly from Equation 1.27. Figures 1.14a and 1.14b illustrate the effect of coherence length on the distribution of superconducting electrons.

#### **1.2.4** The Isotope Effect

Arguably, the most valuable discovery for the development of a theoretical description of superconductivity came from the isotope effect. As will become clear later, it was the connection between the mass and the superconducting  $T_c$  that would eventually lead to the famous microscopic theory of Bardeen, Cooper, and Schrieffer.

As early as 1920, Onnes and Tuyn attempted to investigate the superconducting isotope effect in lead using "Kahlbaum" lead and uranium lead, <sup>207</sup>Pb with an average mass of 207.2 and <sup>206</sup>Pb with an average mass of 206.06 respectively[75]. Unfortunately, the resolution of their helium gas thermometer, which they claimed to be 0.025 K, was not great enough for the researchers to distinguish the two superconducting transitions. A later investigation by E. Justi in 1941 also failed to detect the isotope effect despite claiming a temperature



Figure 1.15: Data plotted to show the relationship between the square-root of mass and  $T_c$ . Note that each datum point is also labeled with the atomic mass. Figure (a) shows data from Reynolds et al. and Maxwell for the isotope effect in mercury[77, 78]. Figure (b) shows data from Maxwell, Laurmann et al., Lock et al., Olsen-Bär et al., and Serin et al. for the isotope effect in tin[79–83]

On March 24th, 1950, two groups independently led by Charles Reynolds and Bernard Serin at Rutgers University, and Emanuel Maxwell at the National Bureau of Standards, simultaneously published their works on the effect of isotopic mass on the critical temperature of mercury[77, 78]. They noted an increase in  $T_c$  with decreasing mass as shown in Figure 1.15a. This was quickly followed by investigations of the isotope effect in tin by Maxwell on May 19th and expanded by Lock et al. and Olsen-Bär et al. in collaboration with Allen and Dawton in November[79, 81, 82]. Data for tin can also be seen in Figure 1.15b.

A few months after the initial discovery in mercury on May 16th, 1950, Herbert Fröhlich submitted a theoretical paper which claimed  $T_c \propto \frac{1}{\sqrt{M}}[84]$ . It is not entirely clear whether this work was completed without knowledge of the work of Reynolds et al. and Maxwell. The original paper made no mention of the experimental works on the isotope effect and a later letter to the editor clarified Fröhlich recently came to know of these works[85]. Though there is doubt about the independence of the work, it was still a major step toward understanding the mechanism of superconductivity[86].

Worth mentioning is the work of Marianne Olsen-Bär. On June 5th, 1951 she submitted findings on the isotope effect in lead 31 years after the initial experiment by Onnes and Tuyn[75]. It was found that the T<sub>c</sub> of lead 206.15 was  $0.0386 \pm 0.002$  K higher than lead 207.72, concluding that  $T_c \propto \frac{1}{M^{0.73}}$ [76]. A few months later Serin and Reynolds confirmed the work of Olsen-Bär on lead in their investigation of the isotope effect of tin and lead[83]. It is interesting to consider how the field of superconductivity may have developed had Onnes detected the isotopic T<sub>c</sub> shift in 1920.

#### **1.2.5** Theory of Conventional Superconductivity

Up to the 1950s, all that was known about superconductivity came from experiments and phenomenological theories. There was no microscopic description of superconductivity at the time leaving, researchers to hypothesize about its mechanism. It was not until the breakthrough research on the isotope effect that the path forward became clear. The fact that the  $T_c$  depended on the mass of superconducting elements implied an interaction with the crystal lattice.

The discovery of the isotope effect attracted the attention of John Bardeen who then set out to describe the mechanism of superconductivity[52]. He proposed a mechanism involving a weak attraction among electrons in a free electron gas, which was mediated through lattice phonons. In 1955, with the help of David Pines, Bardeen was able to show electrons could overcome Coulomb repulsion at low temperature[87].



**Figure 1.16:** This figure illustrates the effect of conduction electrons on the crystal lattice. As electrons travel through the crystal, they attract the positive nucleus inducing phonon motion and creating an area of higher positive charge density. It is this region of higher positive charge density that overcomes the Coulomb repulsion between electrons, allowing the formation of Cooper pairs. Note the two electrons are represented by different colors to indicate opposite spin.

Around this time, Bardeen was joined by his graduate student Robert Schrieffer and Leon Cooper to tackle the challenging problem. A big advancement in the project occurred in 1956 when Cooper found that electrons would pair to form a condensation at the fermisurface leading to a protective energy gap[41, 88]. These pairs, now called Cooper pairs, have equal and opposite momentum and spin which allows electrons to travel through the crystal lattice without a net exchange of momentum. Furthermore, they only experience an attractive force at a distance close to the coherence length. If they are much further or closer than this distance the electrons will not interact with or will repel each other.

A year after the development of Cooper pairs, Schrieffer had the final breakthrough finding a way to mathematically represent the many-body problem with a single wavefunction[89]. With this, the group had finally solved the mystery of superconductivity known today as BCS theory after the authors[90]. Later that year, the group successfully



**Figure 1.17:** The Feynman diagram of the phonon mediated interaction responsible for Cooper pairing. The fermion creation and annihilation operators are placed next to the respective section of the Feynman diagram to help illustrate the process. Initially, two electrons of opposite spin and momentum k exist. These particles are then annihilated as they transfer momentum q through the lattice via phonon interaction. Then, two electrons are created with the momentum k+q and -k-q conserving the net-zero momentum in the Cooper pair.

used their new theory to calculate the properties of a superconductor including heat capacity, penetration depth, energy gap, etc.[91]. The resulting relationship for the  $T_c$  was shown as:

$$k_B T_c = 1.134 E_D e^{\frac{-1}{N(0)V}} \tag{1.28}$$

where  $E_D$  is the Debye cutoff energy, N(0) is the density of states at the fermi-surface, and V is the electron-phonon coupling potential. Finally, 46 years after the initial discovery by Onnes superconductivity had been explained.

Though BCS theory was able to predict the properties of superconductivity there was no experimental evidence to directly support the newly proposed Cooper pairs. The persistent nature of supercurrent indicated a quantization in the permitted energy. This would necessarily mean that the current could only change incrementally in proportion to the elementary fluxoid h/e. In 1961, experiments to prove the quantized nature of supercurrent were completed independently in two groups led by Bascom Deaver and William Fairbank and R. Doll and M. Näbauer[41, 92, 93]. They used long, thin-walled cylinders of superconducting materials to track the applied flux passing through them. What they found was a quantization of the allowed flux over small ranges of applied magnetic field. The outcome of their experiment was the realization that the fluxoid for the superconducting cylinders was h/2e. The 1/2 factor was, of course, due to the charge of the fundamental particle responsible for the supercurrent, the Cooper pair.

#### 1.2.6 Era of HTS & RTS

In the time from the discovery of superconductivity in 1911 up to 1974, the highest  $T_c$  had increased very little: from 4.2 K in mercury, to 9.2 K in niobium, and finally to 23.2 K in Nb<sub>3</sub>Ge[1, 11, 17, 94]. In fact, in 1968, William McMillan predicted the maximum  $T_c$  based on BCS theory to be about 40 K, leaving little hope for high-temperature superconcuctivity[95]. It was not until 1986 that a major breakthrough in the field of superconductivity bought renewed hope.

For a while after the development of BCS theory it did well to describe many superconductors at the time. However, in 1986 Alex Muller and Johannes Bednorz discovered a new class of superconductors with La-Ba-Cu-O (LBCO) which pushed the record  $T_c$  up to 35 K[2]. Researchers quickly began investigating other cuprates for similarly high critical temperatures. In less than a year a new cuprate, Y-Ba-Cu-O (YBCO), was discovered catapulting the record  $T_c$  to 93 K and shattering the limit set by McMillan[20]. By 1993, the record  $T_c$  had reached 133 K in Hg-Ba-Ca-Cu-O at ambient pressure which was then enhanced to 164 K at a pressure of 31 GPa[23, 24]. It became clear that the cuprates could not be explained by BCS theory and were deemed unconventional superconductors.

After the discovery of the cuprates came the iron-based family of superconductors starting with LaOFeP in 2006[4]. In the years to follow many other iron-based compounds were discovered with  $T_cs$  around 40 K, leaving cuprates unrivaled in terms of critical temperature. Even so, there have been reports of exceptionally high  $T_cs$  in monolayers of FeSe, up to 107 K[26, 96, 97]. Like the cuprates, these high  $T_c$  superconductors could not be understood using BCS theory and were also designated unconventional.

In recent years there have been numerous reports of superconductors with critical temperatures that approach and even exceed room temperature [27–33, 98–101]. All but one of these superconductors are hydrogen based materials known as superhydrides [32, 33]. This new class of superconductors was discovered in 2015 when it was found that a  $T_c$  of 203 K could be induced in H<sub>3</sub>S under 155 GPa of pressure, making it the highest  $T_c$  at the time [27, 98]. This was quickly supplanted by the current record holder, LaH<sub>10</sub>, with a  $T_c$ of 260 K under 190 GPa [28, 99, 100].

Worth mentioning are contested reports of room-temperature superconductivity (RTS) in carbonaceous sulfur hydride (C-H-S) with a  $T_c = 287 \text{ K}$  under 267 GPa[29], in LaH<sub>10-x</sub> with  $T_c$ s potentially well above room temperature under 158 GPa after repeated thermal cycling[30], and the very recent reports of LuH<sub>x- $\delta$ </sub>N<sub> $\delta$ </sub> with a  $T_c = 294 \text{ K}$  at 1 GPa[31, 101] and Pb<sub>10-x</sub>Cu<sub>x</sub>(PO<sub>4</sub>)<sub>6</sub>O (x=0.9-1.0), more commonly referred to as LK99, with a  $T_c$  up to



Figure 1.18: A graph showing the increase in  $T_c$  over time. All data points proceeded by \* are under pressure and the datum point proceeded by \*\* indicates the sample is under pressure and underwent thermal cycling. The region above the dashed line shows RTS that are hotly contested. Data used in this figure was taken from numerous sources[1–33].

400 K at ambient pressure [32, 33]. However, these claims have been heavily scrutinized by the scientific community as other groups have failed to reproduce the reported RTS.

The newest class of superconductors discovered is the family of nickelates. To date, only a handful of reports have documented superconductivity in these materials, which include  $Nd_{1-x}Sr_xNiO_2$ ,  $Pr_{1-x}Sr_xNiO_2$ , and  $La_3Ni_2O_7[7-9, 25]$ . These compounds are similar in structure and chemistry to the cuprates which has excited many researchers about their potential. In fact, a very recent report on  $La_3Ni_2O_7$  claims a  $T_c$  of 80 K at 14 GPa[25].

# Chapter 2

# **Experimental Methods**

This dissertation chapter focuses on the experimental methods employed and goes into the details of this high-pressure work. The methodology used is based on the previous works which developed the diamond anvil cell (DAC), particularly those by Mao and Bell[102–104]. Figure 2.1 shows an overview of the experimental setup. Each component is explored in the corresponding section. Note that the pressure cell and optical system are not present in Figure 2.1 for simplicity, but are also explored in the following sections.

Figure 2.1 shows the three major components of the experimental setup used for measuring resistivity: the double vacuum flask dewar (1), the probe (2), and the data acquisition rack (3). Each component in the figure is also labeled with its major subcomponents, which are briefly described below.

The dewar flask (1b) is used to create a low-temperature environment and is held inside a metal support frame (1a).  $LN_2$  and LHe are cryogens used in the glass dewar to reach temperatures of ~ 1 K. Temperatures below 4.2 K are reached using a vacuum pump which is not visible in Figure 2.1. Further details of the vacuum system are discussed in Section 2.4 on the glass dewar.



Figure 2.1: A summary of the main components used in the data acquisition of high-pressure resistivity.

The probe (2) is used to hold the pressure cell inside the dewar and control its temperature by moving it up (warmer) or down (colder) through a temperature gradient. The pressure cell is contained inside the pressure cell can (2e) which is screwed to the base of the probe. The can also houses a resistance temperature sensor (RTS) not shown in Figure 2.1. The main body of the probe, or probe shaft (2d), supports the can and houses the wires that run between the can and a DB-25 connector in the probe head (2a). Stainless-steel pressure rods (2b) pass through the top plate into the dewar where they can be used to adjust the pressure in the DAC. Finally, the top plate (2c) supports the probe shaft and pressure rods and creates an airtight seal for the dewar.

The data acquisition rack (3) is responsible for collecting resistivity data on high-pressure samples. The data rack frame (3b) holds all the instruments (3e-3h) and the computer (3c/3d). The probe is connected to the instruments using a wire cable (3a) with a DB-25 connector. The instruments are connected to each other and the computer via GPIB cables. The instruments included in the rack include: Keithley 6221 DC and AC Current Source (3e), Keithley 2182A Nanovoltmeter (3f), Keithley 705 Scanner with 7055 and 7059 scanner cards (3g), and Lakeshore LS336 (3h).

## 2.1 Pressure Cell

High-pressure work necessitates a high-pressure environment for exploring the properties of a material. Pressure cells provide such an environment through a number of methods which commonly use opposing anvils, pistons, screws, or levers to apply force to a sample. Distributed over a small contact surface, these cells can produce pressures up to 1 TPa (10 Mbar)[105, 106].

This section will describe the symmetric DAC which was used for measurements in a glass dewar. Details of the cell construction and preparation are discussed in the following

sections.

#### 2.1.1 Physical Description

A diagrammatic summary of the symmetric DAC is show in Figure 2.2 below. Each component is numbered and listed in the Bill of Materials presented in Table 2.1. The numbers used to label each component will be used for all subsequent figures pertaining to this pressure cell. Components appearing outside the pressure cell are labeled accordingly.

The DAC is made of a top (2) and bottom (1) cell half as shown in Figure 2.2. Figure 2.3 shows more detailed views of the top and bottom halves respectively. Each cell half has four M2.5-0.45 set screws (10,11) which hold their tungsten carbide seats (3) in place. The seats support the diamond anvils (4) and are bonded together using a mixture of Loctite Stycast (5) 2850FT and CAT 24LV. These components are clearly shown in the exploded view of each cell half presented in Figure 2.4.

A total of four M5-0.8 screws are used to couple the cell halves and control the cell pressure. Two are left-handed screws (8) and the other two are right-handed screws (9). Each pressure screw has a stack of 25 Belleville washers (13) stacked in alternating groups of 5 washers which act as a spring and help control the addition and removal of pressure. The stacks can be seen in Figure 2.2, but are best seen in Figure 2.4a. The diamond anvils are held apart by M5-0.8 safety screws (12) until the cell is to be closed. These screws also provide a convenient tool for separating the cell halves during disassembly.

During pressure experiments, a metal gasket (6) is placed between the diamond anvils to contain the sample and hold the pressure. This gasket is supported by small pieces of clay (7). An exploded view of the anvil assembly is shown in Figure 2.5a. Close up views



**Figure 2.2:** Exploded view of a diamond anvil cell. Each of the labeled components can be found in Table 2.1.

of the bottom anvil assembly with and without the gasket and clay supports are show in Figure 2.5b. Details and figures of the gasket and sample are given in Section 2.1.2.







(a)

(d)

(b)

(c)

(f)



Figure 2.3: Detailed view of the top (a-c) and bottom (d-f) cell halves.

(e)





**Figure 2.4:** Exploded view of the top and bottom cell halves. (a) shows the top half of the DAC while (b) shows the bottom half. Note the orientation of the Belleville washers (13) grouped in stacks of five.



(a)



(b)

**Figure 2.5:** The diamond anvil, tungsten seat, and gasket. (a) detailed view of the anvil assembly. (b) shows the bottom seat with clay supports and indented gasket (top) and the diamond anvil attached to the bottom seat with Stycast (bottom).

ITEM NO.	PART NAME	DESCRIPTION	QTY.
1	DAC - Bottom Half	Bottom portion of DAC	1
2	DAC - Top Half	Top Half of DAC	1
3	DAC Seat	Tungsten carbide seats for anvils	2
4	Diamond Anvil - 8 Sides	8 sided diamond with 500 um culet	2
5	Stycast	Loctite Stycast 2850FT using CAT 24LV	2
6	Pressure Gasket	Half-hard stainless steel 300 um thick and 1 cm diameter	1
7	Clay Support	Clay for supporting pressure gasket	4
8	Pressure Screw - LH	Left handed screw for adding pressure	2
9	Pressure Screw - RH	Right handed screw for adding pressure	2
10	Set Screw	Screws to hold top seat in place	4
11	Set Screw - Short	Screws to hold bottom seat in place	4
12	Safety Screw	Screws to hold DAC halves appart	2
13	Belleville Washer	Washers used as a spring for adding pressure to DAC	100

Table 2.1: Bill of materials for diamond anvil cell

### 2.1.2 Cell Preparation

Preparation of the DAC can be divided into three main steps: diamond anvil alignment, gasket preparation, and sample installation and wiring. This section will give a general outline of cell preparation.

#### 2.1.2.1 Diamond Anvils & Alignment

To produce the extreme pressures used in investigating properties like superconductivity, an equally extreme material must be used to support compression. For this reason, diamonds are paired with tungsten carbide seats to form the opposed anvils used for compressing samples. Therefore, the first step is to mount the diamonds to their tungsten carbide seats.



Figure 2.6: Diamond anvil jig. (1) bottom half, (2) top half, (3) tungsten carbide seat, (4) diamond anvil, (5) M4-0.70 screw, and (6) M2.5-0.45 screw.

Mounting the diamonds is accomplished by using the mounting jig shown in Figure 2.6. The jig has four screws (6) at its base that are tightened to secure and adjust the position of a tungsten carbide seat (3). The top half (2) of the jig holds the diamond (4) in position, with its table resting against the seat and culet faced upward (see Figure 2.7 for details
on the diamond anvil). Using a microscope, the seat is moved via the four screws to center it with the center of the diamond culet. For details on the alignment process see Appendix A.1. Once centered, a mixture of Loctite Stycast 2850FT and CAT 24LV is used to cover the seat around the diamond crown and slightly above the diamond girdle. The Stycast is typically allowed to cure overnight before the seat is removed from the jig. For more details on preparing the Stycast and alternate curing conditions see Appendix A.2.



Figure 2.7: Detailed view of 8-sided and 16-sided diamond anvils.

Diamond alignment is the key to reaching the highest pressures. All diamond anvils will break at sufficiently high pressures. That said, poor alignment can greatly decrease this pressure, leading to diamond breakage at low to moderate pressure.



Figure 2.8: Using the safety screws to protect the diamond anvils while closing the cell.

To begin the diamond alignment, the seats are fixed in place in the approximate center of each cell half. This step is done by eye and is a very rough approximation. Each cell half is equipped with four set screws, utilized in the same manner as the jig screws, to secure and adjust the positions of the seats. With the anvils in place, the cell is slowly closed with the safety screws (see Figure 2.8) raised to prevent a sudden collision between the diamond anvils, potentially damaging them. Once the top half of the cell meets the safety screws, the latter are lowered in small increments so that the cell can be slowly closed. Using a pressure screw to close the cell gives the user more control than compressing it by hand. The cell is closed until the diamonds are separated by an air gap of a few microns as shown in Figure 2.9. At this distance both diamond culets should be in focus under the microscope.



**Figure 2.9:** A small air gap between diamonds provides the best view of both culets for alignment while preventing damage due to contact.

Adjustments to the top anvil are easy and can be monitored under the microscope as the set screws are accessible when the cell is closed. The set screws for the bottom half can only be adjusted when the cell halves are separated (see Figure 2.8), making it much more difficult to center. Fixing the position of the top diamond is the most effective method for completing the alignment. While the cell is upside-down, the top (now bottom) seat is moved into position. Keeping the bottom half (now top) fixed in place, the top cell half is rotated to compare the images at  $0^{\circ}$  and  $180^{\circ}$ . If the two images look nearly identical it means the top diamond has been properly centered. Note that the images do not need to be perfectly aligned as shown in Figures 2.10a/b, rather they should show the same diamond misalignment without mirroring in both orientations. From here the cell is sat upright, so the bottom anvil can be slowly moved into position. Since the adjustment can only be done when the cell is open this part is a matter of guess work and patience. The permissible misalignment depends on the culet size, but is generally 10 µm to 20 µm for a 500 µm culet and roughly 5 µm for a 150 µm culet. Note that illuminating the DAC from below makes identifying the top and bottom diamond anvil easy as shown in Figure 2.10d.

It is not sufficient to align the diamonds so that they overlap with an acceptable misalignment. The diamonds should be rotationally aligned along the central axis of the cell to ensure even compression. This can be quite difficult to align, but is best done before final translational alignment has been completed. If done carefully, translational adjustments will do little to rotate the diamond. Since the top anvil should be centered first, it is preferable to rotate the bottom diamond. When rotating the diamond, two set screws are loosened (one along each axis) while the others provide a reference for the position of the seat. A reference mark is made on the tungsten carbide seat and the floor/ceiling of the cell half to gauge how much it is rotated. The seat is lifted and rotated with a pair of tweezers while pushing it against the two reference screws. The set screws are then tightened again, and the rotational alignment is checked. Examples of good and bad alignments are given in Figure 2.10.

Once the alignment is complete, four small balls of clay are placed around the bottom diamond anvil to provide support to the gasket as illustrated in Figure 2.5. Then, a final check is done by partially pre-indenting an annealed 301-stainless-steel gasket. Inspecting



**Figure 2.10:** Diamond alignment process. (a) and (b) show the diamonds when they have been properly aligned at  $0^{\circ}$  and  $180^{\circ}$ , respectively. (c) and (d) give examples of poor alignment both rotationally and translationally, also at  $0^{\circ}$  and  $180^{\circ}$ . Note the bright and dark diamond outlines prominently featured in (d) correspond to the lower and upper diamond respectively.

the indentation will show any misalignment of the anvil surfaces, i.e., warping of the gasket indentation when the anvil surfaces are not parallel. This test also checks whether the diamonds will shift under pressure. Anvil surface misalignment is rare, but changes to the alignment are likely if the set screws are not tightened adequately.

