Pressure effects on selected correlated electron systems

Stella Kim
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Pressure effects on selected correlated electron systems

by

Stella Kwi Kim

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Condensed Matter Physics

Program of Study Committee:
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Iowa State University
Ames, Iowa
2013
DEDICATION

I would like to dedicate this thesis to my family, especially my mom, dad, brother, and grandmother.
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This thesis summarizes experimental work using high pressure for materials synthesis and also as a tuning parameter in the study of correlated electron systems at low temperatures. Details of materials growth at high pressure and high temperature are given as well as the details of the assembly and use of the high pressure modified Bridgman anvil cell (mBAC) for resistivity measurements. The mBAC was used to tune the various ground states of several correlated electron systems: the metal-to-insulator transition in V$_6$O$_{11}$, the spin density wave antiferromagnetism in V$_7$O$_{13}$ as well as members of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$, the superconductivity of members of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$, and the heavy fermion state of YbFe$_2$Zn$_{20}$. 
CHAPTER 1. INTRODUCTION

In experimental physics, the furthest reaches of our exploration are achieved only with the tools that we have. With increasing advances in technology, the extent of our reach is ever growing. The focus of this thesis is on the use and ongoing development of my tool of choice, pressure. The effects of pressure on the behavior of matter is not a foreign concept. We have seen the effects of pressure in our day to day lives. For example, at high altitudes water undergoes a phase transition, from liquid to gas, at lower temperatures than at sea level. Moreover, high pressures can be used to stabilize new phases and even create metastable ones as evidenced by the fact that diamonds exist on the Earth’s surface.

In this thesis, the modified Bridgman anvil cell (mBAC) has been used to probe the effects of applying pressure on a variety of systems. The idea was to see how these systems react to a perturbation in the form of pressure. As hydrostatic pressure is applied to a material, the material unavoidably contracts and thus the inter-atomic spacing is decreased. There are several possible consequences to this contraction. There can be greater overlap between neighboring electron orbitals which can change the width of the conduction band. This becomes important in the case of Mott-insulators where the narrow conduction band is widened with pressure, thereby stabilizing a metallic state. Pressure can also change the structure of the Fermi surface which can enhance or inhibit the formation of spin and charge density waves by creating or destroying the nesting of Fermi surfaces. Furthermore, the change in lattice spacings can also probe the competition between local moment formation and long range magnetic ordering at low temperatures. Whereas these topics are explored in this thesis, they are just a few of the many ways that pressure can be used to study the physical properties of materials. In this introductory section, I want to introduce, briefly, the materials and ground states I will examine: iron pnictides, vanadium oxides, and Yb-based heavy fermions, as well as the primary
research tool I will use: the modified Bridgman anvil cell. This is like introducing the players and the stage before the start of the performance. Through the rest of the thesis, I will devote whole chapters to each of these topics.

### 1.1 Iron Pnictides

Since its discovery by Onnes in 1911 [Onnes, 1911], superconductivity has been extensively studied over the past century, bringing a basic understanding of the underlying mechanism for its lossless electrical conductivity and perfect diamagnetism (where the internally generated magnetic field is equal in magnitude and opposite direction to that of the applied magnetic field) at least for “conventional, low-$T_c$, superconductors.”

The more recent discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ with superconducting transition temperature, $T_c$, as high as 26 K for $x = 0.1$ by Kamihara in 2008 [Kamihara et al., 2008] and as high as 43 K under 4 GPa of pressure [Takahashi et al., 2008] instigated a flurry of research as it opened the door to a whole family of iron-based superconductors. The presence of Fe was curious considering it has a large magnetic moment and typically magnetism tends to destroy superconductivity. Due to its similarity to the cuprate superconductors, most notably, its layered structure and the presence of oxygen, it seemed possible that the oxygen content in these new iron-based materials was just as important. In what is now known as the 1111 family, $T_c$ as high as 55 K in SmFeAsO$_{0.9}$F$_{0.1}$ has been seen in ambient pressure measurements [X. H. Chen, 2008; Chen et al., 2008; Ren et al., 2008c,a,b]. Soon after these initial discoveries, superconductivity was found in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [Rotter et al., 2008a] (part of the now known 122 family) suggesting that the oxygen content was not at all vital to the stabilization of the superconducting ground state and instead, the structurally common FeAs layer was the key.

The structures of the 1111 and 122 materials are similar in that they are composed of layers of FeAs$_4$ edge sharing tetrahedra separated by a layer of R$_4$O edge sharing tetrahedra (R = rare earth element) or a sheet of AE (A = alkaline earth element or Eu), respectively, stacked along the $c$-axis (see Figure 1.1). In physical properties measurements, both parent members of the two series, LaFeAsO and BaFe$_2$As$_2$, showed transitions from a high temperature tetragonal and paramagnetic state to a low temperature orthorhombic antiferromagnetic state.
Due to practical considerations, the 122 materials have gained more attention since it was easier to grow large single crystals, unlike the 1111 materials. Other Fe-based superconductors have been found, such as the AFeAs (A = alkali metal) (the 111 family) and the Fe$_{1-y}$Se system, however, I focus on the 122 materials in this thesis, and more specifically, on the BaFe$_2$As$_2$ system [Hosono, 2008; Canfield and Bud’ko, 2010; Johnston, 2010; Paglione and Greene, 2010].

In the parent material, BaFe$_2$As$_2$, the transition from the paramagnetic tetragonal to the antiferromagnetic orthorhombic state occurs below just 140 K [Rotter et al., 2008b] however no bulk superconductivity was found. In the antiferromagnetic state, the moments align antiparallel along the $a$- and $c$-axes (where $a$ is the longer lattice parameter in the orthorhombic basal plane) and parallel along the $b$-axis. In resistivity measurements at the structural magnetic transition, there is an almost imperceptible increase in value associated with a loss of density of states that is overwhelmed by the subsequent decrease in resistivity attributed to the loss of spin disorder scattering due to the antiferromagnetic transition.

For certain substitution of the either the alkaline earth, transition metal, or pnictogen (the Nitrogen group in the periodic table of elements) site, superconductivity can be stabilized at low temperatures [Hosono, 2008; Canfield and Bud’ko, 2010; Johnston, 2010; Paglione and Greene, 2010]. In the case of Co substitutions, less than 4% of Co is needed to bring about supercond-
ducting behavior. At this lower substitution level, which we call underdoped, the structural and magnetic transition occur separately and at reduced temperatures. Higher concentrations of Co lead to further suppression of the split structural and magnetic transitions and an increase of the superconducting transition temperature, until at an optimal concentration where the structural and magnetic transitions occur near the superconducting temperature, \( T_c \), and the latter reaches its highest value. Further increases in Co substitutions, which we call overdoped, causes a gradual suppression of \( T_c \) to zero. These results are shown in Figure 1.2.

![R/R(300 K) curves for Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\). Inset shows the low temperature data for \( x \geq 0.038 \) [Ni et al., 2008].](image)

Surprisingly, substitution of Rh instead of Co (considered an isoelectronic substitution) showed similar behavior for similar concentrations despite clear differences in how Co and Rh changed lattice parameters. When the phase diagrams of the two are superimposed, the suppression of the structural and magnetic transitions and the superconducting dome map onto each other (see Figure 1.3). The similarity of phase diagrams for isoelectronic substitutions was also seen with Ni and Pd doped materials. Although these are isoelectronic substitutions, each elemental substitution causes different changes to the lattice spacings, but the near identical
phase diagrams suggests that perhaps these structural variations play a minor role in the overall behavior of these doped materials.

Alternatively, it is likely that adding electrons to the system may play a more vital role in its behavior. In comparing the phase diagram of Co/Rh and Ni/Pd, it is apparent that Ni/Pd substitution causes the structural and magnetic suppression and superconducting dome to evolve twice as fast as Co/Rh substitution. If the addition of electrons to the system via doping has such a simple yet significant affect on the system, this then raises the question of how BaFe$_2$As$_2$ will respond to isoelectronic substitution.

![Figure 1.3](image)

Figure 1.3  $T - x$ Phase Diagram for Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ for (a) TM = Co and Rh and (b) TM = Ni and Pd [Ni et al., 2009] showing the remarkable similarity between isoelectronic substitutions.

One way of perturbing the system without contributing or subtracting electrons is by applying pressure to the parent BaFe$_2$As$_2$. Under pressure, BaFe$_2$As$_2$ exhibits similar behavior as its Co, Rh, Ni, or Pd doped variants where pressure suppresses the AFM temperature...
and superconductivity emerges. Figure 1.4 shows resistivity measurements under pressure for BaFe$_2$As$_2$.

![Figure 1.4 Pressure dependent resistivity curves for BaFe$_2$As$_2$ up to 7.59 GPa (75.9 kbar) [Colombier et al., 2009b]. Arrows indicate the structural/magnetic transition.](image)

For the parent compound, BaFe$_2$As$_2$, superconductivity can be stabilized under a moderate pressure which varies with the level of hydrostaticity [Alireza et al., 2009; Duncan et al., 2010; Yamazaki et al., 2010; Colombier et al., 2009a]. Pressure dependent studies of Co-substituted BaFe$_2$As$_2$ shows that with pressure $T_c$ can be enhanced for underdoped samples which still have a structural and magnetic transition at ambient pressure, whereas for optimally and overdoped samples with no such transitions, $T_c$ is suppressed with pressure (see Figure 1.5).

Isoelectronic Ru substitutions for Fe in BaFe$_2$As$_2$ also causes a similar progression of the structural and magnetic transition as well as the superconducting dome. In this case, the structural and magnetic transitions occur simultaneously (Figure 1.6). It should be noted that Ru substitution causes an overall increase in the unit cell volume, mimicking negative pressure.

In comparison to Co substitutions, far greater concentrations of Ru are necessary to cause similar changes to the phase diagram. In order to make further comparisons to Co substituted BaFe$_2$As$_2$ and help clarify key factors for inducing superconductivity, a pressure study was done on Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ for several Ru concentrations. The results of this pressure study are given in Chapter 4.
Figure 1.5 Pressure dependent resistivity curves for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ for (a) $x = 0.038$, (b) $x = 0.047$, (c) $x = 0.074$, and (d) $x = 0.1$ [Colombier et al., 2010].