### 2.1.2.2 Gasket Preparation

Once the diamonds have been aligned, the cell gasket can be prepared. This begins with choosing an appropriately sized gasket from the desired gasket material. Gaskets are punched or cut from metal shims or purchased commercially. As an example, the author cut gaskets from 0.012'' (~300 µm) half-hardened stainless-steel shim purchased from McMaster-Carr. The size, material, and thickness of the gasket are typically determined by the ultimate pressure of the experiment and whether a magnetic field is to be applied. Thicker and more rigid materials are used to reach higher pressure, however high pressure is not always desired. When magnetic measurements are planned, materials such as CuBe, rhenium, or Russian alloy (Ni-Cr-Al) should be used to minimize the contribution of the gasket to the magnetic response.

When the gasket is ready, the pre-indentation procedure can commence. During preindentation, pressure is measured using laser spectroscopy by tracking the shift in the fluorescence peak of a small ruby or the frequency edge of the diamond anvil as discussed in Section 2.2.2. Though unnecessary, it is good practice to place a small ruby on one of the diamond anvils for tracking pressure. The ruby is useful for measuring low pressure, as a check against the diamond pressure measurement, and because of the superior response of fluorescence emission.

The ruby can be placed on either diamond anvil, but is most often placed on the bottom cell half of a symmetric cell. This makes it easy, as the gasket can be positioned over the ruby and held in place by the clay. For other pressure cells, the focal length of the optical system and cell dimensions must be considered as well as the difficulty of placing a ruby in the center of each diamond. As an example, rubies are placed on the top diamond of Physical Property Measurement System (PPMS) cells due to the shorter optical path. Viewing rubies from the bottom side of this cell is not possible with the optical system used in these works. The main goal of the gasket is to create a sample space that will keep the sample under pressure. To form the sample space, the gasket is first pre-indented, drilled, and then insulated with cubic boron-nitride (cBN). Closing the cell for pre-indentation follows the same precautions, namely, paying attention to the position of the anvil relative to the gasket surface and utilizing the safety screws. Pressure is added by slowly rotating the pressure screws after the safety screws have been fully lowered. Periodically checking the pressure and keeping a log of rotation angle makes future pre-indentation faster. The pre-indentation pressure determines the ultimate pressure the cell can reach. As a rule of thumb, this is approximately double the pre-indentation pressure; however, this does not serve as a substitute for carefully monitoring the sample shape and size as pressure is increased.



**Figure 2.11:** Gasket realignment markings. (a) mark made with a sharple after completing preindentation. (b) mark made by etching the gasket realigned on the diamond anvil. Note the additional marks made on the clay and cell body made for realignment.

During decompression, it is important that the gasket remains in position so that it may be marked before removal. Marks are made on the gasket as well as the cell or clay supports and are used later to realign the gasket on the bottom diamond anvil. After removing the indented gasket, a permanent mark is etched into the surface. Images of the gasket markings before and after it is replaced are available in Figure 2.11. Next, the bottom of the indentation is drilled out with a jeweler's lathe using an appropriately sized drill bit, i.e., a 500 µm drill bit for a 500 µm culet. Typically, metal burs form around the edge of the hole while drilling which need to be removed before it is replaced. Burs can easily be removed using a hard metal pick or fine tweezers. Before the gasket is replaced the gasket is sonicated in acetone for approximately 10 minutes to remove any remaining oil or debris.



**Figure 2.12:** A good gasket alignment will show both the gasket and culet in focus and have no gaps around the periphery.

To proceed, the gasket is replaced on the bottom anvil using the etched marks to guide the alignment. It is good practice to raise the compressed surface of the clay supports with a toothpick or some other fine tool. This will allow the gasket to be firmly seated on top of the bottom anvil rather than falling to the side. Pressing the center of the gasket with the flat end of a cotton swab helps to seat the gasket without compressing the clay supports too much on any side. An example of a properly realigned gaskets is shown in Figure 2.12. Note that both the diamond culet and base of the gasket are in focus, confirming they are well-fitted.

With the gasket in place, the cell is closed and gently compressed to no more than 1 GPa. This forces the gasket into position where it typically remains when the cell is opened again. This step requires careful attention otherwise the anvils are at risk of breaking. If the diamonds are too far misaligned with the gasket indentation, they will begin to make a second indentation on the hardened surface. In the best case, further compression would ruin the gasket and, in the worst case, could break the diamond. Figure 2.13a shows an example of the additional lines that are formed when the gasket is misaligned and Figure 2.13b shows a diamond broken by compressing a misaligned gasket.

When the cell is opened, the gasket will be correctly centered on the anvil. The next step is to fix the gasket in place using Loctite 416 superglue. The glue is spread from the surface of the gasket up the inner wall of the bottom cell half using a fine point toothpick. The glue needs roughly 3 - 5 hours to fully cure. If desired, the cell can be closed after the superglue is applied to ensure the gasket is held in position. This is sometimes necessary if the clay supports fail to keep the gasket in place. However, this will typically lead to glue deposits on the gasket surface and interior of the cell which will need to be cleaned.



**Figure 2.13:** Results of gasket misalignment. (a) shows an example of a misaligned gasket resulting in multiple indentation marks. (b) a diamond broken during cell assembly due to gasket misalignment.

Insulating the gasket is essential and begins with pressing slivers of a cBN and binder mixture into the sample space. Thin pieces of the cBN insulation are placed around the inside of the sample space to cover the walls and fill in the space between the two diamond culets. This can be seen in Figures 2.14a and 2.14b. When the cBN is lightly compressed to a few GPa it spreads throughout the sample space, insulating it with a thin layer of the material. Typically, cBN insulation must be placed in the sample space 2 - 4 times to fully insulate the walls. Sometimes the insulation will excrete an oily substance that causes the cBN insulation to stick to the top anvil. Cleaning the anvil with ethanol before each compression helps prevent this. Figures 2.14c and 2.14d show cBN that was pulled from the sample space.

After the sample space is insulated, it is compacted to the pre-indentation pressure. As with the pre-indentation, it is good practice to place a small ruby in the center of the sample space to help track the pressure. After compression, the excess cBN that protrudes beyond the boundaries of the indentation is removed in preparation for insulating the



**Figure 2.14:** Filling the sample space with cBN. (a) slivers of cBN placed in the sample space. (b) the sample space filled and compressed with cBN. (c) and (d) show the sample space and diamond, respectively, after a piece of the cBN insulation broke off when compressed to the pre-indentation pressure.

gasket surface with Stycast.

A hole which holds the sample is drilled into the cBN insulation using the jeweler's lathe. The hole diameter is typically  $\frac{1}{3}$  the culet size but no more than  $\frac{1}{2}$ . Since the gasket is in direct contact with the bottom diamond anvil, care should be taken when drilling so that the drill bit does not contact the diamond. Ideally the sample hole depth will be the approximate height of the sample. If needed, the hole can be filled in with cBN again and compressed to the pre-indentation pressure to regenerate the insulation. This can be



**Figure 2.15:** Illustration of the gasket cross-section once the sample space has been drilled and the gasket surface insulated with Stycast.

useful in cases when the hole is drilled too far from the center or if it is too deep. A cross-sectional view of the sample space is provided in Figure 2.15.

One final step in preparing the sample space is adding a pressure medium. This is not always necessary and, in these works, cBN and NaCl were used as pressure media. A commonly used pressure medium is NaCl as it helps provide quasi-hydrostatic pressure. Filling the sample space with NaCl is relatively straight forward but can be a little challenging. The salt is first baked to remove moisture and then ground into a fine powder before loading in the cell. The salt can then be loaded using a sharpened toothpick. Small clumps of NaCl are placed in the sample hole and gently compressed with the diamond anvils, stopping before the anvil touches the cBN. This process is repeated a few more times until the hole is mostly filled. The salt should still have noticeable granules but fill the entire space. The NaCl should only be inside the sample space and should not be compressed to its glassy state.

Once the sample space has been correctly prepared (complete insulation of the sample space, appropriately sized and positioned sample hole, cleaned periphery free of excess cBN, and optional pressure medium), the remaining surface of the gasket is insulated with Stycast. A toothpick with a fine point or a small syringe needle is ideal for spreading the Stycast across the gasket surface. Care should be taken when applying Stycast near the sample space to ensure that it does not enter the sample space. Pulling and pushing the Stycast toward the edge of the sample space gives the most control. Ensuring that the Stycast being brought to the sample space edge is spread thin across the surface also improves control in this step. Spreading the Stycast across the remainder of the surface is rather trivial in comparison. Keeping the Stycast even across the gasket will improve the quality of the gasket and reduce the strain on the sample contact leads. The Stycast typically cures overnight. See Appendix A.2 for more details on preparing the Stycast and alternate curing conditions.

It is worth mentioning that curing the Stycast is almost always the rate limiting step in pressure cell assembly as it takes between 8 and 16 hours to fully cure at 25 °C[107]. If desired, this step can be combined with a later step where the copper wires are affixed to the gasket using Stycast. This will reduce the total preparation time for the pressure cell substantially. See Appendix A.3 for detailed instructions on this alternative method.

#### 2.1.2.3 Sample Installation & Wiring

The final steps in preparing the pressure cell are centered on the sample and making contact with the sample for transport measurements.

To make contact with the sample, copper wires run from within the cell to the outside where they are later soldered to a 4-pin connector. The copper wires are cut from 34 gauge wire to a length of 4 cm or one length of a razor blade. These wires are encased in an insulating enamel which must be removed to expose the bare copper. The enamel is removed with Ambion Insulstrip Jell (dichloromethane 73 WT%, formic acid 12 WT%, phenol 7 WT%, and toluene 3 WT%) or by scrapping it off with a razor blade. If the copper wires were not bound to the gasket when insulating its surface with Stycast, a fresh batch is made to attach the wires. These wires are placed to form a square around the sample space and are affixed with Stycast at the edge of the gasket. Once cured, the wires are wrapped in tight coils and placed inside the bottom cell half as shown in Figure 2.17.

Samples are polished to an appropriate thickness based on the pre-indentation thickness and ultimate pressure of the experiment. However, some samples are limited by the material or sample quality as they become too fragile to work with. Typically, for moderate pressures the sample thickness is from  $20 \,\mu\text{m}$  to  $40 \,\mu\text{m}$ . Polishing the sample is done using 2000 grit sandpaper to produce a clean and smooth contact surface.

Due to the relationship between culet size and ultimate achievable pressure, the sample size scales inversely with the pressure. In other words, high-pressure experiments must use smaller samples. As an example, pressure experiments conducted by the author have used 500 µm culets with samples with a diagonal length of 230 µm up to pressures of 40 GPa. Likewise, samples with a 70 µm diagonal length compressed with 150 µm diamond anvils were able to reach pressures up to 170 GPa[108]. Therefore, an appropriately sized sample should be cut to fit within the sample hole. This is accomplished with a stainless-steel razor blade and a high magnification microscope. The main objective is to produce a nearly square sample with a diagonal length that does not exceed the hole diameter. Further details on polishing and cutting the samples are provided in Appendix A.4.

Wetting a finely sharpened toothpick with ethanol simplifies the task of transferring the sample to the sample space. However, this step is critical and requires patience as it is easy to lose or break the sample while attempting to place it in the sample space hole. Once the sample is inside the hole, the cell is closed to compress the sample into the cBN or NaCl which helps keep it in position. This is necessary before attempting to position the platinum leads. When the sample is in, a ruby chip or sphere is placed near the edge of the sample to track the sample pressure. The cell is then closed a second time to compress the ruby in place. This step can be combined so that both the sample and ruby are compressed at the same time, but is generally not worth the trouble due to the difficulty of placing the ruby without disturbing the sample.

Platinum leads are used to contact the sample inside the sample space. Each lead is cut into a narrow triangle from a platinum foil. The tips should be approximately  $7 \,\mu m$  to  $25 \,\mu m$  wide depending on the sample size. A good rule of thumb is a tip width of about 1/9 the sample's diagonal length. Leads are placed on the insulated gasket perpendicular to the copper wires and are stretched to contact the sample inside the sample space. Contact between platinum leads and copper wires is made by soldering them together with 60/40SnPb solder. These copper wires come out of the cell and allow measurements of the



**Figure 2.16:** Positioning the platinum leads. (a) an example of initial lead alignment, and (b) an example of the final lead alignment. Note the position of the top lead was moved up, closer to the sample corner. The right lead was moved further to the left, and the bottom lead was moved to the right. Ideally, the left lead would be positioned further down, but it is often preferable to minimize the number of times the leads are compressed.

sample. Detailed instructions on cutting, placing, and soldering the platinum leads are given in Appendix A.5.

The final step before closing the pressure cell is to position the platinum leads so that they contact the sample in a van der Pauw configuration. Moving the leads into position is one of the most challenging steps in cell assembly. The best way to check if a lead is in position before closing the cell is to gently force the lead into the sample space with a finely shaven toothpick. More information is provided in Appendix A.6. Figure 2.16 illustrates the process of adjusting the lead position.

Before finishing the cell, the contact resistance is checked for each of the leads. Every sample is different, but resistance over a few kOhm typically indicates an issue with the contact leads. If the cell must be opened to reposition the leads, the copper wires are wound again and pushed into the cell so they will not be cut in the process.



**Figure 2.17:** Detailed view of a completed pressure gasket. Note the copper wires are coiled so that they fit inside the holes of the bottom cell half's inner wall. These holes are clearly visible in Figure 2.3d.

Copper Lead Number	4-Pin Connector Wire Color
1	Red
2	White

Green

Black

3

4

 Table 2.2: Copper wire connections

To create a path from the sample to the instruments a 4-pin connector is soldered to the copper wires. For the sake of consistency, the copper wires are labeled by the screw number to the left. Using this convention, the 4-pin connector is soldered to the copper wires following the listed pairs in Table 2.2. As each pair is soldered the joint is insulated using Kapton tape for simplicity. The wires are then taped to the cell to ensure they are secure and reduce the likelihood of breaking while handling the cell. A schematic of the fully assembled cell is provided in Figure 2.18.



**Figure 2.18:** A fully assembled DAC ready to be wired to the probe. Note the copper wire to the far right is number 2. This is followed by 3 and 4 moving to the left with wire 1 being out of view. Refer to Table 2.2.

# 2.2 Optical System

A number of methods for determining the pressure inside of pressure cells have been developed throughout the history of high-pressure research. Some of the earliest manometers used well-known phase transitions that were easy to detect via abrupt changes in the resistance, such as bismuth. Likewise, one of the commonly used manometers in the earlier days of high-pressure superconductivity research was lead, as the  $dT_c/dP$  was well studied. Other methods include establishing an equation of state for pressure, such as those derived from the lattice parameters in high-pressure synchrotron studies of metals like platinum. In modern times, where the majority of high-pressure research has adopted the use of DACs, optical methods of measuring pressure are more convenient.

## 2.2.1 Physical Description-optical

This section describes the optical system used to determine cell pressure via fluorescence and Raman scattering spectroscopy. It lists each component and describes their function.



**Figure 2.19:** Optical setup for measuring cell pressure. A detailed list of components is given in Appendix B.1.

Figure 2.19 gives a general overview of the optical table and its components. A 50 mW helium-neon (HeNe) laser (1) with a wavelength of 632.8 nm is used as the probe for pressure measurements by exciting electronic states in the ruby or interacting with the vibrational and rotational modes in the diamond. This laser is first cleaned by a band-pass filter (2) that limits the light to  $632.8 \text{ nm} \pm 2.4 \text{ nm}$ . Next it passes through a polarizer (3) used

for adjusting the beam intensity. It continues through a beam splitter (4) before being reflected by a mirror (5) at  $45^{\circ}$  and finally passes through a lens (6) into the pressure cell (7). The pressure cell rests on a 3D platform (8) that is adjusted with three micrometer screws (one for each axis of motion). Reflected laser light  $(632.8 \,\mathrm{nm})$  as well as emission light from the ruby fluorescence ( $\sim 694 \,\mathrm{nm}$  at ambient) or Raman scattered light from the diamond (~ 691 nm at ambient) travel back to the mirror (5) and to the beam splitter (4). At the splitter, the light from the cell is partially reflected at  $45^{\circ}$  toward a Horiba iHR 550 spectrometer (14-18). Between the beam splitter and spectrometer is a movable mirror (9) positioned at  $45^{\circ}$  to the optical path. When positioned between the beam splitter and the spectrometer, light is directed into a camera (10) and is displayed on a monitor (11), providing a view inside the cell. Without the mirror, light continues toward the spectrometer, first passing through a band-stop filter (12) where the excitation laser light is excluded, and then through a focusing lens (13). As the light enters the spectrometer it is shaped by a height limiter and adjustable slit (14). A collimating mirror (15) reflects the light onto a diffraction grating (16) with a groove density of 1800 grooves/mm. The dispersed light then reflects off a focusing mirror (17) which directs it into the charge coupled device (CCD) detector (18).

## 2.2.2 Fluorescence and Raman Scattering

This section discusses the basic theory behind the optical methods used in determining cell pressure. Also discussed are the details of pressure calculation for both the ruby and diamond. Finally, some limitations and considerations for measuring pressure at multimegabar pressures are detailed.

#### 2.2.2.1 Theory Introduction

Fluorescence is a type of photoluminescence that begins with the absorption of a photon with energy  $E = \hbar \omega$  as shown in Figure 2.20a. This causes an electron to be excited to a higher energy level making fluorescence a quantum mechanical phenomenon. During this process the excited state can lose or gain energy through internal conversion (Stokes shift) or thermal excitation/upconversion (anti-Stokes shift), respectively. This change in energy through a Stokes or anti-Stokes shift manifests in the energy of the photon which is emitted as the excited state relaxes back to the ground state as  $E_{Fl} = \hbar(\omega \mp \omega_{Shift})$ . Unlike light scattering processes, which occur on the femtosecond scale, fluorescence sees excited states with an extended lifetime on the nanosecond timescale. This lifetime can be even longer, reaching the millisecond scale for forbidden transitions such as that in ruby.

Raman scattering is a type of inelastic light scattering that leads to a shift in the wavelength of the light source. Light scattering can be conceptualized using virtual energy states where the absorption of a photon excites the scattering center into a higher energy state as shown in Figure 2.20b. In most cases, this excited state relaxes back to its ground state releasing a photon of the same energy in what is known as Rayleigh scattering. Less often, the incoming light interacts with one of the real rotational or vibrational states of the scattering center. The resulting transfer of energy between the scattering center and photon is known as Raman scattering. When the incoming photon loses energy a Stokes shift occurs and when the photon gains energy an anti-Stokes shift occurs.

Beyond the classical nature of Raman scattering and the extended lifetime of excited states in fluorescence, the main difference between Raman scattering and fluorescence is their wavelength dependence. The incident photon energy has a strong effect on the Raman scattering rate, where higher energies scatter more readily In addition, wavelengths that are



**Figure 2.20:** Figures show details of ruby fluorescence and diamond Raman scattering. (a) a Jablonski energy diagram based on the crystal field calculations of  $Cr^{3+}$  that are responsible for ruby fluorescence[109]. Note the ground state can be excited using numerous wavelengths but come to the <sup>2</sup>E states through internal conversion and other non-radiative relaxations. The R1 and R2 emissions are clearly shown as relaxations from the <sup>2</sup>E states to the <sup>4</sup>A<sub>2</sub> state. (b) a modified Jablonski diagram which visualizes the virtual states used to conceptualize Raman scattering. Note the red and blue shift for the Stokes and anti-Stokes Raman scattering and how it differs from Rayleigh scattering.

near a resonant energy level also see enhanced scattering. On the other hand, fluorescence emission rates depend directly on the absorption of photons used to excite the ground state. So long as the energy is sufficient to excite electrons to a state above the emission level, internal conversion can dissipate the excess energy as thermal, vibration, and rotational energy.

#### 2.2.2.2 Pressure Calculations

Conveniently, both ruby fluorescence and diamond Raman scattering can be achieved using an excitation wavelength of 632.8 nm as the resulting radiation occupies roughly the same spectral range around 690 nm. This makes the simultaneous measurement of pressure from ruby pieces and the diamond anvils possible. It is important to distinguish that fluorescence is measured from the ruby, while Raman scattering is measured from the diamond. Therefore, two separate spectra can be expected to coexist at low to moderate pressures when excited with a HeNe laser, so long as the ruby fluorescence does not obscure the diamond signature.

In the ruby fluorescence spectra two emission lines, R1 and R2, are observed via stimulation of the  ${}^{2}T_{1}$  energy levels also called the R' band[109]. At ambient conditions, these emission lines are centered at 694.24 nm and 692.8 nm respectively. Pressure is tracked by monitoring the position of the R1 peak. With increasing pressure, this peak shifts to longer wavelengths. Figure 2.21 provides an example of the spectra at ambient and at 3.5 GPa.

The R1 line as a function of pressure is typically calibrated against the volumes of various metals with well-defined equations of state. The calibration used in this dissertation was given by a least-squares fit of data collected by Mao et al., resulting in the following



**Figure 2.21:** Fluorescence spectra of ruby pieces recorded at ambient pressure (694.24 nm) and 3.5 GPa (695.51 nm).

equation:

$$P = \frac{a}{b} \left[ \left( \frac{\lambda}{\lambda_0} \right)^b - 1 \right]$$
(2.1)

where P is the pressure in GPa, a = 1904 GPa and b = 5 are constants,  $\lambda_0 = 694.24$  nm is the reference wavelength of the R1 line at ambient conditions, and  $\lambda$  is the measured wavelengths of the R1 line[110]. Note that Equation 2.1 was derived from calibration data up to 80 GPa and is therefore unreliable beyond this pressure.

For Raman scattering, cell pressure is determined by tracking the frequency edge of the scattered light. Typically, the frequency edge is not easily distinguished until a pressure of  $\sim 3$  GPa. However, as the pressure increases the edge is extended as shown in Figure 2.22. The midpoint of this edge was used for calculating pressure in this work.



**Figure 2.22:** Raman scattering spectra of the diamond anvil at ambient pressure, 1.60 GPa (691.33 nm), and 10.73 GPa (692.36 nm). Note the Raman spectrum depends on the excitation wavelength unlike the ruby fluorescence. The frequency edges in this figure were determined using the first derivative. The corresponding figure is available in Appendix B.2.

Much like the ruby fluorescence, the equation of state for the volume of platinum was used to calibrate the Raman pressure scale. The pressure calculations in this dissertation were done using the calibration curves created by Akahama et al.[111, 112]. The equation below was used for pressures up to 310 GPa:

$$P \approx A \frac{\Delta \omega}{\omega_0} \left[ 1 + \frac{1}{2} (B - 1) \frac{\Delta \omega}{\omega_0} \right]$$
(2.2)

where P is the pressure in GPa, A = 547 GPa and B = 3.75 are constants,  $\Delta \omega$  is the frequency shift, and  $\omega_0$  is the reference frequency shift. Both frequencies are further explained by the below relationships:

$$\omega_0 = \left[\frac{1}{\lambda_{Ex}} - \frac{1}{\lambda_0}\right] 10^7 \tag{2.3}$$

$$\Delta\omega = \left[\frac{1}{\lambda_{Ex}} - \frac{1}{\lambda}\right] 10^7 \tag{2.4}$$

where frequency is given in  $cm^{-1}$  and wavelength is in nm.

Due to the large deviations from Equation 2.2 above 300 GPa, a separate quadratic function was used to fit the data from 200 GPa to 410 GPa given by:

$$P = 3141 - 4.157\omega + 0.001429\omega^2 \tag{2.5}$$

where P is again pressure in GPa and  $\omega$  is the frequency edge shift.

As shown in Figure 2.23, Equations 2.2 and 2.5 can be plotted together revealing a point of overlap at 253.06 GPa. This allows the two functions to be joined together at  $\omega = 1762.18 \text{ cm}^{-1}$  ( $\lambda = 712.22 \text{ nm}$ ), forming a continuous calibration curve up to 410 GPa.

While the pressure scale based on the data of Akahama et al. was used for the works of this dissertation, it is worth mentioning that Eremets et al. has recently calibrated the



**Figure 2.23:** The pressure scale used to relate cell pressure with observed Raman scattered light. Note that the calibration data from the 2006 and 2010 works by Akahama were limited to 310 GPa and 410 GPa respectively[111, 112].

diamond pressure scale up to 477 GPa[113]. This publication used the equation:

$$P = A \frac{\Delta\omega}{\omega_0} + B \left(\frac{\Delta\omega}{\omega_0}\right)^2 \tag{2.6}$$

where A = 517(5) GPa, B = 764(14) GPa and  $\omega_0 = 1332.5 cm^{-1}$ . This pressure scale is also presented in Figure 2.23.

#### 2.2.2.3 Ruby & Diamond Response

As illustrated in Figure 2.20a multiple wavelengths can be used to stimulate fluorescence in the ruby. While this study used a HeNe laser of 632.8 nm to pump the  ${}^{2}T_{1}$  energy levels, also called the R' band, many others use green or blue lasers for exciting the U ( ${}^{4}T_{2}$ ) and B ( ${}^{2}T_{2}$ ) bands respectively[109]. The choice of excitation wavelength is dependent on the pressure range as each energy band has a different response to pressure. For example, both the R' and B bands shift to longer wavelengths while the U band rapidly shifts to shorter wavelengths with increasing pressure. This makes consistent absorption of the excitation wavelength difficult over a large pressure range.

Fluorescence by exciting the R' band with a HeNe laser, as used in this study, typically becomes weak around 20 GPa–30 GPa. Similarly, green lasers used to excite the U band suffer above 40 GPa–50 GPa while blue lasers generally work best above 50 GPa after the U and B energy bands cross. This is best illustrated in Figure 13 of the review paper by Kurt Syassen[109].

The biggest challenge facing ruby fluorescence measurements in a DAC is fluorescence from the diamond, particularly above pressures of 100 GPa–120 GPa. Typically, at ambient conditions, the fluorescence of diamonds used for high pressure work shows decreasing wavelength from 550 nm to 800 nm[114]. However, as pressure increases above 100 GPa, the diamond fluorescence shifts further toward red until it begins to obscure the ruby signal. Looking at Figure 2.24 it becomes clear why the diamond fluorescence interferes with the ruby fluorescence. This has led researchers to devise workarounds for this issue.

The first solution is to use a tunable red laser to excite the R' band[115]. A red laser is used as it causes much less diamond fluorescence than the shorter wavelengths options.



**Figure 2.24:** Absorption and emission spectra due to H3 defects in a diamond at ambient temperature and pressure. This data was replicated from the work of Eggert et al[114].

The laser can also be adjusted over a large range of excitation wavelengths which improve the overall absorption of the R' band. This technique allows the ruby fluorescence pressure range to extend up to about 250 GPa.

The other workaround is to exploit the extended lifetime of the excited  ${}^{2}E$  state in the ruby. The lifetime of the  ${}^{2}E$  state is longer than 3 ms compared to the nanosecond lifetime of the diamond fluorescence state[114]. This allows timed chopping techniques to block the diamond fluorescence while allowing the ruby signal to be captured, effectively extending the ruby fluorescence pressure scale.

Since pressure studies are often done into the Mbar (100 GPa) pressure range, ruby fluorescence is abandoned for Raman scattering due to the complexity of these workarounds. While any wavelength laser can be used for Raman scattering, there are two main considerations. First, the intensity of the resulting scattered radiation is a function of the frequency to the 4<sup>th</sup> power. This means that shorter wavelengths will scatter more frequently and result in higher intensities for pressure measurements.

The second consideration is the absorption and fluorescence spectra of the diamond as a function of pressure. Depending on the type of diamond and the color center defects present, various absorption and fluorescence spectra can be expected. As an example, at ambient conditions, a diamond with H3 defects absorbs light in the region from about 400 nm to 530 nm, with peak absorption occurring around 470 nm, as shown in Figure 2.24. Fluorescence of these H3 defects is most intense in the region from about 500 nm to 600 nm peaking around 520 nm. The modern technique employed to measure high pressure via Raman is to use a 660 nm laser as it is mostly transparent to the diamond up to about 300 GPa[113, 116]. Because of the substantial shift in the diamond's color center spectra at high pressure, the red laser is swapped for a green, 532 nm laser above 300 GPa. This helps minimize luminescence from the diamond.

## 2.3 Cell Probe

This section discusses some component details of the cell probe and can as presented in Figure 2.25. The section on Probe Operations is a continuation of the experimental procedures presented in Section 2.1.2 on Cell Preparation. The section goes into the details of using the probe, particularly in its operation during pressure quenching experiments. Finally, details of the temperature sensor including the process used to calibrate a new Cernox are discussed.

## 2.3.1 Physical Description

Beginning at the top of the probe is the probe head which consists of a DB-25 connector (2a) contained within a metal housing. Its function is to provide an easy means of connecting the sample leads and temperature sensor to the instruments on the data acquisition rack. Details of the wire connections are shown in Figure 2.26 and Table 2.3. The probe head is connected to the probe shaft (2d) with a specially fabricated copper fitting (not visible). This fitting has a hole drilled through its center to allow wires to pass through to the DB-25 connector.

The wires which run through the probe shaft are twisted in pairs to help reduce the self-inductance. These twisted pairs are bundled together in Teflon tubing (2i) to help prevent shorting as they rub against the interior of the steel probe shaft. Stycast is used in the top of the hollowed fitting to prevent the wires from moving and potentially breaking connections to the DB-25 connector. More importantly, the Stycast seals the probe which allows a vacuum to be pulled within the dewar's sample space.

At the bottom of the probe is another fabricated fitting (2h) which is threaded to provide an easy connection point for the pressure cell can. Like the probe head fitting, it is partially hollowed to allow the wires to pass out and to a 16-pin connector at the base of the can, also shown in Figure 2.25.

A top plate (2c) is fitted around the probe shaft with a quick connect coupling (2c.1) sized to allow the probe shaft to move vertically inside the dewar while also being able to make a vacuum seal. In combination with a metal screw clamp (2f), the top plate supports



Figure 2.25: Detailed view of the pressure quenching probe.



**Figure 2.26:** The wiring diagram for the probe tail (black) and probe head (blue). See Table 2.3 for more details about their connections.

the probe as it rests inside the dewar. The top plate is screwed to the copper flange at the top of the dewar to keep the probe in place and seal the inner dewar space (sample space). A rubber gasket embedded in the flange helps to create a vacuum seal. A rubber stopper (2c.2) plugs a hole in the top plate which is used for transferring LHe to the dewar. More details on the dewar will be provided in the subsequent section.

Probe Tail	DAC Probe Wires	Probe Head
1	Temperature Sensor (Current)	1
2	Temperature Sensor (Potential)	2
3	Disconnected	N/A
4	Disconnected	N/A
5	Cell (Black)	5
6	Cell (Green)	19
7	Not Used	8
8	Not Used	9
9	Temperature Sensor (Current)	14
10	Temperature Sensor (Potential)	15
11	Not Used	16
12	Not Used	17
13	Cell (Red)	18
14	Cell (White)	6
15	Not Used	21
16	Not Used	22

 Table 2.3:
 Wire connections between probe head and tail

Four more quick connect couplings are attached to the top plate which provide access into the dewar and down to the pressure screws via long stainless-steel pressure rods (2b). These rods pass through the top plate and a guide (2g) attached lower on the probe shaft to prevent lateral movement. Holes in the lid of the can (2e.1) allow the rods to pass through so that the Allen wrenches at the ends of the steel rods can mate with the pressure screws. Hex heads at the top of the steel rods are used to rotate the rods and adjust the pressure within the cell while it is held at low temperature.

The last part of the probe is the can (2e), which holds the pressure cell (2l) and houses the temperature sensor(2e.4). The can consists of a lid and a cup (2e.2), which are made of copper to improve thermal contact with the surrounding, low-temperature environment. As mentioned, the lid has a threaded hole at its center so that it can easily connect with the probe shaft. It also has four holes on the top surface to allow the steel rods to connect with the pressure screws. On the periphery of both the lid and cup are three small screw



Figure 2.27: Detailed view of the pressure cell and can assemblies.

holes used to hold the two parts of the pressure can together.

The cup has two holes in its base where screws are used to hold the pressure cell in position for pressure quenching experiments. Two small tapped holes are used to attach the male 16-pin receptacle (2k) to the underside of the cup. One final hole at the inner edge of the cup allows wires to run from the 16-pin receptacle to the temperature sensor and a female 6-pin connector (2e.3), used to connect with the pressure cell. A small piece of Teflon tubing is also placed in the hole to prevent shorting of the wires as employed inside the probe shaft.

### 2.3.2 Probe Operations

This section can be treated as a continuation of the Cell Preparation section. fter soldering the 4-pin connector to the pressure cell and securing the wires with Kapton tape, the cell is placed in the pressure cell can, as shown in Figure 2.27. The two holes without safety or pressure screws are aligned with the two holes in the bottom of the cup (2e.2) and fastened with M5-0.8 screws. Next, the temperature sensor is positioned on the top optical window and attached to the cell with copper grease. Following this, the male 4-pin connector from the cell is connected to the female 6-pin connector (2e.3) so that the red wire matches a red mark on the edge of the 6-pin connector. Finally, a piece of Kapton tape is placed over the top of the cup to hold down the wires. If no pressure quenching is planned the lid is attached using three screws and then fastened to the probe.

For pressure quenching experiments the can is only closed after the pressure rods are aligned with the pressure screws. The four pressure rods are put through the quick connect couplings, run through the guide, and finally through the can lid which is fastened to the base of the probe. Each quick connect is tightened to hold the rods in place. Finally, the
rods are aligned with the pressure screws and the cup is fastened to the lid.

After the can is closed, a metal clamp is placed above the pressure rods to keep them from coming out of the pressure screws while moving the probe in the dewar. A second metal clamp (not shown) is fastened to the probe shaft just above the central quick connect coupling to prevent the probe from falling into the dewar. The connectors at the head and tail of the probe are connected to the data acquisition rack and pressure cell respectively. The can is then moved as far up as possible and placed in the dewar to begin cooling.

When adjusting the cell pressure with the pressure rods, the metal clamp above the rods is removed so that the hexagonal heads can be accessed. Two ratchets with 1/4'' sockets are used to rotate the pressure rods at low temperature. After the pressure is released, the rods are removed from the probe and the quick connect couplings are plugged to reduce the mass inside the dewar.

### 2.3.3 Temperature Sensor

The temperature sensor (2e.4) is one of the most vital components of the experimental setup, as it is responsible for accurately tracking the temperature of the pressure cell. The earliest temperature sensors relied on the relationship of pressure or density to track changes in temperature. Although any property that changes with temperature could be used as a temperature sensor, resistance temperature sensors are one of the most ubiquitous. The predictable resistance response to changes in temperature along with their size and overall simplicity make this fact clear.

#### 2.3.3.1 Cernox & Si Diode

Two temperature sensors, a zirconium oxy-nitride Cernox and a silicon diode, were used at different times to determine the temperature of the pressure cell and are discussed below. Although they fundamentally functioned in the same manner, there are a few details that differ between the two.

The main difference in these two sensors comes from the excitation current provided. For the Cernox sensors the current polarity is continuously flipped so that averaging of the measured voltage drop can eliminate any thermal electromotive force (EMF). This is obviously impossible for the silicon diode due to its directionality. The second difference comes from the voltage response of each sensor. A single excitation current of  $10 \,\mu\text{A}$  is used for the silicon diode, as the voltage only changes by one order of magnitude over the temperature range of  $1.2 \,\text{K}$  to  $500 \,\text{K}$ . For the Cernox sensor four to five different excitation currents ( $1 \,\text{mA}$  to  $100 \,\text{nA}$ ) are needed to cover a similar temperature range as the voltage response changes by four orders of magnitude.

#### 2.3.3.2 Calibration

For a temperature sensor to be useful, the response as a function of temperature must be known. Unless an equation of state can be used to compute the temperature, a temperature sensor must be calibrated to determine this relationship. Calibration is done using welldefined data points, such as a triple-point or other calibrated sensors.

While the silicon diode had a very well-known calibration curve, the Cernox temperature sensor had to be calibrated. This was done using pre-calibrated germanium and platinum resistors purchased from Lakeshore. The platinum resistor was used to calibrate the temperature range from 30 K to 360 K while the germanium resistor was used for calibrating from 1.2 K to 30 K. The Cernox calibration was carried out over the entire temperature range at a cooling rate of roughly  $0.5 \text{ K} \text{min}^{-1}$ . The voltage response was recorded, and excitation current was controlled by a Lakeshore 336 Temperature Controller. The excitation current was autoranged from 1 mA to 300 nA to maintain a voltage response < 10 mV to help mitigate sensor heating. Current reversal was also used during calibration to eliminate potential thermal EMF.

Region	Excitation Current	Range in $Log(R)$	Range in Temperature (K)
Ι	$1\mathrm{mA}$	1.72830 - 2.05667	360.413 - 160.001
II	300 µA	2.05667 - 2.43441	160.001 - 60.0001
III	100 µA	2.43441 - 2.78541	60.0001 - 22.0091
IV	30 µA	2.78541 - 3.19446	22.0091 - 7.00122
V	10 µA	3.19446 - 3.72901	7.00122 - 2.50191
VI	300 nA	3.72901 - 4.35361	2.50191 - 1.20162

 Table 2.4:
 Temperature regions for Cernox-X147966

The data were fitted using 10<sup>th</sup> degree Chebyshev polynomials over six temperature ranges. Details of the calibrated sensor regions are given in Table 2.4.

Chebyshev polynomials are given as:

$$C_n(x) = \sum_n a_n T_n(x) \tag{2.7}$$

where  $a_n$  are the Chebyshev coefficients calculated in the fitting and  $T_n(x)$  are the Chebyshev polynomials of order n. Chebyshev polynomials have a recursive relationship defined as:

$$T_n(x) = \cos(n \cdot \arccos(x)) \tag{2.8}$$

$$T_{0}(x) = 1$$

$$T_{1}(x) = x$$

$$T_{n+1}(x) = 2x \cdot T_{n}(x) - T_{n+1}(x)$$
(2.9)

The first eleven Chebyshev polynomials, those that were used to fit the Cernox calibration data, are:

or

$$\begin{split} T_0(x) &= 1 \\ T_1(x) &= x \\ T_2(x) &= 2x^2 - 1 \\ T_3(x) &= 4x^3 - 3x \\ T_4(x) &= 8x^4 - 8x^2 + 1 \\ T_5(x) &= 16x^5 - 20x^3 + 5x \\ T_6(x) &= 32x^6 - 48^4 + 18x^2 - 1 \\ T_7(x) &= 64x^7 - 112x^5 + 56x^3 - 7x \\ T_8(x) &= 128x^8 - 256x^6 + 160x^4 - 32x^2 + 1 \\ T_9(x) &= 256x^9 - 576x^7 + 432x^5 - 120x^3 + 9x \\ T_{10}(x) &= 512x^{10} - 1280x^8 + 1120x^6 - 400x^4 + 50x^2 - 1 \end{split}$$

The Chebyshev coefficients calculated through the function fitting are provided in Table 2.5.

	Region I	Region II	Region III	Region IV	Region V	Region VI
$a_0$	243.177	110.237	41.8714	14.3481	4.73859	1.91899
$a_1$	-103.925	-61.3079	-24.4776	-9.41705	-2.94110	-8.49895E-1
$a_2$	11.9056	7.81262	3.37292	1.82639	6.80785E-1	1.541480E-1
$a_3$	-1.28531	-5.77232E-1	-2.71756E-1	-2.06302E-1	-1.27054E-1	-2.54033E-2
$a_4$	1.37789E-1	4.97278E-2	1.35102E-2	5.03478E-3	1.96385E-2	3.26089E-3
$a_5$	-1.59912E-3	-1.52103E-2	-3.63097E-3	1.80825E-3	-4.45393E-3	-5.44652E-5
$a_6$	-6.76760E-3	-1.05346E-3	8.00089E-4	-3.70198E-4	4.92086E-4	3.97832E-4
$a_7$	3.99385E-3	3.01561E-3	4.03234E-3	-7.51006E-4	8.13174E-4	3.56411E-4
$a_8$	-3.58337E-3	1.49018E-4	1.47715E-3	-3.39761E-4	-6.07646E-4	-1.37728E-4
$a_9$	4.85673E-3	-1.50878E-3	-1.01720E-3	-5.38179E-4	-1.18196E-3	-4.79727E-5
<i>a</i> <sub>10</sub>	6.24178E-4	5.10826E-4	-2.09120E-3	-4.17702E-4	1.66467E-4	6.6613E-6

 Table 2.5: Chebyshev coefficients for Cernox-X147966

Given the Chebyshev coefficients and Equations 2.7 and 2.8, the temperature is calculated using the  $\log(R)$  response of the Cernox, which has been rescaled to the range [-1,1]. This is necessary to fit the limits of the Chebyshev polynomials as  $\cos^{-1}(x)$  is not defined outside this range. Rescaling a range to [a,b] is done as follows:

$$x_{rescaled} = (b-a)\frac{x - x_{min}}{x_{max} - x_{min}} + a$$
(2.10)

Therefore, rescaling  $\log(R)$  to the range [-1,1] for each region is given by:

$$log(R)_{[-1,1]} = 2 \frac{log(R) - log(R)_{min}}{log(R)_{max} - log(R)_{min}} - 1$$
(2.11)

It is worth noting that the max and min referred to in Equation 2.11 are not the values presented in Table 2.4. To better blend the regions, they were extended beyond the determined region transition limits. This extension helped smooth out the regional boundaries when fitted with a Chebyshev polynomial. For this reason, the max and min in Equation 2.11 are the bounds of the Chebyshev fitting and not the of the temperature-based regions in Table 2.4. The fitting bounds which can be used in scaling the region ranges are provided in Table 2.6 below.

Region	Lower Bound in $\log(R)$	Upper Bound in log(R)
Ι	1.7282969547	2.0827961378
II	2.0086384902	2.4582600374
III	2.3775448289	2.8090072371
IV	2.7316532197	3.2212890178
V	3.1171519312	3.7656685548
VI	3.6450487334	4.3536065968

 Table 2.6: Chebyshev fitting bounds for Cernox-X147966

# 2.4 Glass Dewar

Vacuum flask dewars are integral to low-temperature experiments. A vacuum flask creates a highly insulated environment, which prevents the rapid evaporation of cryogens and maintain a low-temperature environment.

## 2.4.1 Physical Description

The glass dewar comprises two separate vacuum flasks with silvered interior walls to help minimize heat exchange with the interior sample space. The two flasks can be seen in Figure 2.28. These vacuum flasks are placed one inside the other and are referred to as the inner (1b) and outer vacuum jackets or flasks (1a). Both flasks have a valve (1a.3/1b.4) which are used to flush and pump the vacuum space (1a.2) when the dewar becomes "soft" or otherwise contaminated with air or helium. Pumping the vacuum jackets is done with external oil and turbomolecular pumps (not shown), not to be confused with the high-vacuum system (1e) used for pumping the sample space.



Figure 2.28: Detailed view of the glass dewar.

The inner flask is bolted to a large metal plate (1b.3) which rests on a Unistrut frame (1c). The outer vacuum flask is positioned below the inner flask so that it rests at its center when fixed to the dewar frame.  $LN_2$  is pumped into the space between the outer and inner vacuum flasks (1a.1), keeping the sample space at 77 K. This  $LN_2$  bath helps reduce boil off of lower temperature cryogens, namely LHe. With the addition of LHe to the sample space temperatures can reach 4.2 K or lower by pumping the space.