Figure 1.6 Phase diagram for Ru-substituted BaFe$_2$As$_2$ [Thaler et al., 2010].
1.2 Vanadium Oxides

In 1946 Foëx discovered $V_2O_3$ manifested a temperature dependent metal-to-insulator (MI) transition; Conductivity measurements showed a pronounced hysteretic jump in value between 150 and 160 K, signalling the onset/offset of the lower-temperature insulating behavior [Foëx, 1946; Morin, 1959]. The low temperature state is well known today as a prototypical Mott-Hubbard insulator [Mott, 1990] where intra-atomic Coulomb forces causes a metal to insulator transition. An antiferromagnetic transition also occurs at the same temperature [Shinjo and Kosuge, 1966; Moon, 1970]. By applying pressure to $V_2O_3$, the metal-to-insulator (MI) transition was gradually suppressed, reaching zero at 2.6 GPa [McWhan and Rice, 1969]. Beyond 2.6 GPa, $V_2O_3$ remained metallic throughout the measured temperature range and showed a growing temperature range of Fermi liquid (FL) behavior at low temperatures where $\rho \propto AT^2$.

Figure 1.7(a) shows the MI transition phase diagram for $V_2O_3$.

![Figure 1.7](image_url)

(a) (b)

Figure 1.7  (a) Phase Diagram of MI transition of $V_2O_3$ as it is suppressed with pressure.  (b) Resistivity of $V_2O_3$ for $P \geq 2.6$ GPa. Inset shows the quadratic $T^2$ dependence of the resistivity at low temperatures [McWhan and Rice, 1969].
The $T^2$ coefficient $A$, where $\rho(T) = \rho_0 + AT^2$, was surprisingly large for a metal ($A = 0.042 \mu \Omega \text{ cm K}^{-2}$ at 2.6 GPa whereas for a normal metal it is on the order of $10^{-3} - 10^{-4} \mu \Omega \text{ cm K}^{-2}$), suggesting that in the metallic state, $V_2O_3$ was a correlated electron system (see Figure 1.7).

When small amounts of Ti$^{3+}$ were substituted for V, the changes in temperature dependent data resistivity data were similar to those caused by the application of pressure in $V_2O_3$, with the MI transition gradually suppressing with increasing Ti concentration and leading to an ambient pressure metallic state. Heat capacity measurements (see Figure 1.8) for $V_2O_3$ doped with Ti$^{3+}$ also showed that in the metallic state the linear term in the specific heat was quite large for a normal metal with $\gamma$ (for $C/T = \gamma + \beta T^2$) increasing with greater Ti concentration. This corroborated the evidence from pressure dependent resistivity measurements that the low temperature metallic state of $V_2O_3$ was a correlated electron system.

![Figure 1.8 Low temperature specific heat measurements of $V_2O_3$ doped with Ti$^{3+}$ showing the large value of the linear coefficient, $\gamma$, where $C = \gamma T + \beta T^3$ [McWhan et al., 1971].](image)

In 1959, VO$_2$ was discovered to also have a MI transition [Morin, 1959]. However, unlike $V_2O_3$, VO$_2$ showed no corresponding antiferromagnetic ordering at the MI transition temper-
ature, $T_{MI} = 340$ K [Kosuge, 1967]. Furthermore, the application of pressure seemed to have the opposite effect on $T_{MI}$, increasing it at a rate of 0.82 K/GPa (see Figure 1.9).

Figure 1.9 Phase diagram showing the progression of the MI transition temperature with pressure for VO$_2$ [Berghund and Jayaraman, 1969].

Remarkably, the vanadium Magnéli series, V$_n$O$_{2n-1}$ with $n = 3 - 9$ exists as a series of compounds that structurally spans these two end members $n = 2$ (V$_2$O$_3$) and $n = \infty$ (VO$_2$). Structurally a member of this series can be thought of as being n-units of VO$_2$ joined to the next n units by a V$_2$O$_3$-like shear plane. A diagram of this is shown in Figure 1.10. Other Magnéli series (TM$_n$O$_{2n-1}$) exist with TM = Ti, Cr, Nb, and Mo [Glasser, 2009].

This series has been extensively studied over the past years, and with the exception of V$_7$O$_{13}$, all undergo a MI transition. Figure 1.11 shows $T_{MI}$ for several members of V$_n$O$_{2n-1}$. V$_7$O$_{13}$ remains metallic to lower temperatures and manifests what is thought to be a spin density wave/antiferromagnetic (SDW/AFM) transition at $T = 43.5$ K [Griffing et al., 1982; Canfield, 1990] where the magnetic moments have a spatial periodicity across the sample.

Pressure dependent resistivity measurements of almost all members have been made up to moderate and high pressures [Åsbrink and Malinowski, 1987; Terukov et al., 1979; Canfield et al., 1990a,b; Canfield, 1990; Sidorov et al., 2003; Ueda et al., 2003]. Measurements of V$_3$O$_5$
up to 10 GPa showed that pressure suppresses the insulating ground state and above 8 GPa, a metallic state is stabilized [Sidorov et al., 2003]. The metallic state resistivity showed a remarkable broad maximum at low temperatures and then $T^2$ dependence at base temperatures (see Figure 1.12). The large $T^2$ coefficient, $A = 10 \mu\Omega \text{ cm K}^{-2}$ at 9 GPa, and the broad peak below 100 K have been interpreted as signs of strongly correlated behavior, suggesting this could possibly be an example of a 3d heavy fermion compound [Sidorov et al., 2003].

Resistivity measurements of $V_4O_7$, $V_5O_9$, and $V_6O_{11}$ under pressure of up to 1.8 GPa, 1.73, and 1.84 GPa [Canfield, 1990] showed a similar suppression of $T_{MI}$, however these were not large enough pressures to reveal the emergence of any new ground state. Measurements
Figure 1.11  $T_{\text{MI}}$ for $V_nO_{2n-1}$ $(n = 3 - 8)$ and VO$_2$ [Canfield, 1990; Schwingenschl"ogl and Eyert, 2004].

of metallic $V_7O_{13}$ [Canfield et al., 1990b; Canfield, 1990; Ueda et al., 2003] revealed that the SDW/AFM transition can also be suppressed by pressure, reaching $T_N = 0$ at roughly 3.4 GPa. Surprisingly, for $V_8O_{15}$, near 1 GPa and above $T_{\text{MI}}$, an anomalous hump appeared in the resistivity, resembling the SDW/AFM feature seen in $V_7O_{13}$. This splitting of the two features continued until at 1.7 GPa where the MI state is fully suppressed and the AFM feature still appears. Pressures up to 3.5 GPa are necessary to finally suppress the AFM feature to $T_N = 0$. A phase diagram summarizing these findings are shown in Figure 1.13.

As we go across this Magnéli series, the gradual change in structure provides a way to try to find a unifying physics that underscores this family. Applying pressure could cause these compounds to instigate a common response and reveal some characteristic family traits. With this in mind, the pressure dependent electrical resistivity of $V_6O_{11}$ was measured to see if it contributes to the insights gained from pressure dependent studies of $V_7O_{13}$ and $V_8O_{15}$, and also to look for exotic behavior as $T_{\text{MI}}$ or $T_N$ is suppressed to zero in $V_6O_{11}$ and $V_7O_{13}$.

Historically, the difficulty in measuring the transport properties of these materials under high pressure is due to the difficulty of appropriately attaching contacts onto the sample. For
Figure 1.12  Resistivity of $\text{V}_3\text{O}_5$ at 9 and 10 GPa showing broad maxima below 100 K. Inset shows $T^2$ dependence at low temperatures [Sidorov et al., 2003].

Figure 1.13  $T-P$ Phase Diagram of $\text{V}_8\text{O}_{15}$ showing the emergence of AFM feature at $\sim1$ GPa (10 kbar in the figure) [Canfield et al., 1990b].
pressures higher than 3 GPa, typically, a diamond anvil cell would be used, however the sample space is quite small. For the vanadium oxides, good strong electrical contacts using silver paint resulted in a somewhat large cross-sectional profile. In this case, the modified Bridgman anvil cell, with a larger sample space is ideal for measurements of poor metals like the vanadium oxides.

1.3 Ytterbium-based Heavy Fermions

Heavy fermion behavior arises from strong electron correlations in materials reflected in the large effective masses of the electrons, ranging from several tens to thousands of times that of the free electron. In these cases, the strong correlations are mainly due to the hybridization between the local moment electrons and the conduction electrons and is predominantly seen in certain rare earth-bearing intermetallic compounds (e.g. Ce and Yb compounds). In general, for many rare earth-bearing compounds, the rare earth atoms retain their $4f$ electron(s) whereas their $5s$, $5p$, and $5d$, electrons have a larger radial extent from the nuclei and tends to join the conduction band. Hybridization of the $4f$ electrons with the conduction band leads to heavy fermion behavior and occurs in several Ce and Yb-based compounds where the $4f$ shell favors a fully empty or occupied state. In Ce-based heavy fermions, the Ce $4f^1$ electron may join the conduction band and empty the $4f$ shell, whereas for Yb-based heavy fermions, the Yb $4f^{13}$ electrons can borrow a conduction electron to completely fill the $4f$ shell.

For many Ce-based heavy fermions, this hybridization leads to a low temperature magnetic ordering mediated by an indirect exchange interaction from one moment to its neighbors via the conduction electrons, known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. In a well known model (the Doniach model [Doniach, 1977], described more extensively in Chapter 2), the RKKY interaction can be suppressed with a non-thermal control parameter such as an applied magnetic field, small changes to the elemental composition, or pressure. As shown in Figure 1.14, increasing pressure moves the system from left to right on the Doniach phase diagram. It is expected that at some critical value of the control parameter, e.g. pressure, the magnetic ordering can be fully suppressed to zero and a different ground state may emerge. Beyond this critical region, the material’s low temperature behavior can be dominated by
the Kondo interaction where the local moment is screened by a cloud of conduction electrons [Kondo, 1964]. This Kondo screening gradually turns on at a characteristic temperature, $T_K$, called the Kondo temperature.

In contrast to Ce-based heavy fermions, several Yb-based heavy fermion compounds show the opposite response to applied pressure, where increasing pressure shifts the system from Kondo behavior to one dominated by RKKY interactions. On the Doniach phase diagram (Figure 1.14), this moves the system from the left to the right. The low temperature state of the Kondo dominated material is a Fermi liquid state with the hybridized electrons acting as the quasiparticle pairs and can be used to track the dominance of the Kondo state.