A copper T-joint flange (1b.2) is connected to the top of the support plate so that the top of the T is parallel to the dewar axis, and the center flange is pointed toward the vacuum manifold (1e) behind the dewar. Each flange of the T-joint has a gasket to create a vacuum seal. The top flange connects to the probe top plate while the center flange connects to a butterfly valve (1d). This valve opens to the vacuum manifold and facilitates pumping of the sample space (1b.1).

# 2.4.2 Dewar Operations

As mentioned, the vacuum jackets are vital for dewar operations. They provide the necessary insulation to maintain the low-temperature environment within the sample space by reducing cryogen boil off. Because of this, it is very important to maintain a high vacuum in these flasks. The most obvious sign of a "soft" jacket is extensive icing on the dewar exterior and frequent activation of  $LN_2$  auto-filler (not shown). Otherwise, if the dewar has been sitting unused for a period more than a month it likely needs to be pumped to ensure a good insulation.

As mentioned, a mechanical oil pump and turbomolecular pump are used to produce the high vacuum in the vacuum jackets. The pumps are connected to the dewar jackets via a three-way ball valve. The vacuum lines up to the flask valves are first evacuated using the oil pump. Next, one of the vacuum jackets is slowly opened to the pump and pumped for roughly 20 min. Refer to Figure 2.29 for details of the valve positions. With the oil pump running, the turbomolecular pump is turned on to achieve a high vacuum. The pump is left on for 1 - 2 days before closing the vacuum jacket valve and switching to the other for another 1 - 2 days. Note that the turbo pump should be turned off and allowed to spin down before opening the pump up to the other vacuum jacket. Low vacuums can quickly overwhelm the turbo causing it to shut off and potentially damaging the turbine.

# **Outer Vacuum Jacket**



# **Inner Vacuum Jacket**



Figure 2.29: Figure showing the two vacuum jacket valves and their open/close positions.

Typically, this procedure will provide adequate insulation for the dewar flasks. However, in some cases the dewar will still condense ice on the outside walls away from the neck, indicating a poor vacuum. This is a clear sign of helium contamination and is handled by flushing the vacuum jackets with  $N_2$  gas and then pumping it out with the oil pump. The added  $N_2$  gas helps to displace the smaller helium gas atoms, which are much harder for the turbo to remove. Flushing and pumping each jacket about 20 times typically solves this issue.

When pumping is done, the outer vacuum flask space is filled with  $LN_2$  until it reaches the upper limit of the fill sensor (not shown) and turns off the auto-filler. The sensor will reactivate the auto-filler as the  $LN_2$  level falls below the fill limit.

As the inner vacuum flask cools, the air inside the sample space will also cool and begin to condense. If left open, the atmosphere will continue to condense, filling the sample space with ice and other liquefied gases. This is a big problem not only because it fills the sample space and makes viewing the probe difficult, but because the added thermal mass increases the volume of cryogens needed to cool the sample space. This poses a significant challenge for LHe due to its very low heat capacity, while ice, in contrast, has a very high heat capacity. In fact, if the dewar fills with too much ice, it becomes virtually impossible to condense helium in the sample space. For this reason, the sample space is always sealed with a lid or by the probe to prevent the cryopumping of atmospheric gases.

After the initial cooldown, the sample space is allowed to cool for 1 - 2 hours before LHe is transferred. This helps save LHe by allowing the  $LN_2$  to pre-cool the sample space to 77 K. The LHe is transferred into the dewar through a hole in the top-plate lid, similar to the one shown in Figure 2.25. Once LHe has condensed in the sample space, the probe

is placed inside. The temperature of the pressure cell is then controlled by changing its vertical position.

To cool the cell below 4.2 K (the boiling point of LHe at 1 atm), the vapor pressure is lowered by pulling a vacuum in the sample space. At this point, the cooling rate is controlled by how wide the butterfly valve is opened. Note that the temperature sensor used was only calibrated to 1.2 K despite the dewar's capacity to go to lower temperatures. The main reasons for stopping at 1.2 K, other than a lack of a standard to calibrate against, are practical considerations. Firstly, the cooling rate drops off dramatically below about 2 K, making the helium cost too great. Secondly, a different low-temperature sensor would be required to accurately measure this range, as self-heating becomes an issue due to the exponential increase in the RTS used.

Warming the cell from 1.2 K begins with closing the butterfly valve. Next, ultra-high purity helium gas (> 99.999%) is connected to a valve (not shown) in front of the butterfly valve. The valve is slowly opened to allow warm helium gas into the sample space, which increases the vapor pressure and warms the LHe. Once the sample space reaches atmospheric pressure, the butterfly valve and helium gas line are fully closed. The vacuum pump is then turned off, and the line is vented to atmospheric pressure. Finally, the cell can be raised to further warm it to room temperature or other desired temperature.

# 2.5 Data Acquisition

This section discusses the instruments used in the low-temperature pressure experiments and how they interact with a custom LabVIEW program to collect resistivity data. Details of resistivity measurements and calculations are also provided.

## 2.5.1 Equipment

The equipment used for data collection consists of two groups and is shown in Figure 2.1. The first is the Lakeshore 336 Temperature Controller (3h), which is used for measuring the cell temperature. The second group includes the Keithley 6221 DC and AC Current Source (3e), Keithley 2182A Nanovoltmeter (3f), and Keithley 705 Scanner (3g) for measuring the transport properties.

#### 2.5.1.1 Temperature

A Lakeshore 336 Temperature controller is used for monitoring the temperature. Channel A is configured for an NTD Cernox temperature sensor using auto-ranging and current reversal. The auto-ranged currents and their temperature ranges are provided in Table 2.4. As mentioned, current reversal mode is used to eliminate the effects of thermal EMFs. A user defined calibration curve is saved to curve 30 on the LS336 as 200 breakpoints consisting of temperature and log(R) data. This allows the LS336 to use linear interpolation to determine the temperature.

#### 2.5.1.2 Resistivity

The Keithley 6221 and Keithley 2182A are used in combination to measure transport properties in the van der Pauw configuration using the built-in delta mode. This mode changes the current polarity and averages the measured potential to eliminate contributions from thermal EMFs. These instruments are connected to the sample through the Keithley 705 via two scanner cards, a 7055 General Purpose Relay Scanner and a 7059 Low Voltage Scanner. This allows connections to the sample leads to be switched so that the four van der Pauw measurements can be made as shown in Figure 2.30. Further details of the wiring to the Keithley 705 are provided in Figure 2.31.



**Figure 2.30:** Idealized van der Pauw configuration depicting the four resistance measurements taken using the Keithley 705, 6221, and 2182A.

### 2.5.1.3 Equipment Wiring

Table 2.3 from the section discussing the cell probe shows the connections between the pressure cell and the probe head. Here, the connections from the probe to the abovementioned equipment are briefly discussed.



**Figure 2.31:** Wiring diagrams for the two scanner cards. (a) Wiring diagram of the 7055 scanner card which connects the Keithley 6221 to the pressure cell. (b) Wiring diagram of a 7059 low voltage scanner card which connects the Keithley 2182A to the pressure cell. Connections labeled S1-S4 are connections between the scanner cards while those labeled C1-C4 connect to the pressure cell. Channels 1 & 11, 2 & 12, 3 & 13, and 4 & 14 are closed at the same time to collect a complete set of van der Pauw resistance data. More details covering the channel handling for the scanner cards is provided in the section on LabVIEW.

From Table 2.3, it is clear that the probe head relays eight wire connections to the instruments. This includes four leads for the pressure cell (5, 6, 18, & 19) and four more for the temperature sensor (1, 2, 14, & 15). The wires for the temperature sensor are connected to one of the four LS336 channels (A-D) using a 6 pin DIN connector as illustrated in Figure 2.32. The pressure cell wires are connected to the 7059 scanner card as shown in Figure 2.31. Also shown in Figure 2.31 are the connections between the Keithley 6221 current source and the 7055 card, and the Keithley 2182A nanovoltmeter connection to the 7059 card.



**Figure 2.32:** The male (left) and female (right) 6 pin DIN connectors used to connect the temperature sensor (left) to the LS336 (right). Note that the two center pins were not used.

### 2.5.2 Resistivity

#### 2.5.2.1 Standard Resistivity

As zero resistance is one of the hallmarks of superconductivity, resistivity measurements, particularly as a function of temperature, are very important in confirming the existence of the phenomenon in a material. In a classic resistivity measurement the 4-probe measurement is used as illustrated in Figure 2.33. Two leads on either end of a bar shaped sample are used to pass a current through the sample while the two near the center are used for measuring the potential difference. It is well known that conductors that follow Ohm's law show the linear response:

$$V = IR \tag{2.12}$$

where V is the voltage measured, I is the current passed through the conductor and R is the resistance of the sample.

Though constant for a given configuration at reasonable currents, the dependence of resistance on the probes and sample geometry means it is not an intrinsic property. For this reason, it is preferable to measure a sample's resistivity which is given as:

$$\rho = R \frac{l}{A} \tag{2.13}$$

where  $\rho$  is the resistivity, R is the resistance for the measured geometry, l is the distance between the voltage leads and A is the cross-sectional area of the sample.

The simplest method of measuring resistance is the 2-wire method which can be accomplished with a simple handheld multimeter. However, this method is prone to error, particularly when dealing with samples having high contact resistance. This comes from the fact that the probing current passed through the sample is also passed through the probes themselves. Therefore, instead of measuring the voltage drop across the sample (a single resistor), the voltage drop is measured across the two probes as well as the sample (three resistors in series). This is represented in Figure 2.33a, illustrating how the measurement by the 2-wire method results in the sum of these three contributions.



**Figure 2.33:** Difference between 2-wire and 4-wire measurements. (a) 2-wire measurements include the contact resistance while (b) 4-wire measurements only measure the sample resistance.

To eliminate contact resistance, the 4-wire method is instead used as shown in Figure 2.33b. In this configuration it is easy to understand how the contact resistance is eliminated. Instead of the current passing through the voltage probes and sample, the current is only passed through the sample. Due to the high impedance of the voltmeter, little to no current can pass through the voltage probes, meaning that the voltage dropped measured is that of the sample.

#### 2.5.2.2 van der Pauw Resistivity

In pressure cell experiments the size and geometry of samples are tightly constrained due to the limited space. For this reason small square samples, typically no more than 300 µm along the diagonal, are used in place of the more traditional bar-shaped samples. These geometric constraints have led high-pressure resistivity measurements to follow the van der Pauw method. The van der Pauw method is capable of determining the resistivity of an arbitrary shaped sample, given it adheres to the following conditions.

- 1. The contact leads are positioned along the periphery (corners)
- 2. The contacts are small in comparison to the surface area
- 3. The sample surface is continuous (no holes)
- 4. The sample is of uniform thickness
- 5. The sample is thin compared to the surface area (A/t > 10)
- 6. The sample is isotropic

With these conditions satisfied, the resistivity of a sample can be determined from the horizontal  $(R_H)$  and vertical resistance  $(R_V)$  presented in Figure 2.30.

In the high-pressure experiments conducted, the resistivities in all four configurations were used to find resistivity via the van der Pauw method. Averaging the resistance of channels 1 & 3 and channels 2 & 4 (see Figure 2.30) gives the aforementioned  $R_H$  and  $R_V$ , respectively. From these, the resistivity can be calculated given a correction factor f which is a function of  $R_H$  and  $R_V$ . This factor becomes 1 when  $R_H = R_V$ , further simplifying Equation 2.15.

$$R_{vdP} = \frac{R_V + R_H}{2} \tag{2.14}$$

$$\rho = R_S t = \frac{\pi t R_{vdP}}{\ln 2} f(\frac{R_V}{R_H}) \tag{2.15}$$

Here  $R_S$  is the sheet resistance, t is the sample thickness,  $R_{vdP}$  is the van der Pauw resistance, and f is the aforementioned correction factor. In general, the correction factor f is given by the following transcendental equation:

$$\frac{R_V - R_H}{R_V + R_H} = \frac{f}{\ln 2} arccosh \frac{e^{\ln 2/f}}{2}$$
(2.16)

In the context of high-pressure measurements, where the samples are cut into squares of high-quality single-crystals, it is usually the case that  $R_H \approx R_V$ . This allows f to be approximated by the equation:

$$f \approx 1 - \left[\frac{R_V - R_H}{R_V + R_H}\right]^2 \frac{\ln 2}{2} - \left[\frac{R_V - R_H}{R_V + R_H}\right]^4 \left[\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right]$$
(2.17)



Figure 2.34: A sample represented as the upper-half of a semi-infinite plane.

In the original paper by van der Pauw, he derived the above equations and criterion for a sample of arbitrary shape. His derivation began by representing the sample as a semi-infinite plane with points P, Q, R, and S as illustrated in Figure 2.34.

If a current is injected into point P and exits at point Q, the potential difference measured between points R and S is:

$$V_S - V_R = -\int_R^S \vec{E} \cdot d\vec{r} \tag{2.18}$$

The current density entering point P will propagate through the sample as a short halfcylinder with a height equal to the thickness of the sample. The current density is thus given by:

$$\vec{J} = \frac{I}{\pi \vec{r} t} \tag{2.19}$$

where  $\vec{J}$  is the current density, I is the current,  $\vec{r}$  is the distance from point P, and t is the thickness of the sample.

Using the continuum form of Ohm's Law and Equation 2.20,  $\vec{E}$  is found to be:

$$\vec{E} = \rho \vec{J} = \frac{\rho I}{\pi \vec{r} t} \tag{2.20}$$

Note that  $\vec{E}$  contains a contribution from both the current injection at P and the exit point at Q. Therefore, using the given definition of  $\vec{E}$ , Equation 2.18 can be rewritten as:

$$V_S - V_R = \frac{\rho I}{\pi t} \left[ -\int_R^S \frac{1}{\vec{r}} \cdot d\vec{r} + \int_R^S \frac{1}{\vec{r}} \cdot d\vec{r} \right]$$

$$= \frac{\rho I}{\pi t} \left[ \int_{a+b+c}^{a+b} \frac{dr}{r} + \int_b^{b+c} \frac{dr}{r} \right] = \frac{\rho I}{\pi t} \ln \frac{(a+b)(b+c)}{b(a+b+c)}$$
(2.21)

Likewise, if the orientation were to change so that the current was passed through points Q and R, while the potential was measured between S and P, the potential difference would be:

$$V_P - V_S = \frac{\rho I}{\pi t} \left[ \int_a^{b+c} \frac{dr}{r} + \int_c^{a+b} \frac{dr}{r} \right] = \frac{\rho I}{\pi t} \ln \frac{(b+c)(a+b)}{ac}$$
(2.22)

When solving for the potential difference  $V_Q - V_P$  and  $V_R - V_Q$ , it can be determined that they are equal to  $V_S - V_R$  and  $V_P - V_S$  respectively. Therefore, knowing  $R_{RS}$  and  $R_{SP}$  is sufficient for describing the sample.

$$R_{RS} = R_{PQ} = \frac{\rho}{\pi t} \ln \frac{(a+b)(b+c)}{b(a+b+c)}$$
(2.23)

$$R_{SP} = R_{QR} = \frac{\rho}{\pi t} \ln \frac{(b+c)(a+b)}{ac}$$
(2.24)

Using the definition of the sheet resistance from Equation 2.15, Equations 2.23 and 2.24 can be added to get:

$$e^{-\pi R_{RS}/R_S} + e^{-\pi R_{SP}/R_S} = \frac{b(a+b+c)}{(a+b)(b+c)} + \frac{ac}{(a+b)(b+c)}$$
(2.25)

Since it can easily be shown that b(a+b+c) + ac = (a+b)(b+c), Equation 2.29 becomes:

$$e^{-\pi R_{RS}/R_S} + e^{-\pi R_{SP}/R_S} = 1 \tag{2.26}$$

Equation 2.26 can be shown to be of general validity through conformal mapping. This is accomplished by mapping the upper-half plan to a sample of arbitrary shape (within the listed constraints) as shown in Figure 2.35.

Further manipulation of Equation 2.26 reveals the origin of the correction factor f given in Equation 2.16. In transforming the arbitrary sample shown in Figure 2.35 into an idealized sample, as presented in Figure 2.30, it becomes easy to relate  $R_{RS}$  and  $R_{SP}$  to  $R_V$  and  $R_H$ , which yields the following:

$$R_{RS} = R_H = \frac{1}{2} \left[ (R_V + R_H) - (R_V - R_H) \right]$$
(2.27)

$$R_{SP} = R_V = \frac{1}{2} \left[ (R_V + R_H) + (R_V - R_H) \right]$$
(2.28)



Figure 2.35: A sample of arbitrary shape mapped from the upper-half of a semi-infinite plane.

Inserting Equations 2.27 and 2.28, Equation 2.26 can be rearranged in the form:

$$e^{\frac{-\pi(R_V+R_H)}{2R_S}} \left[ e^{\frac{-\pi(R_V-R_H)}{2R_S}} + e^{\frac{\pi(R_V-R_H)}{2R_S}} \right] = 1$$
(2.29)

Next, the definition of cosh(x) is used to get:

$$e^{\frac{-\pi(R_V+R_H)}{2R_S}}\cosh\frac{\pi(R_V-R_H)}{2R_S} = 1$$
(2.30)

The value of the exponential is then related to the correction factor f as:

$$\frac{\pi(R_V + R_H)}{2R_S} = \frac{\pi R_{vdP}}{R_S} = \frac{\ln 2}{f}$$
(2.31)

Now in terms of f, equation (2.29) is written as:

$$e^{-\frac{\ln 2}{f}} \cosh\left[(R_V - R_H)\frac{\ln 2}{f(R_V + R_H)}\right] = \frac{1}{2}$$
 (2.32)

From this point it is rather trivial to rearrange Equation 2.32 to the form presented in Equation 2.16.

## 2.5.3 LabVIEW

LabVIEW is a visual programming software from National Instruments that facilitates quick development of custom programs for experimental control and data acquisition (DAQ). This section will not discuss the details of using the LabVIEW software, rather it will serve as a guide for the functionality of the custom programs used in the works pertaining to this dissertation.

#### 2.5.3.1 User Interface

The front end of a LabVIEW program is known as the Front Panel or user interface (UI). This is used to make operating the program more intuitive to users. It also serves as an important tool for monitoring data acquisition through interactive objects like graphs. The program interface is used to set the parameters for the temperature sensor and for data collection.



Figure 2.36: The GUI for the custom LabVIEW program used for data acquisition.

The program has two modes for data acquisition (1), using a time step or temperature step. If a calibration curve is uploaded to the LS336, the Boolean toggle on the LS336 Interface panel (2) can be set to interpolate the temperature from its user curve. The ability to load factory curves in the LS336 is also helpful in cases where standard calibration curves exist for the temperature sensor. Examples include Si diodes and thermocouples. Note that the LS336 must have the 3060 thermocouple option card installed to make use of thermocouples. Alternatively, the Boolean on the LS336 Interface panel (2) can be toggled to use the Chebyshev fitting VI to calculate temperature directly. The Chebyshev calculator is more accurate than the LS336 fitting, but if an appropriate dataset is chosen for the user curve the difference can be negligible. The Temperature Sensor Interface (3) also provides control over which sensor is used in the program-side calculations and some other related options.

After the temperature sensor is configured, the DAQ settings are next. This configuration includes assigning DAQ instruments appropriate General Purpose Interface Bus (GPIB) addresses, setting the sample excitation current (4), and choosing a file path where the data will be saved (5). The two standout controls are the d (cm) and # of CH, which are used as the sample thickness and number of channels for the van der Pauw resistance measurement.

When all controls have been set, data collection can be initiated by running the program (6). Two graphs can be used to display data that is collected during the DAQ sequence (7). Each graph has a Boolean which will toggle the graph on/off, and two axis rings (8) used to select the dependent and independent variables, such as R(T) or R(t). Two more controls can be used to change the graph update frequency from Auto to Manual (9). This allows the user to choose between updating the graph after each data point is collected (Auto) or updating after a period of time (Manual).

One point worth noting is the Graphing File Path is separate from the Data File Path. This allows the user to print the data of any file, not just the current data collection file.

#### 2.5.3.2 Program Details

On the other side of the user interface is the block diagram. This window is where the visual programming is done. The program is split into two parallel functions, the Data Acquisition, and the Graph Printing functions. The following images taken from the program's block diagram highlight the main function of the program.



Figure 2.37: First iteration case to initialize and create a header.

The Data Acquisition function begins by initializing the Keithley 6221 and 2182A (1) to function in delta mode. Moving into the main loop the first iteration of data acquisition collects an initial reference time and temperature (2) from the computer's internal clock and the LS336 respectively. At the same time, a special function is used to create the data file header (3).



**Figure 2.38:** Main case that shows the data acquisition waiting step (time or temperature).

Once the header has been created, the function enters the main sequence for data acquisition. At the beginning of every loop (including the header iteration), the Keithley 705 scanner is activated (4) to close channels 1 and 11 on the 7055 and 7059 cards respectively. This corresponds to the first van der Pauw wiring configuration as described in the previous section. In Case 0 of the stacked sequence, the program activates the temperature sampling VI (5), which returns information from the LS336, including the temperature (T1\_N) and the time (t1\_N) when the measurement was taken. For more details on the temperature sampling VI see Appendix B.3.

As discussed in the section on the user interface, data can be collected in specified time or temperature steps. The Time/Temp Boolean is used to toggle the temperature step check (6). When activated, the 1st Measure T-t loop will run until the difference between the previously measured temperature and the current temperature matches or surpasses the desired temperature step, before terminating the loop. If the time step option is chosen, the loop will terminate on the first iteration and move to Case 1.



Figure 2.39: The cases (0-5) for the main DAQ sequence.