Figure 1.14 Doniach Phase Diagram showing the RKKY-mediated AFM state on the left and the Kondo dominated state on the right [Doniach, 1977; Coleman, 2007]. Ce-based heavy fermions typically manifest an RKKY-mediated AFM which is suppressed with pressure (or other perturbations) with the direction denoted by the right-pointing arrow. Whereas Yb-based heavy fermions start in the Kondo-dominated regime and AFM can possibly be induced with pressure, denoted by the left-pointing arrow.

The family of YbTM$_2$Zn$_{20}$ with TM = Fe, Co, Ru, Rh, Os, and Ir, proves to be a good system for studying the effects of strong correlations [Torikachvili et al., 2007]. In the unit cell,
the Zn atoms are in a nearly spherical distribution around the Yb atom. This arrangement of Zn atoms creates a small crystalline electric fields which lead to relatively small splittings of the degenerate ground state of the 4f electrons. For most of these compounds, the temperature scale of the crystalline electric field splitting is on par with that of the Kondo effect which offers a rich, isostructural series in which to study Kondo physics and quantum criticality.

Magnetic susceptibility measurements made on the YbTM$_2$Zn$_{20}$ compounds show paramagnetic Curie-Weiss behavior, where $\chi = C/(T - \theta)$ ($C$ is the Curie constant and $\theta$ is the Curie temperature) at high temperatures which saturates at low temperatures. The resistivity measurements show a broad shoulder or local maximum at the Kondo temperature, then a sharp drop down to low temperatures at which point, Fermi liquid behavior sets in showing $\rho(T) = \rho_0 + AT^2$ dependence. Specific heat measurements where $C/T = \gamma + \beta T^2$ show a large electronic contribution, $\gamma$, revealing the heavy effective mass of the electron. Figure 1.15 shows the temperature dependent physical properties measurements of YbTM$_2$Zn$_{20}$.

According to the Doniach model [Doniach, 1977], the Fermi liquid behavior at low temperatures indicates that these compounds are in the Kondo dominated regime. Pressure can be used to drive the system into an RKKY-mediated, magnetically-ordered state. To this effect, resistivity measurements of YbCo$_2$Zn$_{20}$ under pressure have been carried out [Saiga et al., 2008; Matsubayashi et al., 2010]. These measurements showed a small feature at may be associated with magnetic ordering in the low temperature data starting at $\sim$1 GPa and reaching as high as $\sim$0.5 K at $P = 2.37$ GPa. This provides an impetus to pursue pressure measurements on other members of the YbTM$_2$Zn$_{20}$ family and reveal some insight into the subtle changes of the correlated electron behavior brought about by the presence of the different transition metals.

The YbFe$_2$Zn$_{20}$ compound is a tantalizing choice as it is also a member of the RFe$_2$Zn$_{20}$ (R = rare earth) family that exhibits notable magnetic behavior [Jia et al., 2007, 2009]. YFe$_2$Zn$_{20}$ and LuFe$_2$Zn$_{20}$ were found to be nearly ferromagnetic Fermi liquid materials with a large Stoner enhancement factor of $Z = 0.88$ (for $\chi_T = \rho_{Pauli}/(1 - Z)$). By replacing Y or Lu with a moment bearing rare earth element, RFe$_2$Zn$_{20}$ compounds for $R =$ Gd-Tm manifest ferromagnetic ordering, with a rather high ordering temperature for GdFe$_2$Zn$_{20}$ at 86 K. If applying pressure on YbFe$_2$Zn$_{20}$ can stabilize magnetic ordering, an intriguing question is
whether it will exhibit something other than simple antiferromagnetic ordering.

At ambient pressure, resistivity measurements [Torikachvili et al., 2007] have already shown that there is a clear $T^2$ region at low temperatures. Initial measurements under pressure using a piston cylinder cell with a maximum pressure of 2.03 GPa revealed promising results. Mainly, the low temperature Fermi liquid region was suppressed with pressure, going from $\sim$11 K at ambient pressure to less than 8 K at 2.03 GPa. In a simple linear approximation, this suggests that the Fermi liquid behavior can be suppressed by $\sim$7 GPa which is well within the pressure range of the modified Bridgman anvil cell. These results and higher pressure measurements on YbFe$_2$Zn$_{20}$ are given in Chapter 6.
1.4 The Modified Bridgman Anvil Cell

Measurements of transport properties of materials under pressure are typically performed in a piston cylinder cell for lower pressures (less than 3 GPa) and a diamond anvil cell for higher pressures (greater than 3 GPa and up to 36 GPa for transport measurements). In most cases, for high pressures, a diamond anvil cell is used, however, the sample space is at times too restrictive. The great benefit of the modified Bridgman anvil cell (mBAC) is that it provides a relatively large sample space for pressure measurements up to about 9 GPa. The relatively large sample space of the mBAC provides a way to more readily measure a wide range of research samples up to intermediate pressures.

The process for preparing and using the mBAC was introduced to our group by the time the iron pnictide research was in full swing and so it behooved us to use the mBAC to measure these new exciting materials under pressure. From then on, the mBAC has seen regular use for pressures $3 < P < 9$ GPa. This pressure range has proven to be very useful for $V_nO_{2n-1}$ and YbFe$_2$Zn$_{20}$ as well as for FeAs-based superconductors.