In Case 1, the multichannel VI (7) is used to record the resistance of the four van der Pauw configurations. See Appendix B.3 for more details. Next, the sequence enters

Case 2 where the temperature sampling VI is used again (8) to get a second temperature (T2\_N) and the time (t2\_N) measurement. These values are then averaged (9) with the first measurements to better represent the temperature (Tavg\_N) and the time (tavg\_N) when the measurement was taken. Note that both Tavg\_N and tavg\_N are passed to the next iteration of the data acquisition as references, but only Tavg\_N is passed in Case 3. Other calculations in Case 3 include the time step between data acquisition iterations, the relative time, and temperature rate (9). Finally, Case 3 calls the van der Pauw calculation VI (10) which returns the resistivity of the sample based on Equations 2.15 and 2.17.

With all calculations completed, the sequence proceeds to Case 4 where the relevant data is collected into an array and then written to a text file using LabVIEW's provided "Write to Spreadsheet File" VI. Finally, the stacked sequence reaches Case 5 where tavg\_N is passed to the next iteration for reference. In the case that the temperature step is chosen, the average time is directly passed to the shift registry. If the time step is active the sequence will enter a while-loop which delays the next data acquisition iteration until the time step is reached.

The Graph Printing function runs in parallel with the Data Acquisition so that it can be decoupled from data collection. This is useful when data files are very large and would slow down data collection.

A series of Boolean logic (1) is used to determine if the graphs will be updated. If the Auto Update mode (2) is active, the program updates only when a new data point has been collected since the graphs were last updated. If the program is running in Manual mode, it will loop without updating the graphs until the Update Timer is reached. This works as each iteration waits at least 50 µs. If either graph is active, and the graph update



Figure 2.40: The graph printing sequence that runs in parallel to the main DAQ sequence.

Boolean is true, the sequence will enter the graphing case.

The file path given in the Graphing File Path is used to read the data file (3). Since the header occupies the first 3 rows, these are removed before sending the data to the two graphing cases. In the graphing cases (4), the appropriate data columns are selected for printing based on the axis rings.

# Chapter 3

# **Results and Discussion**

It is clear from Figure 1.18 that there has been a recent and rapid increase in the critical temperature of superconductors. What is also apparent is the importance of high pressure in facilitating high critical temperatures. However, the extreme pressure required to induce and enhance the  $T_c$  makes it impractical for commercial use. Therefore, the objective of this dissertation was to provide a path to broaden the application of materials that develop or enhance superconducting properties at high pressure via pressure quenching. In particular, the pressure enhanced  $T_cs$  of Bi, FeSe, and  $Cu_xFe_{1.01-x}Se$  were targeted to exhibit the potential pressure quenching has for retaining metastable superconducting phases at ambient pressure. Further, testing with bismuth was conducted to investigate the possibility of retaining a specific superconducting state at ambient with more desirable properties.

In the following section, the results of the pressure quenching work for a number of superconductors are presented. These results show that metastable superconducting phases can be retained at ambient pressure in a variety of materials. The stability of these metastable states is also discussed.

# 3.1 Experimental Techniques

For clarity the experimental techniques used to collect the pressure quenching data are discussed ahead of the results of this dissertation. Details about the equipment itself can be found in the chapter on Experimental Methods.

## 3.1.1 Pressure Quench

The sequence for pressure quenching is laid out in Figures 3.1 and 3.2. Every experiment began by consulting the phase diagram of the material to determine at what pressure it would become superconducting and how it would respond to pressure, known as the  $T_c$ -P relationship.

From here, a superconducting phase was targeted for the pressure quenching experiment and pressure in the DAC was increased accordingly. Once at the desired applied pressure ( $P_A$ ), resistivity was measured to a temperature below the superconducting transition temperature. After the superconducting state was confirmed the sample temperature was adjusted to a desired quenching temperature ( $T_Q$ ) which was usually 4.2 K



Figure 3.1: Pressure quenching sequence. Note each step is colored to match the corresponding data plotted in Figure 3.2

(LHe) or 77 K (LN<sub>2</sub>) in the studies conducted. At this point  $P_A$  was released to ambient while the cell was held at constant temperature. The sample was then cooled again from  $T_Q$  to low temperature to check if the sample remained in a superconducting state. Finally, the sample was annealed to room temperature and subsequently cooled back to low temperature to check if the metastable superconductivity persisted.



**Figure 3.2:** An example of the resistivity measured during a pressure quench experiment with bismuth. Note the left and right axes provide two resistance ratio scales which are normalized to the value of the sample resistance at 10 K, immediately after pressure quenching.

Since the pressure could not be measured in-situ, it was measured after the quenched sample was annealed to room temperature. During pressure quenching the screws were loosened by rotating them back to approximately the zero-degree position. Often, a small pressure was required to keep the platinum leads in contact with the sample, but this pressure was typically less than 0.50 GPa. In the section on  $Cu_xFe_{1.01-x}Se$ , more details are given to support the validity of this method for confirming a complete pressure quench.

# 3.1.2 Stability Testing

Once a metastable superconducting state was created, the sample was further tested to assess its stability. Since one of the goals of pressure quenching was to provide a route to produce metastable superconducting phases at ambient conditions, testing the stability of these retained phases was important to evaluating their success and application.

Stability testing was done in two ways. Pressure quenched samples were tested for temporal stability at a given  $T_Q$  by monitoring changes to the resistivity and  $T_c$  over the course of a few days. Thermal stability was also tested to determine when the metastable phases began to disintegrate and when they were completely destroyed via thermal cycling.

# 3.2 Development of Pressure Quenching & Targeted Phase Retention with Bi

#### 3.2.1 Motivation

The purpose of this experiment was two-fold. First, bismuth was selected as a starting point for our experimental pressure quenching works. Therefore, the most fundamental goal was to successfully retain a metastable superconducting phase of bismuth at ambient pressure via pressure quenching. Previous works on bismuth and antimony indicated a high likelihood of success in retaining metastable phases in bismuth[117–119]. This would then set the foundation for the development of our pressure quenching technique and subsequent investigations of other materials. The second goal was to selectively retain a metastable phase with desirable properties at ambient pressure. In this regard bismuth also well-suited for the roll as it has multiple pressure induced superconducting phases at moderate pressure. In particular, Bi-III has a distinctly high critical field between about 2.5 T and 4 T and Bi-V is the highest  $T_c$  phase at ~ 8.5 K making them good targets for retention[120–122].

# 3.2.2 Introduction

Bismuth is a well-studied element with four unique structures (Bi-I, Bi-II, Bi-III and Bi-V) at room temperature (RT) with Bi-II, Bi-III and Bi-V developing under pressure[123–126]. Of these, three structures have been shown to persist at T ; 8 K (Bi-I, Bi-III, and Bi-V)[127]. There is also evidence for several additional unconfirmed electronic and metastable phases at low temperature and high pressure[121, 128–131]. The ambient Bi-I phase has an As-type, R3-mh structure and was recently found to be superconducting with a  $T_c \leq 53$  mK[132]. At RT this phase exists under pressures up to 2.55 GPa, where it transitions to Bi-II with a monoclinic, c12/m1 structure. As the pressure increases to 2.7 GPa, Bi-II transforms into Bi-III, resulting in complex host-guest structures, I4/mcm[124]. At RT and pressures greater than 7.6 GPa, it transforms to Bi-V a body-centered cubic (bcc), Im-3m structure which persists up to at least 222 GPa[125, 126]. For completeness, it is worth noting that above 450 K, and from 2.5 - 5.5 GPa, Bi-IV can be formed with an orthorhombic, Cmce structure[133]. This high temperature phase has recently been suggested to superconduct at 4.25 K[134].

The phase boundaries of the Bi polymorphs shift at low temperature but can be distinguished by their  $T_c$  and pressure. At atmospheric pressure, Bi-I persists with a  $T_c$  of 0.53 mK and a currently unknown  $dT_c/dP$  relationship[132]. From pressures of ~ 2.5 to 3.3 GPa, a metastable phase with a  $T_c \approx 4$  K, attributed to Bi-II[121, 131], may appear. A recent report on the nature of Bi-II suggests a more reliable way of creating this phase is through decompression (Bi-III to Bi-II) rather than compression (Bi-I to Bi-II)[131]. However, there still remain open questions as the Bi-I-II-III triple point is thought to occur around 160 K - 225 K[121, 130, 135], and structural analysis has failed to confirm the existence of Bi-II at low temperature[127]. It is most often the case that superconductivity is first observed at ~ 2.7 GPa corresponding to Bi-III with a  $T_c$  of 7 K[120, 121, 128–131]. Above pressures of ~ 7 - 9 GPa, Bi-V is formed[120, 129, 131] with the highest  $T_c$  between 8.5 and 8.7 K[128, 136]. Bi remains in this superconducting phase up to at least 34.51 GPa where its  $T_c$  decreases to 3.32 K[137].

Similarly, the phases of bismuth can be distinguished by their differences in critical field. For Bi-I at ambient pressure the critical field is reported to be 0.0052 m T[121, 132]. The H<sub>c</sub> of Bi-II is reported to be around 32 m T[120, 121]. Interestingly, Bi-III is thought to be a type-II superconductor with an upper critical field of 2.5 T-4 T[120, 121]. Finally, there is Bi-V with a critical field around 76 m T[138].

#### 3.2.3 Data & Discussion

Figure 3.3 shows the phase diagram of bismuth by plotting the critical temperature as a function of applied pressure. The figure includes data collected in this work, as well as data from previous studies, showing general agreement with slight shifts in the pressure scale[128, 129, 131, 137, 139]. This information was vital in characterizing the retained superconducting phases.


Summary of Bi T<sub>c</sub> Under Pressure

Figure 3.3:  $T_c$ -P diagram of Bi under pressure. Blue & light blue data points represent major and minor superconducting phases respectively. See Figure 3.4 b for an example. Details on the determination of  $T_c$  are provided in Appendix Figure C.1. Diagonal dashed lines show the phase boundaries based on the  $T_c$ -P relationship. Orange indicates Bi-II, green indicates Bi-III and purple indicates Bi-V. Solid vertical lines indicate RT phase boundaries based on structure, whereas dashed vertical lines show low-temperature phase boundaries derived from resistance in this work and others. Note that data from Rabin'kin was collected as pressure was released near LHe temperatures. The single large purple datum point was taken by Lotter during decompression. This represents the highest recorded  $T_c$  in Bi prior to this work and is marked by a solid blue line.

#### **3.2.3.1** Pressure Quenching at 77 K

The first set of pressure quenching experiments on bismuth were completed at  $T_Q =$  77 K. Various pressures throughout the phase diagram were selected to target the three superconducting phases. Some results of pressure quenching are shown in Figure 3.4. It is clear from the figure that the  $T_c$  changed with increasing pressure. However, the retained

superconducting phases were effectively independent of  $P_A$ , resulting in a band of retained  $T_cs$  from ~ 6.6 K–7.3 K as shown in Figure 3.5. The consistency of this result indicates Bi-III was consistently retained near the Bi-III/I boundary and is a robust metastable phase, likely protected by the latent energy of the structure transition.



**Figure 3.4:** Examples of pressure quenching at 77 K across a wide pressure range. Figure (a) shows the results of quenching in Bi-III. Figure (b) is near the Bi-III/V boundary, made clear by the two superconducting transitions of  $\sim 6$  K and 8 K. Figure (c) and (d) are both in Bi-V. These show the best quench results at 77 K with full zero-resistance drops.

Only one pressure quench from  $P_A = 2.62 \text{ GPa}$  and  $T_Q = 77 \text{ K}$  resulted in a distinctly different retained  $T_c$  of 5.51(43) K. Given the low  $P_A$ , this retained phase may be a novel



Pressure Quench: Summary @ 77 K

Figure 3.5: Summery of retained  $T_cs$  pressure quenched at  $T_Q = 77$  K. Horizontal dashed lines give an indication of the likely phase which is retained based on the retained  $T_c$  and follows the same color scheme as Figure 3.3. Almost all retained phases resulted in a  $T_c$  onset around the value expected for Bi-III, near the phase boundary. Note that the minor phases shown do not have a full zero-resistance drop. An example can be seen in Appendix Figure C.2. The fine dotted line at 5.5 K marks the lower boundary of what has been observed in Bi-III/128].

metastable phase as  $T_c$ s below 5.5 K have only been detected above pressures of ~ 21 GPa in Bi-V[137]. Furthermore, only the study by Il'ina provides any indication that a  $T_c$ around 5.5 K could exist in Bi-III, but occurs at pressures above ~ 10.5 GPa[128]. Both seem unlikely as the initial  $P_A$  of 2.62 GPa is far from the pressure required to suppress the  $T_c$  to such an extent. A better interpretation of this unexpected  $T_c$  is that an amorphous superconducting phase is formed, similar to those seen in bismuth thin films as a result of quench condensation at 4 K[140]. The T<sub>c</sub> of 5.51 K fits well between the T<sub>c</sub> of 6 K initially recorded by Buckel after quench condensing Bi and the T<sub>c</sub> of ~ 5 K after the film was annealed to 20 K. This becomes even more sensible when considering the initial phase under pressure is Bi-III prior to pressure quenching at 77 K and cooling to 4.2 K. It then seems likely that before reverting to Bi-I, Bi-III underwent a transition into an amorphous phase in which it was trapped as the sample cooled.

#### **3.2.3.2** Pressure Quenching at 4.2 K

To further investigate bismuth, pressure quenches at  $T_Q = 4.2$  K were conducted in the hope that the reduced thermal energy would enable the targeting of the other superconducting phases and improve the quality of metastable Bi-III phases. Figure 3.6 shows the results of these pressure quenching experiments.

The result of pressure quenching from  $P_A < \sim 6.5$  GPa was a band of retained  $T_cs$  corresponding to Bi-III. Additionally, two outliers were observed, likely arising from minor phases and suggesting the potential presence of the amorphous phase, as previously mentioned. For pressure at and above 6.5 GPa an abrupt drop in the  $T_c$  of the retained phases was observed near the Bi-III/V boundary. The retained  $T_cs$  then continued to increase along with  $P_A$ , reaching a max  $T_c \approx 9$  K when pressure quenched from a  $P_A$  of 26.5 GPa.

At first glance, the low  $T_cs$  retained by pressure quenching near the Bi-III/V boundary appear to be an extension of the long-established negative  $dT_c/dP$  relationship for Bi-III present in Figure 3.3[129, 139]. As previously noted, the literature only provides evidence for  $T_cs$  near and below 5.5 K at higher pressure[128, 129, 137]. This would indicate that Bi-III could exist with a  $T_c$  as low as 4.5 K and implies pressure quenching has the potential



**Figure 3.6:** Summery of retained  $T_cs$  pressure quenched at  $T_Q = 4.2$  K. Many of the retained phases were Bi-III and occurred below  $P_A = 6.5$  GPa. In the transition region  $T_cs$  that fall below the Bi-III limit were retained. Beyond the transition region,  $T_c$  increased with pressure up to a maximum of  $\sim 9$  K, denoted by the blue star.

to probe for even lower  $T_cs$  near, and possibly beyond the established phase boundaries. This region also contains low  $T_cs$  that match with the previously mentioned amorphous phase of Bi as well as Bi-II. Even so, the pressure quenches from pressures below 6.5 GPa and at 4.2 K exclusively resulted in  $T_cs$  corresponding to Bi-III at the phase boundary, save for the minor phases observed at 2.12 GPa. Furthermore, it seems unlikely that Bi-II would result as the evidence for its formation at low temperature is lacking[121, 127, 130, 135].

One final possibility worth posing is that a novel structure supporting superconductivity was retained which was not previously observed under pressure. Recent computational work on the structure of Bi under pressure indicates a hexagonal close-packed (hcp) structure should be preferred over the bcc phase of Bi-V starting around 14 GPa[141]. According to the authors, this phase should be superconducting with a  $T_c$  of 4.8 K at 15 GPa which decreases to 4.1 K at 20 GPa. The  $T_c$  of this theoretical hcp phase fits well with the phases retained near the Bi-III/V boundary and may be accessible through pressure quenching.

When looking at  $P_A$  beyond the transition region, the retained  $T_cs$  become ambiguous and do not seem to follow the expected T<sub>c</sub>-P relationship; instead, an increase in retained  $T_{\rm c}$  with pressure is observed. The ambiguity of this region follows the fact that nearly all retained  $T_c$ s in this pressure region falls below 7.3 K. This is crucial as the retained phases could be either Bi-III or Bi-V due to the negative  $dT_c/dP$  relationship in both phases. Not until  $P_A = 23.6$  GPa was Bi-V unambiguously retained, with a  $T_c$  around 8 K. However, the most impressive result came during pressure quench from  $P_A = 26.5$  GPa, which yielded numerous superconducting transitions as shown in Figure 3.7. A  $T_c$  of  $\sim 9$  K was the most notable, as this  $T_c$  surpasses the previously held record for Bi under pressure of between 8.5 and 8.7 K. This novel  $T_c$  may also represent Bi-V as it can be expected that the T<sub>c</sub> should increase as pressure is removed while retaining the same structure. In fact, a noticeable increase in the  $T_c$  of Bi-V to  $\sim 8.7$  K is observed in the datum collected by Lotter during decompression, presented as a dark purple triangle in Figure 3.3[131]. However, the fact that a  $T_c > 8.7$  K has never been observed under pressure, and this record  $T_c$  was retained only after quenching from a  $P_A$  far beyond the Bi-V onset only serves to confuse the situation.



**Figure 3.7:** Temporal stability testing of the record  $T_c$  phase retained in bismuth. The solid horizontal lines show the effective width of the superconducting transition for each phase. This line connects the vertical dashed line representing the  $T_c$  offset to the solid vertical line representing the  $T_c$  onset. The solid vertical line between the other lines denotes the  $T_c$  at 50% integration (see Appendix Figure C.1 for more details).

Another possible explanation for this enhancement may be lattice dislocations. When Brant and Ginzburg induced Bi-III through repeated pressure cycling at 2.2 K, they eventually recorded a "washed out"  $T_c$  of 7.6 K[117]. Typically, this would have been observed as a sharp transition around 7 K. They justified this  $T_c$  discrepancy, positing lattice dislocations, created by pressure and stabilized at low temperature, had enhanced the  $T_c$  of Bi. With this in mind, it seems likely that the  $T_c$  of Bi-V is likewise enhanced to ~ 9 K through a combination of the innate negative  $dT_c/dP$  relationship and presence of lattice dislocations retained after pressure is removed at low temperature, rather than room temperature.

Although  $\rho(T)$  data are inadequate for determining the overall phase composition of the sample, some insight into this novel phase can still be gained. Upon further inspection of Figure 3.7, a sharp superconducting drop at 9.05 ± 0.07 K can be observed, which is distinctly separate from the second most prominent drop rather than being a single broad transition. This lesser but substantial drop at 8.15 ± 0.10 K likely corresponds to Bi-V near the Bi-V/III boundary. Also retained was a minor superconducting phase with T<sub>c</sub>s below 7 K that seemed to develop into two broad transitions after the initial warming cycle following the pressure quench. Using the magnitude of the drop as a stand-in for overall phase composition, it can be said that both superconducting phases with T<sub>c</sub> = 9.05 K and 8.15 K seem to be more favorable than the 7 K phase. Therefore, assuming the novel T<sub>c</sub> phase is also Bi-V, the majority of the sample should be a metastable phase of Bi-V.

#### 3.2.3.3 Phase Stability Testing

A few samples were thermally cycled to identify the temperature at which the metastable phases would degrade. Figures 3.8 and 3.9 provide insight into the thermal stability of Bi-III retained by quenching at  $T_Q = 77$  K. In the former, the metastable phase is shown during warming immediately after pressure quenching at 77 K and 3.53 GPa. Perfect overlap between warming (red) and cooling (black) was observed up to ~ 71 K. Above this temperature the resistance began to rapidly increase, indicating further degradation to the metastable state. This is made clear in the subsequent temperature cycles of cooling (blue), warming to 92 K (orange), cooling (cyan), and warming to 151 K (magenta). During these cycles, the R(T) curves showed near perfect overlap, but began to diverge



**Figure 3.8:** Thermal stability testing of metastable Bi-III pressure quenched at 77 K and 3.53 GPa. Vertical lines at 77 K, 104 K, 92 K, and 151 K indicate the turning points during thermal cycling and are colored accordingly. All data presented are normalized to the resistance of the metastable phase measured at 10 K during cooling (black).

noticeably around 60 K. This behavior was also observed in two other quenches at 77 K and is presented in Appendix Figures C.3 and C.4. The  $T_c$  onset did not change from the initial quench, but developed a broad secondary drop around 4 K. Only this secondary  $T_c$  experienced a shift in the thermal cycling below 104 K. Once the sample was warmed to 151 K and cooled once more (purple), all signs of superconductivity disappeared, indicating the complete destruction of the metastable superconducting phase.



**Figure 3.9:** Thermal stability testing of metastable Bi-III pressure quenched at 77 K and 11.70 GPa. All curves shown were taken during cooling. Unlike Figure 3.8, each curve is normalized to its resistance at 10 K. Note that the cooling data for 65 K (navy) perfectly overlaps the initial measurement taken from 77 K (cyan).

In Figure 3.9 a more detailed investigation of the disintegration temperature was carried out (see Appendix Figure C.3 for an extended view). In this pressure quench, the retained phase did not exhibit a zero-resistance drop as observed in Figure 3.8 but did reinforce the overall experimental results. The initial cooling data (navy) following the pressure quench overlapped perfectly with the cooling data after a warming cycle to 65 K (cyan). The thermal cycles to progressively higher temperatures also showed there was little change to the T<sub>c</sub> onset of the retained phase, rather the magnitude of the superconducting drop decreased until it was completely destroyed between 120 K and 130 K.

The results of thermal cycling following pressure quenches at 77 K were in good agreement and provide the following insights about the metastable Bi-III. First, it is apparent that below ~ 60 K–70 K the retained phase remains stable even after being partially degraded. This manifests as a retraceable  $\rho(T)$  curve that produces a hysteresis only when the sample is annealed to a sufficiently high temperature, suggesting a lower temperature limit for perfect phase stability. Next, the critical temperature of the metastable Bi-III does not change noticeably during phase disintegration. Instead, the normal state resistance sees a marked increase and the zero-resistance drop degrades. Finally, the retained phase fully disintegrates upon warming the sample to ~ 130 K indicating an upper temperature limit for successful pressure quenching of Bi-III.