The difficulties in preparing a Bridgman cell stem from the fact that for every component of the cell, there is an opportunity for failure. Often, this failure is an explosion of the gasket, which obscures the source of the failure. Most of these had been addressed before my interest in pressure work, however, the unexpected difficulties due to humidity problems and the desire to improve the hydrostaticity of the sample space led to several setbacks and innovations. Eventually, these setbacks were overcome with small modifications to the pressure cell. These efforts are explained more thoroughly in Appendix A.

The bulk of the experimental results presented in this thesis are from measurements of temperature dependent electrical resistivity in a modified Bridgman Anvil cell (mBAC), which can generate pressures up to 8.4 GPa. To put this pressure scale into context, consider the static pressures that we encounter day to day. The atmospheric pressure at sea level is about 101 kPa. For road bikes, the average tire pressure is about a 100 psi which is nearly 6.9 kPa above atmospheric pressure. If I (a $\sim$50 kg person) balance my weight on a single stiletto heel with a $1 \times 1$ cm$^2$ cross section, then the pressure generated under the heel is about
49 bars. Another pressure scale commonly used in the scientific community is the kbar which is equivalent to 0.1 GPa. In this body of work, the GPa scale is used.

1.5 Outline of the Thesis

The following is an outline of the thesis: Chapter 2 is a description of the theoretical physics underlying the materials studied in this thesis, covering Fermi liquid theory, heavy fermion behavior, density waves, metal to insulator transitions, superconductivity, and quantum criticality. Chapter 3 covers the experimental methods used in this body of work, focusing on pressure cells. Experimental results are summarized in chapters 4, 5, and 6. Chapter 4 discusses the pressure dependence of the antiferromagnetic ordering and superconductivity in Ru substituted BaFe$_2$As$_2$. Chapter 5 summarizes the study of V$_6$O$_{11}$ and V$_7$O$_{13}$ in the hopes of finding a “unifying trend” amongst the vanadium oxide Magnéli series, and exploring the correlated electron behavior in their metallic states. Chapter 6 delves into the world of heavy fermion physics with the study of the Yb-based heavy fermion, YbFe$_2$Zn$_{20}$ and tackles the question: Can pressure stabilize a magnetically ordered ground state in this material? Chapter 7 summarizes the results of these studies and provides direction for future pressure related research. Appendices A and B detail the preparation of the modified Bridgman cell and Appendix C goes over the operation of the High Pressure Furnace. Finally, Appendix D is a list of publications and accomplishments and Appendix E is a catalog of high pressure materials growth and high pressure mBAC cell preparations.
CHAPTER 2. OVERVIEW

In modeling the behavior of electrons in materials, there were early successes by treating the electrons as non-interacting particles. However, the richer and more exotic behaviors of materials can be understood only when we consider that the electrons interact with each other and their environment in ways other than ballistic collisions. In this chapter, I will briefly review the theories behind a variety of effects caused by electron interactions. For subsequent chapters, familiarity with these theories will be important in order to understand the interpretation of the data.

2.1 Landau Fermi Liquid Theory

One of the earliest descriptions of resistivity was created by Drude [Drude, 1900a,b; Ashcroft and Mermin, 1976], by considering only the scattering of electrons in a uniform electric field. Drude described the electrons in metals as scattering like point particles without any interactions [Ashcroft and Mermin, 1976]. The resistivity was expressed as:

\[ \rho = \frac{m}{ne^2 \tau} \]

where \( m \) is the electron mass, \( n \) is the density of states, \( e \) is the electron charge and \( \tau \) is the time between collisions. This is in good agreement with resistivities of metals at room temperature.

There are several different scattering mechanisms that contribute to the resistivity, and assuming that the sources of this scattering are independent of each other, these can be summed up according to Matthiesen’s rule:

\[ \frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_e} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{LM}} \]

where \( \frac{1}{\tau_0} \) is the temperature-independent scattering off of impurities, and \( \frac{1}{\tau_e}, \frac{1}{\tau_{ph}}, \text{ and } \frac{1}{\tau_{LM}} \) are the temperature dependent scattering off of the electrons, lattice (or phonons), and local
moments, respectively. The resistivity is then:

$$\rho = \rho_0 + \rho_e + \rho_{ph} + \rho_{LM}$$

In the case where a system undergoes magnetic ordering, a noticeable decrease in resistivity is expected, reflecting the loss of spin disorder scattering.

In many metals at low temperatures, resistivity measurements show a quadratic dependence with temperature, $\rho(T) = \rho_0 + AT^2$. The electron-phonon scattering that was dominant at high temperatures diminishes at low temperatures and the electron-electron scattering dictates the temperature dependence. Consider a system at very low temperatures where the only available electronic states are within a thermal layer of $k_B T$ about the Fermi surface. An electron with energy $E_1(K_1)$ above the Fermi surface that resides within $k_B T$ about the Fermi surface scatters off of an electron below the Fermi surface which has an energy $|E_2(K_2)| < E_1(K_1)$. The absolute value of the energy of the second electron needs to be less than that of the first electron for the final states to be above the Fermi surface and contribute to the conduction. In the final state, the electrons have energies $E_3(K_3)$ and $E_4(K_4)$. Figure 2.1 illustrates a single scattering event [Kaveh and Wiser, 1984].

![Figure 2.1](image-url)  
Figure 2.1 Diagram showing the initial ($K_1$ and $K_2$) and final states ($K_3$ and $K_4$) of a single electron-electron collision [Kaveh and Wiser, 1984].
The scattering rate is:
\[
\frac{1}{\tau(K_1)} = \sum_{K_2, K_3, K_4} P(K_1, K_2, K_3, K_4)
\]
Conservation of energy and momentum (neglecting Umklapp scattering where the initial and final momenta of an electron collision with a lattice differs by a reciprocal lattice vector [Ashcroft and Mermin, 1976]) and the Pauli exclusion principle places restrictions to the final state so that
\[
\frac{1}{\tau(K_1)} \propto \sum_{q, E(K_2), E(K_3)} P(E(K_2), E(K_3))
\]
where \(q = K_2 - K_3\). In other words, the scattering rate depends on the number of electronic state with energy \(E(K_2)\) available for scattering and the number of empty states with energy \(E(K_3)\) available for scattering into. Since both are proportional to \(k_B T N(E_F)/E_F\) where \(N(E_F)\) is the density of states at the Fermi surface, then finally \(\frac{1}{\tau} \propto T^2\) and also, \(\frac{1}{\tau} \propto m^2\) where \(N(E_F) \propto m\).

As the name suggests, heavy fermion materials display a strongly enhanced electron mass (as inferred from the linear coefficient of the low temperature specific heat), sometimes 100 to 1000 times the free electron mass. Landau’s phenomenological Fermi-liquid theory [Landau, 1957b,a, 1959] describes this renormalization of the electron mass as a result of electron-electron interactions [Harrison, 1970; Ziman, 1972; Ashcroft and Mermin, 1976; Kaveh and Wiser, 1984; Singleton, 2001].

Consider a system of a non-interacting Fermi gas. There are three assumptions made in Landau’s Fermi liquid theory [Harrison, 1970]:

- There is a one to one correspondence between the low-lying excitations of the electrons in the Fermi-gas and the quasiparticles in the Fermi-liquid. The spin and momentum quantum numbers of the electrons are still good for the quasiparticles.

- The interaction between electrons are turned on adiabatically, very slowly, so as to prevent any phase transitions and ensure that the new density of states is a smooth change from that of a free electron gas. These interactions are non-zero only at low energies.

- The quasiparticles retain the electron charge (-e).
At this point, we have recast the main characters of our working model from electrons to fermionic quasiparticles. These quasiparticles stem from the fact that we are working with interacting particles, in other words, electron hole pairs or “elementary excitations” of the gas, or electrons with a screening cloud. To calculate the total energy of the system, a simple summing up of the energies of the individual quasiparticles will not suffice. The interaction between the quasiparticles means their energies are functionals of the distribution function, \( n(\mathbf{p}) \) [Abrikosov and Khalatnikov, 1959; Pathria and Beale, 2011]. To a first approximation, the additional interaction energy of the quasiparticle can be written as

\[
\delta\varepsilon(\mathbf{p}) = \int f(\mathbf{p}, \mathbf{p}') \delta n(\mathbf{p}') d\tau'
\]

where \( \mathbf{p} \) is the definite momentum of the electron \( f(p, \sigma; p', \sigma') \) is the strength of the interaction between the quasiparticles, and \( d\tau = 2d^3p/\hbar^3 \). In an isotropic system, there is no energetic difference between different spin orientations but the relative spins of the interacting quasiparticles come into play. The function \( f \) can be rewritten as only dependent on the relative spins of the electrons.

\[
\frac{1}{m} = \frac{1}{m^*} + \frac{p_F}{2\hbar^3} \cdot 4 \int f(\theta) \cos \theta d\omega'
\]

where \( m \) is the mass of the free electron, \( m^* \) is the effective mass of the quasiparticle, \( p_F \) is the Fermi momentum of the quasiparticle, \( \hbar \) is Planck’s constant, \( \theta \) is the angle between the quasiparticle spins, and \( d\omega \) is a solid angle. This can also be simplified to

\[
\frac{m^*}{m} = 1 + \frac{1}{3} F_1^{(s)}
\]

where \( F_1^{(S,A)} \equiv N(0) f_1^{(S,A)} \) is the Landau parameter, \( N(0) \) is the density of states at the Fermi surface and \( f_1^{(S,A)} \) is the interaction strength expressed in terms of Legendre polynomials [Abrikosov and Khalatnikov, 1959; Pathria and Beale, 2011]. Here we find an effective electron mass emerging from a consideration of the electron-electron scattering events.
2.2 Heavy Fermions

2.2.1 Kondo Effect

As early as the 1930’s, measurements of resistivity of what were thought to be high purity, elemental metals and metallic compounds revealed a characteristic minimum at low temperatures followed, upon further cooling, by a resistivity upturn that ultimately saturated to some finite resistivity at base temperatures. Subsequent measurements of susceptibility revealed that there was a small, high temperature, free local moment contribution that would disappear at low temperatures in the same region as the resistive minimum. In addition, the low temperature linear temperature dependent term of the specific heat would increase and saturate in this same temperature range as well. Prompted by these findings, Jun Kondo derived a theory that linked the behavior of the low temperature resistivity to the loss of localized impurity moments [Kondo, 1964]. At the time, there were already several models that considered a system where the conduction electrons would screen the local impurity moment, described as the $s-d$ model.