More insight on the stability of the retained phases was gathered from thermal cycling the superconducting phases retained at  $T_Q = 4.2$  K. Figure 3.10 shows the change in resistance of two warming cycles up to 30 K. An initial hysteresis is observed between the warming (red) and cooling (blue) after the initial pressure quench. Three additional warming and cooling cycles to 10 K were conducted (not presented) between the initial warming cycle to 30 K (red) and the second cycle to 30 K after being held at 4.2 K for 48 hours (orange), with minimal effect on the resistance. The second 30 K cycle also showed a hysteresis between warming (orange) and cooling (cyan), further increasing the resistance with little to no effect on  $T_c$  onset. Notably, the second warming curve (orange) followed the previous cooling curve (blue) well but diverged around 25 K.

The first derivative of the initial warming curve (Q 0h W dR/dT) reveals the approximate temperature where the initial warming curve (red) becomes non-ohmic to be  $\sim 20$ 



**Figure 3.10:** Stability testing of Bi-III via thermal cycling to 30 K. The horizontal dashed line represents the mean value for  $d\rho/dT$  in the ohmic region above the  $T_c$ . The yellow region centered around 20 K gives an indication of when the non-ohmic response begins.

K. At this temperature the metastable phase likely begins to revert to the ambient Bi-I phase leading to the observed hysteresis. This is notable as the stability of the superconducting amorphous phase in Bi thin films reportedly begins to rapidly degrade around 20 K, suggesting part of the metastable composition could be amorphous[140]. Another pressure quench from 1.78 GPa showed a similar response when cycled to 30 K and can be seen in Appendix Figure C.5. This thermal cycle showed good overlap when cycled between 1.2 K and 30 K. However, the resulting phase was diminished substantially more than what is presented in Figure 3.10.Furthermore, the T<sub>c</sub> onset decreased by  $\sim 0.25$  K. This discrepancy in the level of phase decomposition is likely a product of the lower applied pressure.



**Figure 3.11:** Thermal cycling of the record  $T_c$  phase. Vertical lines have been drawn at 115 K, 130 K, 22 K, and 71 K to mark noticeable changes in dR/dT. The remnant superconducting phase present after annealing to 140 K has a broad  $T_c$  with an onset of 5.3 K and centered around 3.1 K.

Thermal cycling was also conducted on the high- $T_c$  phase retained at 4.2 K when quenched from 26.53 GPa, as presented in Figure 3.11. Throughout warming, the sample resistance gradually increased until ~ 115 K where it began to rapidly increase. The resistance then peaked at 130 K before beginning to drop. After reaching 140 K the sample was cooled again revealing a residual superconducting phase with a broad  $T_c$  onset at 5.3 K and centered around 3.1 K. During the final warming cycle (orange) the curve diverged from the cooling (blue) near 24 K. Then around 71 K the resistance reached a turning point and began to decrease substantially until about 125 K, when the rate slowed.



**Figure 3.12:** An expanded view of the warming curve from Figure 3.11. A noticeable peak near 49 K could indicate a Bi-V to Bi-III metal-metal phase transition. The region between 80 K and 115 K shows the beginning of major phase decomposition from Bi-III to Bi-I.

Taking a closer look at the initial warming curve shown in Figure 3.12 reveals a slow initial increase in resistivity up to a minor peak around 49 K. Knowing that Bi-V was retained in this sample would indicate this peak is potentially the metal-metal transition

of Bi-V decomposing into Bi-III. This would also help explain why there was no indication that Bi-V was retained when pressure quenching at 77 K.

As the sample continues to warm it comes to a region from about 80 K–115 K where the resistivity begins to increase at a much faster rate. The increase beginning around 80 K seems to be a common feature of Bi-III converting to Bi-I based on the results of thermal cycling metastable phases with  $T_Q = 77$  K. This is most noticeable in the large resistivity increase and shift from an overall metallic to insulating character observed in the  $\rho(T)$  curve at its peak. Therefore, from ~ 115 K–130 K the transformation of Bi-III to Bi-I occurs rapidly implying pressure quenches, at least up to 26.5 GPa, should not be expected to retain any metastable superconducting phases.

What is interesting is the lack of an inflection point near 20 K in the initial warming curve and its appearance during the second warming cycle around 24 K. Why the overlap is only observed up to 24 K is at first puzzling. However, considering the extreme changes in phase composition around 130 K it makes sense that the phase would continue to transform throughout cooling leading to a hysteresis. Based on the similarity between the final warming curve and the warming curves shown in the pressure quenches at  $T_Q = 77$  K, it is likely that, had the sample been cooled after warming to ~ 70 K, it would show good overlap similar to that in Figure 3.8.

A possible explanation for this is that during the cooling from 140 K, some of Bi-III was caught in the amorphous phase as it transformed to ambient Bi-I. This would explain both the broad drop associated with the amorphous bismuth, and the appearance of the hysteresis around 24 K. However, this point is confused by the thermal cycle presented in Figure 3.8. No signature of the amorphous phase decomposition is present in the initial

warming cycle or subsequent cycles below 104 K. This is despite the evidence for amorphous bismuth indicated by the slight reduction of the secondary  $T_c$  when cycled to 92 K.

Interestingly, a peak in the resistance during the final warming cycle (orange) occurs around 65 K–70 K before it begins to decrease. This seems to indicate that the weak, residual bismuth phase observed after strongly annealing it near 130 K is similar to that seen in 77 K thermal cycles. Following that logic, it would make sense that the  $d\rho/dT$  in the final warming curve suddenly decreases near 125 K as this temperature coincides with the complete destruction of the superconducting phase. Likewise, it seems reasonable to infer that the initial destruction of Bi-III in the region of 60 K–150 K proceeds through the amorphous phase before recrystallizing as the ambient Bi-I. This then gives rise to a weak and broad superconducting transition that corresponds to a metastable composition of Bi-III, amorphous Bi, and Bi-I.

To further test the stability of the retained superconducting phases, samples were kept submerged in LHe for several days after pressure quenching at  $T_Q = 4.2$  K. During stability testing, samples were warmed just above the retained  $T_c$  ranging from 7.25 K - 11 K. However, in a few instances, the samples were warmed as high as 20 K, 30 K, 50 K, and 140 K between stability measurements as described above. The results of temporal stability testing are shown in Figure 3.13. The region in blue shows the  $T_c$  at the respective  $P_A$  before pressure quenching for reference. After the initial shift in  $T_c$ , due to pressure quenching, the retained phase remained stable for the duration of the experiment, so long as the temperature was not increased. In general, only minor changes to the  $T_c$ superconducting phase showed excellent stability over ~ 96 hours, as shown explicitly in Figure 3.7. The noticeable shifts in the  $T_c$  of the quenches from 6.90 GPa and 15.64 GPa



**Figure 3.13:** The stability of  $T_cs$  over time for the major retained phase. Typically, only slight changes to the  $T_c$ , and more often, increases to the resistance were observed in the retained phases. Major changes in  $T_c$  occurred when the sample was warmed beyond 10 K. For instance, the  $T_c$  for  $P_A = 26.53$  GPa changed dramatically during a thermal cycle to 140 K as shown in Figure 3.11.

may indicate an instability in the retained phase. More likely, this was due to a brief moment of warming during helium transfer.

## 3.2.4 Field Effect

In an attempt to better distinguish the retained phases of bismuth, plans for a field effect study were made to determine the critical field after pressure quenching. As mentioned, the critical field of Bi-III is substantially higher than those of the other two superconducting phases. In combination with pressure prior to quenching and  $T_c$ , phase distinction would be possible.

Initially, a new pressure quenching platform was planned for this experiment—a system that would permit pressure quenching in a cryogenic dewar with a strong magnetic field. To that end, a probe was designed, which is detailed in Appendix D. However, due to time constraints the system could not become operational for use in this work. Other paths were considered, such as creating an electromagnet for basic phase distinction, but calculations of field strength and heat dissipation showed it unlikely to succeed.

As a final resort, a bismuth sample was loaded into a PPMS DAC to be pressure quenched and then transferred into the PPMS near room temperature. The sample was cooled to 77 K and pressure quenched. The cell was then transferred into a bucket of liquid nitrogen and subsequently loaded into the PPMS, rapidly cooling from 300 K to 12 K to minimize gas condensation in the sample space. Once at 12 K, the sequence was set to measure the resistivity down to 2 K.

Unfortunately, the results of this attempt were inconclusive. By the time the cell had been cooled to 2 K all signs of superconductivity were gone. As the PPMS has a maximum cooling rate of ~  $6 \,\mathrm{K\,min^{-1}}$ , it would take roughly 50 min to cool to 12 K or about 40 min to cool to 70 K, where the metastable phase might stop degrading. Apparently, this cooling rate is insufficient to retain the metastable bismuth phase so that critical field measurements can be conducted.

# 3.3 Metastable FeSe

The following section and the subsequent discussion of results are, in part, the published work titled "*Pressure-induced high-pressure superconductivity retained without pressure in FeSe single crystals*" [142]. Further insights and unpublished data are also presented in this dissertation section.

## 3.3.1 Motivation

There were two main motivations for investigating FeSe using the pressure quenching technique. First, FeSe is a different class of superconductor than elemental bismuth. This provided an opportunity to explore the applicability of pressure quenching across multiple classes of superconductors to test its universality. Since FeSe also has a pressure-induced structure transition that happens to produce a very large increase in the  $T_c$  from ~ 8 K up to a max of ~ 40 K, it seemed like an ideal material to attempt pressure quenching.

## 3.3.2 Introduction

FeSe has a simple but very sensitive chemical formula. Superconductivity will only appear in a very narrow composition range of ~  $\pm 1\%$  Fe, producing the best superconducting phase with a slight excess of iron to give Fe<sub>1.01</sub>Se[143]. Its simplicity and large dT<sub>c</sub>/dP relationship make it a model material for testing the iron-based superconductors.

Three crystal structures can be produced in FeSe in various pressure and temperature ranges, two of which support superconductivity. The phases are the superconducting orthorhombic (Cmme) and tetragonal (P4/nmm) phases, and the non-superconducting hexagonal (P6<sub>3</sub>mmc) phase. At room temperature and low pressure, FeSe exists in its tetragonal phase. However, as the temperature falls below ~ 87 K, FeSe undergoes a structural transition to the orthorhombic phase. With increasing pressure, the transition temperature from tetragonal to orthorhombic polymorph decreases until it is finally suppressed around 2.3 GPa[144]. Reports show the transformation of the tetragonal to hexagonal phase beings around 7 GPa to 12 GPa[144–148]. These two phases have been observed to coexist up to pressures between 12.4 GPa and 38 GPa, at which point FeSe transforms entirely into the hexagonal phase, indicating a mixture of  $Fe_{1-x}Se$  polymorphs[145, 146].

The implications of the described phase diagram are as follows. From ambient to  $\sim 2 \text{ GPa}$  the superconductivity observed is due to the orthorhombic phase which starts with a T<sub>c</sub> around 8 K and reaches a maximum of  $\sim 12 \text{ K}$  to 20 K near the phase boundary[144, 145]. Beyond 2 GPa, the T<sub>c</sub> sees a rapid increase corresponding to the transition from orthorhombic to tetragonal. By 3 GPa, the T<sub>c</sub> is roughly 25 K and peaks between 35 K–40 K at 6 GPa to 7 GPa. At higher pressures, the superconducting offset broadens and does not drop to zero resistance, due to a combination of impure Fe<sub>1.01</sub>Se and the natural pressure gradient of the DAC. Eventually, the superconductivity is suppressed entirely by the continued development of the non-superconducting hexagonal phase.

## 3.3.3 Data & Discussion

In Figure 3.14, the low-temperature phase boundaries are overlaid with the corresponding  $T_cs$  and room temperature resistances as functions of pressure. The sharp initial drop in room temperature resistance and jump in  $T_c$  both correspond with the orthorhombictetragonal phase transition. Likewise, the region where the resistance started to increase and the  $T_c$  began to noticeably decrease, around 7 GPa, aligned well with the emergence of the hexagonal phase. The phase boundaries shown are based on the works of Medvedev et al. and Miyoshi et al[144, 145].



**Figure 3.14:** Phase diagram of FeSe. The left y-axis is a temperature scale and is used to measure the  $T_c$  under pressure and defines the phase boundaries denoted by dashed lines. The right y-axis shows the resistance at room temperature for a given  $P_A$  normalized to the resistance at room temperature and ambient pressure. The white line running through the  $T_cs$  above 8 GPa is offset from the x-axis for better visibility, but represents the insulating phase.

Unlike bismuth, the ambient phase of FeSe is superconducting, with an initial critical temperature of ~ 9 K as shown in Figure 3.14 and more explicitly in Figure 3.15. Initially, the T<sub>c</sub> increased slowly up to ~ 15 K below 1.9 GPa. At 1.9 GPa the T<sub>c</sub> saw a dramatic increase to ~ 32 K, indicating the structure transition from orthorhombic to tetragonal. With increasing pressure up to roughly 4 GPa, the critical temperature was further increased to ~ 40 K. Pressure added beyond this point led to decreases in the critical temperature, resulting in a superconducting dome. This decrease continued until ~ 8 GPa, where all



**Figure 3.15:** Example of pressure quenching FeSe 4.2 K. The curves shown represent a typical pressure quenching cycle. Pressure is applied (blue) and is then quenched to ambient (red) at  $T_Q = 4.2$  K. When the sample is annealed to room temperature a superconducting phase is recovered with a  $T_c$  onset around 20 K. For comparison the pristine FeSe sample at ambient pressure is plotted as well and has a  $T_c$  of ~ 9 K.[142]

signs of superconductivity disappeared due to the development of the insulating hexagonal phase.

#### 3.3.3.1 Pressure Quenching

The same procedures previously discussed were used for pressure quenching FeSe. One major difference is in the definition of the critical temperature. For this work the  $T_c$  onset was used rather than the more involved method presented in Appendix Figure C.1.

As an example, the highest retained  $T_c$  through pressure quenching at 4.2 K is shown in Figure 3.15. For comparison, the highest  $T_c$  retained by quenching at 77 K is provided in Appendix Figure C.6.



**Figure 3.16:** Summary of pressure quenching FeSe. Blue data points represent the  $T_c$  under pressure and produce the expected phase diagram. Red and green data points show the  $T_c$  onset for phases retained by pressure quenching at 77 K and 4.2 K respectively. Dashed lines are a guide meant to represent the superconducting dome.

As in the previous study, samples were pressure quenched first from  $T_Q = 77$  K and then  $T_Q = 4.2$  K from various pressures. As might be expected, pressure quenches from 4.2 K resulted in metastable phases with higher critical temperatures. The max  $T_c$  retained at  $T_Q = 77$  K was  $\sim 25$  K (Figure C.6) pressure quenched from 4.15 GPa, whereas the maximum  $T_c$  retained at  $T_Q = 4.2 \text{ K}$  was ~ 37 K (Figure 3.15) pressure quenched from 5.22 GPa. An interesting feature of the metastable phases retained at both quenching temperatures was their similarity to the superconducting dome observed under pressure. At the end of the dome, where pressure is above 8 GPa, pressure quenching from either 77 K or 4.2 K in this phase region resulted in retained insulating phases.

One key discovery from these pressure quenches was the critical temperature of the metastable phase after annealing to room temperature. Based on the results of the bismuth work it, was expected that the phase would return to its ambient state. In this scenario it would produce good overlap with the curve for the pristine sample at  $\sim 9$  K. However, this was never the case, made apparent by the room temperature annealed curve with a T<sub>c</sub> of  $\sim 19.6$  K in Figure 3.15. In fact, the T<sub>c</sub> after annealing was 15 K–22 K throughout the quenching experiments. This indicated that moderate enhancement of the superconducting phase could be retained even at ambient pressure and temperature via pressure quenching.

#### 3.3.3.2 Thermal Cycling

Stability testing of a sample, pressure quenched at 77 K, was carried out via thermal cycling as presented in Figure 3.17. The initial phase retained in the pressure quench could be cycled up to 77 K with no signs of degradation. Staring at 100 K, the critical temperature began to shift to progressively lower temperatures in both  $T_c$  onset and offset. The largest change in  $T_c$  seemed to occur between 100 K and 150 K. After annealing to room temperature, an enhanced superconducting phase with a  $T_c \sim 15.5$  K, was formed, again highlighting the moderate enhancement of  $T_c$  after annealing to room temperature.



**Figure 3.17:** Thermal cycling of pressure quench from 4.13 GPa at  $T_Q = 4.2$  K. Thermal cycles below 77 K reproduced the retained phase perfectly. At progressively higher cycle temperatures the  $T_c$  decreased from 26.0 K to 15.5 K after annealing to room temperature.[142]

Thermal cycling performed on a sample pressure quenched at  $T_Q = 4.2$  K produced similar results. Figure 3.18 highlights the key differences between quenches at 77 K and 4.2 K. Cycling the sample from the initial quench at 4.2 K to 40 K produced a small but noticeable hysteresis in the cooling and warming data. Since the metastable sample must first be warmed to 40 K from 4.2 K, it makes sense that a small difference in  $T_c$  would result from a gradual phase decomposition. This would explain why there is perfect overlap in the cycles below 77 K in Figure 3.17, but changes in  $T_c$  are observed up to 80 K in Figure 3.18.



**Figure 3.18:** Thermal cycling of pressure quench from 5.22 GPa at  $T_Q = 77$  K. Thermal cycles below 77 K reproduced the retained phase perfectly. At progressively higher cycle temperatures the  $T_c$  decreased from 36.7 K to 20.2 K after annealing to room temperature.[142]

Unlike the pressure quench at 77 K, only the  $T_c$  onset shifted when cycled to progressively higher temperatures, until the abrupt jump after warming to 200 K. What is evident is that the lower temperature quench resulted in a higher decomposition temperature and better overall stability, despite the lower applied pressure. Since both the retained  $T_c$  and  $T_c$  after complete annealing are noticeably lower in the 77 K quench, it seems that the initial metastable phase plays a big role in the subsequent thermal stability of the phase.



Figure 3.19: Results of pressure quenching from 15.14 GPa at 77 K to 0.50 GPa. With successive warming and cooling cycles, the initial insulating phase developed into a superconducting phase with an onset  $T_c$  near the dome peak. The warming curves are not presented but overlap perfectly with the cooling curves up to ~ 120 K where a slight hysteresis developed as shown in Appendix Figure C.7.

A particularly important result was produced by pressure quenching at 15.14 GPa as shown in Figure 3.19. Initially, the phase was insulating while under pressure. After pressure quenching at 77 K the insulating hexagonal phase remained. The interesting outcome came during the second day of the experiment, after the sample was cooled again from room temperature. A broad and weak superconducting transition appeared with a  $T_c$  of ~ 28.5 K. When the sample was warmed again to room temperature, it showed perfect overlap up to ~ 120 K as shown in Appendix Figure 3.19. When it was cooled once more to low temperature on day 3, the resulting superconducting drop was complete and the  $T_c$  had increased to ~ 34.5 K. Over six days, the sample was cycled between room temperature and 4.2 K, resulting in further improvement to the superconducting phase. Both the  $T_c$  onset and offset increased, narrowing the transition width noticeably. On the final day of cycling, the  $T_c$  onset shifted to ~ 32.6 K while the offset remained the same.

From these results, it can be surmised that pressure quenching from 15.14 GPa produces a phase that retraces the  $T_c$ -P dome as it slowly relaxes back to its ambient phase. This is made clear by the initial increase and subsequent decrease in critical temperature. Furthermore, from the temperature cycle to 77 K on the sixth day of annealing, it is clear that the phase can be stabilized by keeping it at  $LN_2$  temperature. The hysteresis around 120 K also gives an indication of the upper temperature limit for long term phase stability. This provides an extremely useful method of enhancing the superconducting properties of FeSe. By pressure quenching the non-superconducting phase and slowly annealing, it is possible to produce a metastable phase with the maximal  $T_c$ , which can be retained if kept below 77 K.

# 3.4 Metastable $Cu_xFe_{1.01-x}Se$

Like the section on FeSe, the following section and the subsequent discussion of results are, in part, the published work titled "*Pressure-induced high-pressure superconductivity retained without pressure in FeSe single crystals*" [142]. Further insights and unpublished data are also presented in this dissertation section.

## 3.4.1 Motivation

One major concern in the pressure quenching study of FeSe was the potential for residual pressure to be the cause of the observed metastable phase. This concern was exacerbated by the inability to measure pressure in-situ following the pressure quench. This was especially true when considering the difference in the  $T_c$  of the pristine sample and that of the pressure quenched samples after annealing to room temperature. To validate these results, we investigated FeSe doped with small amounts of copper to create  $Cu_xFe_{1.01-x}Se$ , where x = 0.03 and 0.035.

Unlike its parent compound,  $Cu_xFe_{1.01-x}Se$  is not superconducting at ambient pressure. By applying pressure, superconductivity can be induced. The study of  $Cu_xFe_{1.01-x}Se$  sought to leverage this property and prove that the enhancements to its critical temperature were due to pressure quenching, rather than residual pressure. Normally, if the cell pressure was released the sample would return to the non-superconducting state. However, if the pressure quenching technique produced a metastable superconducting state that vanished upon room temperature annealing, it would support the technique's effectiveness. This property of  $Cu_xFe_{1.01-x}Se$  would also provide another check, in addition to the residual pressure of the sample post-quench.

## 3.4.2 Introduction

 $Cu_xFe_{1.01-x}Se$  is similar to its parent compound FeSe, both in structure and  $T_c$ -P relationship. As the copper dopant is increased to 1.4%, superconductivity in  $Cu_xFe_{1.01-x}Se$  is suppressed below 2 K[149]. For samples with 3 % to 4 % copper, superconductivity can be restored with the addition of pressure above ~ 1 GPa[150]. When the dopant reaches 2.45%, the orthorhombic phase observed at low temperature and pressure is completely

suppressed, being replaced by the tetragonal phase. As in FeSe, the tetragonal to hexagonal phase transition is present in  $Cu_xFe_{1.01-x}Se$ , which begins around 8 GPa[151]. The two phases coexist like in the parent compound, again indicating the presence of multiple sample compositions and a pressure gradient. This coexistence persists from ~ 8 GPa to 14 GPa before completely transforming into the hexagonal phase[150, 151].

Strangely, the reemergence of superconductivity in  $Cu_xFe_{1.01-x}Se$ , with x = 0.03, 0.035, does not correspond to a return of the orthorhombic phase. This is illustrated in the phase diagram of Figure 3.20. Instead, there is evidence that copper doping leads to magnetic ordering in  $Cu_xFe_{1.01-x}Se$  at low temperature[151]. The application of pressure between 1 GPa and 2 GPa is enough to disrupt this competing magnetic order and restore superconductivity.

## 3.4.3 Data & Discussion

As with FeSe, the phase diagram for  $Cu_xFe_{1.01-x}Se$  was determined using the resistivity and  $T_c$  as a function of pressure. The data collected for compositions x = 0.03, 0.035 under pressure are presented in Figure 3.20. Though there is no structure transition from orthorhombic to tetragonal as in FeSe, the sudden drop in resistivity and appearance of superconductivity coincided around 2 GPa. A similar increase in the resistivity and development of non-zero resistance superconducting drops signaled that the tetragonal to hexagonal transitions occurs around 8 GPa.

A superconducting dome can be observed for both compositions with a maximum  $T_c$  around 24 K to 27 K. The domes peak between 6 GPa and 7 GPa before beginning to



**Figure 3.20:** Phase diagram of  $Cu_x Fe_{1.01-x}Se$ . The y-axes are the same as shown in Figure 3.14, but the orthorhombic phase is not present. The  $T_c$  data from samples with x = 0.03, 0.035 are presented alongside resistivity data for x = 0.03 samples.

decrease. Soon after the peak, the superconducting phases no longer exhibited a zeroresistance drop down to 1.2 K as the hexagonal phase developed. By 9.35 GPa the superconducting drop was almost completely suppressed. When considering the sample composition, it seems that the increased copper content pushes the superconducting dome toward higher pressure while decreasing the maximum  $T_c$ . This is in general agreement with the observations of previous work[150].

#### 3.4.3.1 Pressure Quenching

Pressure quenching experiments for  $Cu_xFe_{1.01-x}Se$  were quite similar to those for bismuth, owing to their non-superconducting phase at ambient pressure. Figure 3.21 highlights the obvious success of pressure quenching. The initial superconducting phase under pressure (blue/cyan) has a gradual zero-resistance drop, which is shifted to slightly lower temperature after pressure quenching (red/magenta). The room temperature annealed curve (green) shows the return to the non-superconducting ambient phase.



**Figure 3.21:** Comparison of pressure quenching  $Cu_{0.03}Fe_{0.98}Se$  at 77 K and 4.2 K. Both samples were quenched from roughly the same  $P_A$  but resulted in slightly different retained  $T_cs$ . The 4.2 K quench resulted in a higher  $T_c$  onset than the quench at 77 K. Overall, the impact of  $T_Q$  on the retained phase was much less in  $Cu_{0.03}Fe_{0.98}Se$  than in FeSe. Only the annealing data for the 4.2 K quench are shown, but is representative of all pressure quenches on the copper doped FeSe.[142]

When comparing the results of pressure quenches, there is a small increase to the  $T_c$  at  $T_Q = 4.2$  K over 77 K. However, the majority of the phase has good overlap showing that the quenching temperature plays a less crucial role in retaining the metastable phase. This contrasts with the results of FeSe, which seemed to produce better quality phases from LHe pressure quenches. Again, the retained phases seemed to trace out the superconducting dome, with the peak lining up well with the dome peak under pressure.



**Figure 3.22:** Summary of the pressure quenching work on  $Cu_xFe_{1.01-x}Se$ . Blue data points represent the  $T_c$  under pressure for the 3% copper samples while cyan data shows the 3.5% copper samples. Red and green data points show the  $T_c$  onset for phases retained by pressure quenching the 3% copper samples at 77 K and 4.2 K respectively. The lime data shows the retained  $T_c$  for pressure quenches at 77 K in the 3.5% copper samples. Some data points correspond to non-superconducting phases and are offset to 5 K for better visibility. The one half-filled blue circle represents a superconducting phase with a non-zero resistance drop.



**Figure 3.23:** Thermal cycling of  $Cu_{0.03}Fe_{0.98}Se$  pressure quenched from 5.95 GPa at 77 K. All data are taken during the cooling cycle. The red curve corresponding to 77 K is the initial cooling curve after pressure quenching while the yellow-green curve is the second cooling curve after cycling up to 77 K. Each curve is normalized to its value at 25 K./142]

The results of thermal cycling  $Cu_{0.03}Fe_{0.98}Se$  after pressure quenching at  $T_Q = 77$  K are presented in Figure 3.23. There was perfect overlap between the thermal cycles below 60 K, but a small hysteresis upon warming to 77 K indicated a potential lower temperature limit for perfect phase stability between 60 K and 77 K. Below this temperature, the  $\rho(T)$ curve can be perfectly retraced. After the sample was cycled to ~ 200 K the metastable superconducting phase was effectively suppressed. Likewise, thermal cycling presented in Figure 3.24 showed the complete destruction of superconductivity upon warming to  $\sim$  200 K, suggesting an upper limit for successful pressure quenching. Temperature cycles below 77 K experienced a shift in T<sub>c</sub> with successively higher temperatures, but retained strong superconducting drops. Notably, the warming and cooling curves at 25 K show a hysteresis like that seen in Figure 3.18, but with more prominence indicating superior stability in the parent compound FeSe.



Thermal Cycle: 6.08 GPa PQ @ 4.2 K

**Figure 3.24:** Thermal cycling of  $Cu_{0.03}Fe_{0.98}Se$  pressure quenched from 6.08 GPa at 4.2 K. All data are taken during the cooling cycle. The red and light blue curves corresponding to 25 K highlight the change in phase due to initial warming from 4.2 K. Each curve is normalized to its value at 25 K.[142]



**Figure 3.25:** Shows the effect pressure quenching at different  $T_Qs$  has on the room temperature annealing curve of  $Cu_{0.03}Fe_{0.98}$ . Note all three curves share a common peak around 175 K, indicating a large change in the phase composition. The inflection point around 235 K likely indicates the end of phase decomposition. Labeled arrows indicate the local minimum in resistance revealing a potential lower temperature limit for perfect phase stability.[142]

Much of these findings are also manifested in Figure 3.25, which shows the room temperature annealing curves after pressure quenching from 4.2 K, 77 K, and 120 K near the  $T_c$  dome. Notably, quenches at 77 K and 120 K saw a minimum at 65 K and 69 K, respectively, indicating the continuation of phase degradation around 67 K and providing further evidence of a lower temperature limit for phase stability. On the other hand, the pressure quench at 4.2 K saw no such minimum in resistance, but increased linearly after transitioning back to the normal state. This is to be expected, as there is no prior annealing
history. All three pressure quenches showed a common peak around 175 K and a final inflection point around 235 K. An appropriate interpretation of the observed peak is the temperature at which most of the phase has reverted to the ambient phase. Likewise, the upper temperature bound indicates the completion of this process.



**Figure 3.26:** Stability testing of metastable  $Cu_{0.03}Fe_{0.98}Se$  phase after pressure quenching from 6.67 GPa at 77 K. The sample was kept below 77 K for the duration of the experiment. The resistivity ratio is calculated using the value of resistivity at 50 K after pressure quenching. The size of the data points is varied to better illustrate the perfect overlap between successive curves.[142]

As shown in Figure 3.21, there was little difference between the retained superconducting phases at 4.2 K and 77 K near the peak of the dome, with regard to critical temperature. Because of this, a sample of  $Cu_{0.03}Fe_{0.98}Se$  was pressure quenched from 6.67 GPa at 77 K

to test the stability of the resultant phase as a function of time. The sample was measured from 4.2 K to 50 K over the course of seven days. The results presented in Figure 3.26 demonstrate a perfect overlap between the initial cooling curve, after quenching at 77 K, and the subsequent thermal cycles. The data for each curve is normalized to the resistivity value of the pressure quenched phase at 50 K. This shows that not only was the  $T_c$  stable, but the sample resistivity was as well, confirming the overall stability of the phase. From this, it can be concluded that the metastable phase in  $Cu_{0.03}Fe_{0.98}Se$  can likely be retained indefinitely, so long as it is not warmed beyond 50 K.

## Chapter 4

## **Conclusion and Paths Forward**

## 4.1 Conclusion

In this final dissertation chapter, the work conducted is summarized and evaluated. Following this is a discussion of the shortcomings of the investigation into bismuth, FeSe, &  $Cu_xFe_{1.01-x}Se$ . The final section outlines some related projects and provides a starting point for future investigations.

### 4.1.1 Bismuth

Pressure quenching bismuth was successful in retaining metastable superconductivity at ambient pressure. This heavily favored the formation of what seems to be a metastable Bi-III phase. This phase was overwhelmingly retained when pressure quenching at 77 K and dominated the retained phases for pressure quenches below 6.5 GPa at 4.2 K, indicating the robust nature of the metastable Bi-III phase. For quenches above 6.5 GPa and at  $T_Q$ = 4.2 K, the retained phases showed an increase in  $T_c$  from ~ 5K up to ~ 9 K. This revealed a very unexpected response and a record  $T_c$  for bismuth. Due to the limited characterization that could be performed in these pressure quenching experiments, Bi-III and Bi-V could not be distinguished in this region, except for two phases with  $T_{cs} > 8 \text{ K}$ , which likely correspond to Bi-V. Furthermore, unexpectedly low  $T_{cs}$  near the Bi-III/V boundary were not readily explained but may be the extension of the  $dT_c/dP$  relationship for Bi-III.

Investigation into the stability of the metastable phases via thermal cycling revealed some key insights. First, metastable Bi-III begins to degrade around 20 K in pressure quenches at 4.2 K which show near perfect retraceability of the warming curve up to 60 K–70 K. For quenches at 77 K or in phases that were cycled above ~ 60 K the phase stability was effectively ensured due to this lower temperature limit. Cycling above 60 K to 70 K caused further decomposition of metastable bismuth where a hysteresis was always present. This decomposition typically became very pronounced around 100 K and caused a rapid increase in the overall sample resistivity. Annealing the sample between 120 K to 150 K would cause the complete disintegration of all metastable phases.

Overall, it was difficult to determine when different phases began their decomposition, but a few points can be established. First, if it is to be assumed that the high  $T_cs$  above 8 K are due to Bi-V, it is clear that this phase must decompose before 77 K, potentially around 49 K. Next, the 77 K thermal cycles show that Bi-III begins degrading above ~ 71 K and will be completely destroyed by ~ 120 K to 150 K. Finally, when weak and broad superconducting phase develops due to quenching or thermal cycling, a hysteresis around 60 K typically appears which might indicate the development of the amorphous like bismuth phase. The results of temporal stability testing provide further support for the lower temperature retraceability limit seen in thermal cycling. In almost every case, the metastable phase retained at 4.2 K would remain stable when kept at 4.2 K. Both the  $T_c$  and resistivity of the metastable phase would remain unchanged after the initial warming and cooling cycle to measure the  $T_c$ . Only if the phase was warmed further, as shown in Figure 3.10 would a change be observed.

Significant progress toward establishing a pressure quenching system capable of completing a field effect study was made, unfortunately time did not permit its completion. In lieu of this, an attempt to measure the critical field of the retained phases was made using a PPMS but was ultimately unsuccessful in retaining the initial metastable phase.

The initial goals to establish a system for pressure quenching and prove the viability of pressure quenching to enhance superconductivity at ambient pressure were met. Attempts to target and retain a specific phase of bismuth also saw some success but suffered from limited characterization. In particular, Bi-III and Bi-V could be targeted and retained with different pressure quenching sequences. In the process other novel phases may have been retained but require further characterization to confirm. Finally, thermal cycling provided an upper temperature limit between 120 K and 150 K for phase stability.

### 4.1.2 FeSe & $Cu_xFe_{1.01-x}Se$

Taken as a whole, the pressure quenching works on FeSe and  $Cu_xFe_{1.01-x}Se$  were quite successful. Not only was it possible to retain enhanced metastable superconducting phases at low temperature, but it was also found that pressure quenching FeSe produced enhanced phases at room temperature. In particular, pressure quenching from 15.14 GPa followed by phase annealing can be used to slowly transform the insulating phase into a metastable superconducting phase at the dome peak. After this annealing, the metastable phase can be stabilized by keeping it below 77 K.

The results of thermal cycling obtained from FeSe and  $\text{Cu}_{x}\text{Fe}_{1.01-x}$ Se seem to support a lower temperature retraceability limit in the metastable phase below ~ 120 K and 67 K respectively. For FeSe, this is apparent in the small hysteresis in warming and cooling curves of Appendix Figure C.7. On the other hand,  $\text{Cu}_{x}\text{Fe}_{1.01-x}$ Se shows a hysteresis in the thermal cycling of Figure 3.17 and minima around 67 K for the pressure quenches at 77 K and 120 K of Figure 3.25. As with bismuth, the  $\rho(T)$  curve can be perfectly retraced below this temperature allowing metastable phases to persist for extended periods of time, as was highlighted in Figure 3.26.

When looking at the results of room temperature annealing across the pressure quenches, more information about thermal stability was gathered. As shown in Figure 3.25 a large increase in the resistivity, that peaked around 175 K, was commonly found in the case of  $Cu_xFe_{1.01-x}Se$ . Similarly, Appendix Figure C.7 shows there was a noticeable hysteresis in warming and cooling curves of FeSe, starting around 120 K. The way in which these inflection points presented themselves can be accounted for by the overall phase composition. Where FeSe was transitioning to another a metallic phase,  $Cu_xFe_{1.01-x}Se$  was becoming an insulator. Since the resistance in a metallic material is only ever expected to increase with temperature it makes sense that no peak was observed.

In addition to the observed low-temperature retraceability limit, it seems that at temperatures above 120 K-200 K the phase should continue to disintegrate slowly over time. The rate of this decomposition seemed to depend on the initial pressure before quenching and the annealing temperature. In the case of  $\text{Cu}_{x}\text{Fe}_{1.01-x}\text{Se}$ , the return to the ambient phase was much more rapid and complete. This is obvious as only weak signs of superconductivity around 4 K could be observed after annealing to room temperature, likely due to residual deformations disrupting the nematic phase. FeSe, on the other hand, had a much slower return to its ambient phase, with  $T_cs$  as high as ~ 25 K after room temperature annealing, excluding the pressure quench from 15.14 GPa.

Pressure quenching, particularly in FeSe, has exhibited the potential of this technique in enhancing the superconducting properties of a material at ambient pressure. In this regard, the prolonged room temperature stability of the enhanced phase observed in FeSe is particularly promising. With further investigation, it may be possible to prevent disintegration of the enhanced phase in FeSe at room temperature or utilize a pressure treatment to enhance the phase for long-term, low-temperature operation.

### 4.2 Paths Forward

### 4.2.1 Experimental Improvements

One of the biggest weaknesses of the work conducted was its reliance on critical temperature and initial pressure to characterize the resultant metastable phase. This was particularly troublesome for the work with bismuth due to the similarity in  $T_c$  between Bi-III, Bi-V, and the amorphous phase. Although the picture was much more straight forward in the case of the metastable phases in FeSe and  $Cu_xFe_{1.01-x}Se$ , more methods of phase characterization would provide further insight into the phase stability and composition.

#### 4.2.1.1 Structure Analysis

Ideally, the metastable phases would be pressure quenched and characterized using synchrotron radiation. This would provide critical structure data to confirm the retained phase and the overall composition. Unfortunately, limitations in the high-pressure capabilities at these synchrotron sources make this proposed study quite challenging.

Some issues include facility closures, cryogen scarcity, residual pressure, and limitations with gas membrane cells and beamline. That said, further investigations into pressure quenching via structure analysis should be possible once the Advanced Photon Source comes back online in mid-2024. With a double membrane cell it would be possible to completely remove pressure on the sample above  $\sim 10$  K. However, through personal communication with Dr. Changyong Park it was found that the beamline itself has a lower temperature limit of 11 K–15 K. This would, of course, preclude pressure quenching at 4.2 K but should still enable the collection of vital structural information.

For bismuth this would provide much needed structure analysis to help distinguish the retained phases near and above 6.5 GPa. It would also be able to discern the structure of the record 9 K phase and detect the presence of other novel phases, such as the hcp phase that was recently proposed[141]. In the case of FeSe and  $Cu_xFe_{1.01-x}Se$ , structure analysis would mainly help distinguish the phase composition and confirm the tetragonal structure of the metastable phase. This analysis would also provide information about the height of the selenium anion defined as the distance between the selenium anion and the nearest iron layer, which has been shown to correlate strongly with the  $T_c[147]$ . In this way, phase annealing in FeSe could be coupled with structure analysis to monitor the anion height. This information could then be used to determine the optimal point to halt annealing and stabilize the phase corresponding to the maximal  $T_c$ , namely, when the Se is at a height

of  $\sim 1.38$  Å.

#### 4.2.1.2 Critical Field Distinction

Another, more indirect method of distinguishing the retained phases is through their critical field. The basic outline for this kind of experiment is to manually pressure quench the DAC inside a dewar system that can apply a magnetic field at low temperature. By doing this, the metastable phase should be retained without incident and the critical field can be measured.

A system that would support such an experiment was not available at the time of this work. Instead, an attempt to pressure quench a sample and transfer it into a PPMS system was made, as discussed in the results of the bismuth work. Unfortunately, the limited attempts did not prove successful in the initial phase retention. As mentioned, this failure was likely due to rapid warming during the cooldown procedure eliminating the metastable phase. However, a suitable system could enable successful pressure quenching and provide additional information about the retained phases via critical field measurements.

In an effort to facilitate this experiment, a probe was designed for a custom Janis SVT 400-T cryogenic dewar with HTS-110 LM-80-3T magnet. This system would create an environment that could support temperatures from 1.5 K-300 K and a magnetic field up to ~ 3.1 T, while accommodating a pressure quenching probe. Due to time constraints, the system could not be made operational to attempt this experiment. For the sake of posterity, the probe designs and description are included in Appendix D.

### 4.2.1.3 In-situ Pressure Measurements

Though steps were taken to prove pressure had been fully released in the pressure quenching process, in-situ pressure measurements provide the highest level of certainty. Not only could the residual pressure be determined, but experiments in which pressure is partially released or increased could be executed. This tool would expand the potential of the pressure quenching technique by incorporating pressure cycling to attain metastable phases.

Unfortunately, access to this type of pressure monitoring system was not available during the work of this dissertation. However, with the recent purchase of the Almax easyLab gas membrane cell and Optiprexx RubyLux fluorescence systems, future experiments of this type can be conducted. This system can fit inside the Quantum Design PPMS, and when combined with the portable ruby fluorescence system, it provides in-situ pressure measurements.

Since this system was designed to operate with a PPMS, it could be used for the previously mentioned critical field measurements. However, two issues challenge the effectiveness of this solution. First, the gas membrane cell reportedly has a substantial pressure hysteresis, especially at low temperatures, making pressure quenching to ambient unlikely. Second, due to the design of the gas membrane cell, the helium that is used to compress the bellows and provide pressure in the DAC will solidify at low temperature. This would prevent adjustments to the pressure making it impossible to conduct pressure quenches below  $\sim 10$  K. For these reasons, the custom probe solution designed for the Janis system is recommended for future critical field studies.

### 4.2.1.4 Magnetization Measurements

It is safe to assume that the metastable phases retained truly are superconducting based on the resistivity measurements alone. However, to eliminate all doubt about the superconducting nature of the retained phases, magnetization measurements would be required. Furthermore, magnetization measurements would provide vital information about the phase composition. This could confirm whether the metastable phase is filamentary or exists in the bulk. It could also be used to detect the presence of multiple superconducting phases, particularly the low  $T_c$  phases like Bi-II, that might otherwise be overshadowed in transport measurements.

This type of study was not conducted in this dissertation due to its current impracticality. Simply put, in-situ pressure quenching is not currently possible and would require a highly specialized platform to perform. The only viable solution for such a study would require the pressure quenched sample to be stable at ambient conditions so that it could be extracted and prepared for magnetization measurements in the Quantum Design Magnetic Property Measuring System (MPMS). Furthermore, the process of extracting a sample after pressure quenching is difficult. The samples used are typically no bigger than 100 µm and can easily break leaving behind miniscule amounts of the sample for measurements.

### 4.2.2 Other Related Projects

Beyond the works presented, there are many tangential investigations that are worth exploring. A few potential projects are briefly outlined below.

#### 4.2.2.1 Critical Field Characterization of Bismuth Metastable Phases

Some details of this proposed investigation were already mentioned but are reiterated here. Due to the large difference in critical field between Bi-III and the other superconducting phases it should be possible to distinguish these metastable phases. With a combination of  $T_c$ , applied pressure, and critical field Bi-III and Bi-V can be discriminated in the high-pressure region.

### 4.2.2.2 Investigation of hcp in Bismuth

If the report of Chaimayo et al. is to be believed, it should be possible to experimentally simulate their theoretical calculations[141]. Since the structural phase transitions were calculated ignoring the effects of entropy, i.e., T = 0 K, an experiment in which pressure is increased at 4.2 K could provide a good check on this work. With the current pressure quenching probe, it should be possible to execute this experiment with some additional modification. Initial trials between 1.2 K–10 K could be attempted to observe the described phase transitions from Bi-I to Bi-III around 4 GPa, Bi-III to Bi-hcp around 14 GPa, and then continue to high pressure to investigate whether the phase changes back to Bi-V or another novel phase. Each of these phases should be distinguishable since the T<sub>c</sub> of Bi-hcp is expected to be ~ 4.5 K.

### 4.2.2.3 Investigation of Superconductivity in Bi-IV

Another paper by Chaimayo et al. suggests superconductivity should be present in the high-temperature high-pressure phase Bi-IV[133]. Since it has been shown that bismuth supports metastable phases at low temperature, both from the works presented on pressure quenching and earlier works discussing the metastable nature of Bi-II, it seems likely Bi-IV could also be retained at low temperature. This would enable the study of its potential superconducting properties. Such an investigation would make use of temperature quenching rather than pressure quenching but would try to exploit the same underlying low-temperature mechanism.

### 4.2.2.4 Low-Temperature Investigation of FeSe T<sub>c</sub>-P Relationship

It is well known that FeSe exhibits a superconducting dome under pressure. Coincidentally, the peak of the dome typically occurs at a pressure in close proximity to the phase boundary with the non-superconducting hexagonal phase. Shortly after the dome peak, the quality of the superconducting phase degrades as more hexagonal phase develops, until there is no longer a zero-resistance drop. A worthwhile experiment would be to investigate the effects of increasing pressure on FeSe at low temperature, rather than at room temperature, as is the norm. In this way, it may be possible to delay the development of the hexagonal phase. Such a study would allow the dome shaped superconductivity to be probed at higher pressures before its disappearance. This experiment would be a great proof of concept for suppressing competing phases and may also reveal new insights about the superconductivity in FeSe.

# Appendix A

## Pressure Cell

## A.1 Diamond Alignment

Aligning the diamond with the center of the tungsten seats is an important step which will help ensure the DAC can reach the highest pressures and make the alignment of the diamonds easier.

The process begins with installing the tungsten carbide seat into the diamond jig described in Figure 2.6. The base of the seat should rest at the bottom half of the jig, centered over the small hole at its base. Once in position, the four adjustment screws are tightened to hold the seat in place. Next, the diamond is placed so that the table is in contact with the seat, and the culet is pointed up. Note that both the seat and diamond can be inserted into the jig through one of the four holes in the jig sidewall.

With the diamond in place, the top half of the jig is slowly lowered into the bottom half. The position of the diamond can be monitored with the microscope as the top half of the jig is lowered. So long as the diamond is near the center of the opening in the top half, it should move into position as the jig is closed. If the diamond is too far to the side of the opening, it may get stuck. In this case, the jig is gently opened, and the diamond repositioned with a toothpick or tweezers. Once the jig is closed, the screws are hand tightened to minimize the pressure between the diamond and tungsten seat. This will help reduce the friction between the two as the tungsten seat is centered with the diamond culet.

To begin the alignment, double-sided tape is placed on the microscope stage to help reduce jig movement. The jig is then flipped so that the microscope is looking through the base of the jig and positioned on the tape so that the opening in the tungsten seat fills the field of view. Next, the microscope is focused on the diamond culet and the center is determined using the distance tool provided in the Leica software. By refocusing on the opening in the top of the tungsten seat, without changing magnification, the center point of the culet can be used to determine the relative position of the seat. The screws are adjusted to move the opening in the tungsten seat until it is equidistant from the culet center. Note that the jig can still shift as the screws are adjusted. Therefore, it is important to periodically check that the distance tool is still positioned at the culet center.

Once the seat has been centered, Stycast is used to fix the diamond to the seat. Using a syringe needle or other fine tool, the Stycast is spread along the surface of the seat to the edge. Sycast is pulled under the girdle to improve the binding strength. The Stycast is also pulled up and over girdle so that there is a small edge to help hold the diamond down. The surface tension of the Stycast can be used to do most of the work. Placing small drops of Stycast around the edge will fill out the connection, making the liquid slightly convex. If a spot looks slightly concave, more Stycast should be added.

## A.2 Stycast Preparation

Stycast is made using the Loctite Stycast 2850FT and Loctite CAT 24LV. The mixture requires 8 wt% CAT 24LV to activate. Typically, about 1 g of the Stycast is used for covering the gasket. Curing times are provided in the table below. Before the Stycast is applied, it is mixed thoroughly with the wooden end of a Q-tip or toothpick for approximately 10 minutes. For a more viscous consistency, wait an additional 30 minutes before applying the Stycast. Note that the Stycast will often be oily even after the stated cure time. This can cause issues when trying to use Kapton tape to mount the platinum leads. It can also contaminate the sample space and make the cBN sticky.

Table A	<b>1:</b> Loctite	Stycast 2	2850FT	with Lo	$pctite C_{\perp}$	AT	24LV
	mnoratu	$ro(^{\circ}C)$	Curo	Timo	(hour	e)	

Temperature (°C)	Cure Time (hours)
25	8 - 16
45	4 - 6
65	2

Other catalysts can be used for activating the Stycast. The ratios, curing times, and physical properties are available in the technical data sheet[107].

## A.3 Gasket Preparation Alternative

After following all the steps up to drilling the sample space in the cBN, an alternative method can be used to insulate the gasket surface and attach the copper wires in tandem. First, the four copper wires are cut to be larger than needed. The wires are then passed through the holes as they normally would but are then pulled over the interior wall at the notches cut for the tungsten carbide seat screws. The wires are taped down on either end so that they contact the gasket surface at the edge. Stycast is then used to insulate the surface and fix the wires in place simultaneously. Tweezers are used to bend the wires into the Stycast to form a good bond. After the Stycast has dried, the excess wire is cut away and the ends of the copper wires are stripped of enamel. Note that the Insulstrip will dissolve the hardened Stycast. From this point the gasket preparation method follows the same steps as outlined in the main text of this thesis.

## A.4 Sample Preparation

Bulk samples are polished to a target thickness using the sample polisher and high grit sandpaper. The first step to polishing is measuring the puck thickness with an high-precision screw caliper. The sample is then attached to the polishing puck using crystal bond or other low-temperature wax. The melting point for these waxes is below  $\sim 100$  °C. After the puck has cooled it is attached to the polisher using a central screw shaft.

With the sample attached, coarse sand paper is used to quickly reduce the sample thickness. The screw caliper is used to track the sample thickness by subtracting the puck thickness from the thickness of the puck and sample. When a flat surface is established, the sample is removed and flipped over to flatten the other side. Coarse polishing of this side continues until the sample is 3 to 5 times larger than the target thickness.

It is best practice to leave approximately 50 µm on either side of the sample to polish down to the final thickness. It is also helpful to make the initial thickness target slightly thicker than the desired thickness. By cutting the sample in half at this initial target, some sample is saved in case further polishing ruins the sample.

As an example, if the desired sample thickness were  $25 \,\mu\text{m}$  it would be best to use coarse polishing with low grit sandpaper to roughly  $150 \,\mu\text{m}$ . Next, each side would be polished with 2000 grit sandpaper until the sample was 50 µm thick. At this point the sample is cut in half and part is kept as a back-up piece. Further polishing with 2000 grit sandpaper brings the sample thickness to the targeted 25 µm.

It is very important to pay attention to the sample while polishing with high grit sandpaper. This sandpaper has a tendency to stick to the sample and pull it apart. To avoid this, fresh pieces of sandpaper are used regularly.

Once the sample has been polished to the desired thickness, excess wax is removed with acetone and Kimwipes. Next, the puck is heated on a hotplate to melt the remaining wax. A sharp toothpick can then be used to push the sample across the surface of the puck toward the edge. As the sample moves, it will leave behind a trail of liquid wax. Once this trail stops, the sample can easily be removed from the puck with the tooth pick and transferred to a beaker of acetone. After allowing the sample to soak in acetone for 10 minutes, the acetone is decanted and the sample is transferred to a plastic box for later use.

To cut a sample for the DAC, the polished material is measured using the Leica microscope. A sharp stainless steel razor blade is then used to cut the sample to shape. Supporting the razor blade with a fingertip makes controlling the blade much easier. The edge of a glass slide can also be helpful in supporting the razor blade. This allows the blade to be slowly rotated down onto the sample using the slide edge as a fulcrum.

## A.5 Platinum Leads

Platinum leads are cut from 99.95% pure foil, which is 5 µm thick, sourced from Goodfellow. The platinum foil is held in positioned with a gloved finger as the razor blade is used to cut a thin triangle roughly 4 mm in length. Usually, cuts are alternated so that the edge of the foil where the tip is cut switches. This helps ensure that the foil is evenly cut, and it produces more leads.

After a lead is cut, the tip width is measured. If the tip is too narrow it is cut off at a point where the width of the lead is appropriately sized. If the lead is too wide, it can sometimes be cut to a finer point, but can be quite difficult. Ideally, the whole length of the wire would be narrowed, but often it is only possible to narrow a small portion of the tip.

The same tips given for cutting samples apply to cutting the leads. It is recommended to cut the leads closer to the edge of a glass slide to reduce the edge length that is in contact with the slide during cutting. This often makes it easier to cut the leads as more pressure can be applied to the blade edge. Razor blades also tend to develop nicks and dulled points along their length, making it more difficult to cut through the foil. When the blade is close to the slide's edge, it can be gently rocked to help cut through the foil. Gently pulling the foil away from the razor blade is helpful in knowing when the foil is cut. Sometimes the blade will slip or must be repositioned to complete the cut. It is important that the blade is realigned with the previous indention or cut slightly above so that the lead will not split while in the DAC.

Once the leads are done, small pieces of Kapton tape are cut with the razor blade to affix them to the gasket. Tweezers are used to grab the tape strips and pick up the platinum leads. The leads are then placed around the gasket surface so that they are perpendicular to the copper wires as shown in Figure 2.17. A toothpick is useful in sticking the tape to the gasket and removing it from the tweezers. Sometimes, the tape has difficulty sticking to the Stycast if it has not fully dried. The oily substance can be partially removed by wiping it off with a Kimwipe wrapped around a pair of tweezers. If time is not a factor, giving the gasket more time to fully cure or placing the cell in a furnace at 40 °C for a few hours should resolve this.

### A.6 Positioning Leads

Once the leads are placed and have been soldered to the copper wires, they are positioned inside the sample space to contact the sample. The most effective way to adjust the leads is by pushing them toward the sample using a finely sharpened toothpick. First, leads are adjusted so that the tips are roughly at the edge of the sample. Leads that stretch across the sample are moved back by pushing against the copper wire. Small movements are best, as it is easy to move the wires too far back. Moving the wires forward is much more difficult as they tend to bend. It is sometimes necessary to pick up the tape to move the wire forward. The wires can then be pulled back again using the copper wires if needed.

After the wires are moved to their approximate final location, a second piece of tape is placed close to the sample space to secure the lead position. This tape makes the fine adjustments to the lead position much easier. Before adding the second piece of tape, the wire should be at the correct length or slightly too long so that it can be pulled into position. The same issue mentioned will arise if the wire is not far enough into the sample space. From this point, the position of the wire tip is adjusted by bending the wire at the halfway point between the tip and the second piece of tape to either side.

When the wires are in the correct position, the cell is slowly closed using one of the pressure screws and safety screw to limit movement. The position of the wires is monitored

using the microscope during this process. The cell is closed to the point where the diamond is just above the surface of the sample. This prevents the platinum leads from creating unwanted indention in the sample surface while providing a good picture of the final lead position. One safety screw can be used to mark the approximate height of the diamond to speed up subsequent attempts. If the leads are well positioned (see Figure 2.16b) the cell is fully closed. If the leads must be moved, the cell is opened and the leads are adjusted accordingly. Each time the cell is closed, pictures of the lead positions are taken to reference for lead adjustment. The pictures should be taken with the cell in the same orientation every time for clarity.

The final step is to check the continuity of the platinum leads. Pulling all four wires out at once is not advised, as they will all need to be coiled back into the cell if one of them does not make contact with the sample. Coiling the wires and putting them back in the cell is challenging. If the wires are not pushed in far enough the copper wires will be cut when opening the cell. Since the two wire coils in the large optical ports are easiest to access, they are used first. Typically, if these wires show in contact, the other two will as well. Even so, the two remaining wires should be uncoiled one at a time and checked as a safety precaution.

# Appendix B

# **Optical System**

## **B.1** Optical Components

Number	Component Name	Details			
1	HeNe Laser	$50{\rm mW}~(\sim 16{\rm mW})~632.8{\rm nm}$			
2	Band-pass Filter	Edmund Optics part # 68943: $632.8/2.4$ nm			
3	Polarizer	Edmund Optics			
4	Beam Splitter	50:50 beam splitter			
5	Mirror	Driel 14001			
6	Lens	20 mm focal length			
7	DAC	stainless-steel symmetric cell			
8	3D Platform	custom 3-axis platform			
9	Movable Mirror	Driel 14001			
10	Camera	Sony Hi Resolution CCD-IRIS			
11	Display Monitor	Sony Trinitron			
12	Band-stop Filter	GragGrate			
13	Lens	Horiba iHR550 internal component			
14	Slit	Horiba iHR550 internal component			
15	Collimating Mirror	Horiba iHR550 internal component			
16	Diffraction Grating	1800 Grooves/mm 450-850 nm blaze angle			
17	Focusing Mirror	Horiba iHR550 internal component			
18	CCD	Sincerity BI UV-VIS			

 Table B.1: Optical components list

## **B.2** Spectrometry



**Figure B.1:** The first derivative of the Raman spectra presented in Figure 2.22. The second, smaller dip in the derivative spectra is taken as the frequency edge. Note that the first derivative for the spectra at ambient has no sign of a second dip.

## B.3 LabVIEW

More details of the custom LabVIEW program. The figures in this section give a more complete view of the function of each case in the main data acquisition sequence and the parallel graphing sequence. A brief explanation of each case function is given in the figure captions.



**Figure B.2:** Print Header Case 0 grabs the column titles from the graph x-axis ring to include in the file header.



Figure B.3: Print Header Case 1 creates the header for the file.



Figure B.4: Main loop Case 0 where the temperature is sampled using the temperature step setting.



Figure B.5: Main loop Case 0 where the temperature is sampled using the time step setting.



**Figure B.6:** Main loop Case 1 shows the resistance measurement for the channels selected on the GUI front panel.



**Figure B.7:** Main loop Case 2 shows the second temperature sampling which is used for averaging later in the program.



**Figure B.8:** Main loop Case 3 shows all the calculations. This includes the time and temperature averaging and the temperature rate calculation. At the bottom is the van der Pauw resistivity calculator.



**Figure B.9:** Main loop Case 4 shows the compilation of all the data into an array which is then written to the data file.



**Figure B.10:** Main loop Case 5 shows the final waiting counter used to go to the next loop. Recall that this case series initially used the time step to determine the data collection rate. See Appendix Figure B.5



**Figure B.11:** Main loop Case 5 is blank when the data collection rate is set using the temperature step. See Appendix Figure B.4



Figure B.12: Shows waiting time when the pause button is activated on the GUI front panel.



Figure B.13: Main loop for the Graph Printing function which shows the auto update case activated.



**Figure B.14:** Main loop for the Graph Printing function which shows the manual update timer case activated.



**Figure B.15:** Main loop for the Graph Printing function which shows the case where at least one of the graphs is active and is not set to manually update. This keeps resetting the manual time counter to 0 in the event that it is activated. It will also be reset once the timer value has been met in manual mode.



**Figure B.16:** Main loop for the Graph Printing function which shows both graph displays turned off. Note that individual display control is available for each graph.



**Figure B.17:** Main loop for the Graph Printing function which shows the case in which the function deactivates. Note this will occur during the first loop iteration of the DAQ loop (i.e. no data to display), when manual mode is active and when the timer limit hasn't been reached, or if both graph displays are turned off.

# Appendix C

# **Pressure Quenching Data**



Figure C.1: The definition of  $T_c$  used for the work on bismuth.



Figure C.2: Example of a minor retained superconducting phase that does not have a zero-resistance drop.



Figure C.3: The extended thermal cycles for the pressure quench from 11.70 GPa. The vertical dashed line at 7K shows how the  $T_c$  onset remains constant while the line at 62K highlights the beginning of the hysteresis between warming and cooling cycles. As seen in Figure 3.8, there is a large initial increase in resistance around 71K. Note the retraceability of subsequent thermal cycles where dR/dT only changes noticeably near the previous maximum cycle temperature. Some data is excluded for the sake of clarity.



**Figure C.4:** The extended thermal cycles for the pressure quench from 9.00 GPa. The figure shares the same features seen in Appendix Figure C.3. Again, some data is excluded for the sake of clarity.


**Figure C.5:** Thermal cycle showing the rapid increase in resistivity beginning around 20 K. The sample is cooled after reaching  $\sim 30$  K to reveal a degraded superconducting phase. The second warming curve (orange) overlaps perfectly with the cooling curve (blue) up to  $\sim 28$  K before the rapid increase resumes.



Figure C.6: The highest retained  $T_c$  by pressure quenching near the dome peak at 77 K.[142]



**Figure C.7:** Select annealing curves which show a slight hysteresis between cooling and warming around 120 K. Hysteresis likely indicates the temperature at which phase decomposition resumes. Only three annealing cycles are presented for figure clarity.

## Appendix D

## Janis Probe Design

This appendix is dedicated to a pressure quenching probe designed to work with a custom Janis SVT 400-T dewar and HTS-110 LM-80-3T superconducting magnet. Descriptions of each component are available in the figure caption. Exact measurements are provided for each component. Many components have dual units, where metric (mm) measurements are given at the bottom and the imperial (inch) measurements are provided above in square brackets. Nearly all components that show dual units were created to be imperial, with the remaining being odd measurements required to complete the probe design. Those measurements that lack dual units are meant to be metric. Components with defined threading will mention it in the figure caption. All other threading, such as screws for securing components can be adjusted for easier fabrication.

The proposed pressure quenching probe was designed with a few key features. First and foremost are the pressure quenching rods, which can be used to adjust the PPMS pressure screws at low temperature while simultaneously holding a vacuum in the sample space. These pressure rods can be removed after pressure quenching and the pressure cap replaced with a solid cap to reduce the heat load during phase stability tests. The next feature is the wiring and hermetically sealed feed-through. A hermetically sealed MIL-STD connector was chosen to create a vacuum sealed electrical feed-through. By soldering this connector to a KF25 flange it would allow easy access to the probe wires in the event that a wire is broken or damaged. Without this key feature, repairing damaged wires would be very difficult and involve completely removing the electrical feed-through or potentially replacing the hermetic connector entirely.

The final feature of this probe is the consideration taken to provide compatibility with a portable, fiber-optic-coupled diamond Raman or ruby fluorescence system, to conduct in-situ pressure measurements. The probe baffles were modified to allow a fiber optic cable to run down through the center of the probe, connecting with a custom-built focusing lens assembly, as shown in Figure D.10. The optic fiber would exit the Janis system through a KF16 fiber optic feed-through connected the tee reducer that can be seen in the leftmost image of Figure D.1.

These features provide an optimal platform for studying the transport properties of pressure quenched samples. The ability to apply a magnetic field and monitor the pressure in-situ provide much of the functionality suggested for future works on bismuth. Furthermore, the ability to manually release pressure via the pressure screws overcomes the limitations of gas membrane cells previously mentioned, making it an ideal platform for future pressure quenching works.



**Figure D.1:** Detailed figures showing the fully constructed pressure quenching probe and Janis system. The Janis system is shown in the leftmost figure and includes the probe, Janis dewar, and HTS-110 superconducting magnet. The next figure shows the full probe including pressure rods whereas the figure to the right of this shows the probe without pressure rods. The rightmost figure shows a zoomed in view of the probe so the cell and supporting components can be seen clearly.



Figure D.2: The pressure cap used to compress the pressure rod O-rings and create a vacuum seal for the sample space. Four large holes are for the pressure rods and four small holes are for screws to compress the cap.



**Figure D.3:** A KF50 cap modified to pass four pressure rods into the sample space. These holes have space for O-rings to seal the sample space. Four small threaded holes are for the pressure cap screws. One hole at the outer edge creates and electrical feedthrough for the wires to reach the MIL-DTL-38999/25NC35PN hermetic connector. The hermetic connector would be soldered to a KF25 bored blank. Note the quick flange assembly and wire feedthrough were not modeled in CAD and corresponding schematics are unavailable.



**Figure D.4:** The probe baffles help support the structure and better utilize helium boil off to cool the probe. A central hole is cut for the future use of an optical cable. Four central holes are for pressure rods and the four outer holes are for stabilization rods. One outer hole is for a liquid helium sensor. See Cryomagnetics Model 3D Liquid Helium Level Sensor.



**Figure D.5:** The baseplate supports the pressure cell from below by clamping to the four stabilization rods. The cutouts along the perimeter allow the liquid helium sensor to pass between the baseplate and the sample space walls. The small off center hole is used to help lock the G10 spacer in place. The dimensions shown in the isometric view are the depth of the hole and support ring.



**Figure D.6:** The G10 spacer has four holes to fit the cell mount and insulate the cell from the baseplate. The protruding cylinder at the base is to help lock it in place on the baseplate.



**Figure D.7:** The cell mount provides a point to fix the cell to the probe and a place for a heating element. Four legs are used to fit into the G10 spacer. The central threaded post is for screwing a PPMS cell to. The single hole visible from the top view is for a screw to pass through and fix the PPMS cell in place.



**Figure D.8:** The G10 stabilizer passes through the stabilizer rods and fit around the top of the PPMS cell. The function is to hold the cell in place when the screws are adjusted. A large hole on the outer perimeter is for the liquid helium sensor. The bar shaped cutout and holes are for future optical fiber capabilities.



**Figure D.9:** Pressure rods and stabilization rods. The top part is the pressure rod which are used to adjust pressure at low temperatures. The left hex fitting is the top end and the right Allen key is the bottom end. The stabilization rods are shown at the bottom with the cross-section above it.



**Figure D.10:** The custom optical component that connects to an SMA optical fiber cable. Two large holes allow pressure rods to pass through the piece. Two small holes are used for screwing the piece to the G10 stabilizer.

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