For dilute magnetic impurities immersed in an ordinary metal, there are spin fluctuation interactions between the impurities and the conduction electrons. At low temperatures, these give non-trivial contributions to the thermodynamic and transport properties of these materials.

In the Anderson $s-d$ model, a Coulomb interaction, $H_{\text{corr}} = U n_{d\uparrow} n_{d\downarrow}$ between the local $d$ electrons is included in the $s-d$ model Hamiltonian [Anderson, 1961; Hewson, 1997]:

$$H = H_{0f} + H_{0d} + H_{\text{corr}} + H_{sd}$$

Here, $H_{0f}$ and $H_{0d}$ describe the energies of the $s$ and $d$ electrons, respectively. $H_{sd}$ is the energy of the spin-dependent interaction between the $s$ and $d$ electrons and can be expressed as

$$H = -2JS \cdot s$$

where $J$ is the Heisenberg interaction strength, $S$ is the local moment spin, and $s$ is the spin density of the conduction electrons [Maple, 1978].

Assuming that the interaction between the $s$ and $d$ electrons are antiferromagnetic ($J < 0$), a
third order perturbation of this system shows a scattering rate of [Kondo, 1964; Coleman, 2007]:

\[ \frac{1}{\tau} \propto [JN(E_F) + 2(JN(E_F))^2 \ln \frac{D}{T}]^2 \]

where \( D \) is the width of the electron band and \( N(E_F) \) is the density of states at the Fermi energy level. This logarithmic rise with decreasing temperature, combined with the normal metal’s own decreasing resistivity, well describes the resistance minimum seen in many alloys with dilute magnetic moments. Consider the case of Au alloyed with a dilute concentration of Fe (Figure 2.2) [Kondo, 1964; Franck et al., 1961]. The low temperature logarithmic rise, especially noticeable for 0.006 at. % Fe, is very well fitted with Kondo’s expression for resistivity.

![Figure 2.2](image_url)  
Figure 2.2 A comparison of the resistivity of AuFe from experimental data (in circles and crosses) and from the theoretical prediction of the logarithmic dependence with temperature shown as the solid line [Kondo, 1964].

For Kondo systems, as temperature is lowered, scattering off the screened impurities sites grows stronger, causing the logarithmic increase in resistivity. This Kondo effect gradually
dominates the total resistivity at a characteristic temperature, $T_K$, where:

$$T_K \sim T_F \exp[-1/JN(E_F)]$$

where $T_F$ is the Fermi temperature and $N(E_F)$ is the electronic density of states of the host material at the Fermi surface [Maple, 1978].

As mentioned before, in this temperature region, manifestations of this spin fluctuation interaction can also be seen in the magnetic susceptibility and specific heat. At higher temperatures, the impurities act as free local moments, showing a paramagnetic Curie-Weiss behavior. At lower temperatures, in the Kondo regime, the local moment is screened by the conduction electrons and the magnetic susceptibility saturates to the residual Pauli, Landau, core diamagnetic and Van Vleck paramagnetic contributions. In specific heat measurements, the loss of magnetic spin entropy due to the AFM coupling of the screening cloud to the local impurity, causes a peak at low temperatures near $T_K$.

One disconcerting consequence of the Kondo resistivity is that it predicts a divergent logarithmic rise as $T \to 0$. However, Kondo addresses this by saying that at low temperatures, the local spin undergoes a Zeeman splitting, therefore at some $T \ll T_0$ where $k_B T_0$ is on the order of the energy of this splitting, the logarithmic dependence saturates as $\ln(T) \to \ln(T_0)$. However, a more rigorous solution was sought over the years. Dubbed the “Kondo Problem,” this unphysical, theorized divergence was tackled by Anderson using a scaling method wherein the perturbations for higher order excitations were eliminated for a low energy system, thereby accentuating the interaction strength of the spin-dependent interaction [Anderson, 1970]. Building on this, Wilson used the renormalization group method to find an adequate description for the $S = 1/2$ ground state [Wilson, 1975]. In addition he discovered a linear relationship between $\chi$ and $\gamma$, the susceptibility and specific heat ratio, respectively, known as the Wilson ratio. Later, Nozieres was able to interpret Wilson’s results in terms of Fermi liquid theory at very low temperatures [Nozières and Blandin, 1980]. Although these efforts gave very good interpretations of the Kondo system at $T \ll T_K$, an exact solution for the $s – d$ model for $S = 1/2$ was eventually found by Andrei and Weigmann in 1980 using the Bethe Ansatz method (Bethe solved exactly the system of a one-dimensional Heisenberg interaction) [Vigman, 1980; Andrei, 1980].
2.2.2 Kondo Lattice

In the mid-seventies, the first example of a new class of materials called heavy fermion systems was discovered by Andres et al. in 1975: CeAl$_3$ [Andres et al., 1975]. Since then, a multitude of heavy fermions, most based on Ce, Yb, and U elements have been found [Stewart, 1984, 2001]. Measurements of specific heat and susceptibility for heavy fermions show a strongly enhanced electron mass, generally 100s of times greater than that of the free electron.

In 1977, Doniach proposed that heavy fermion compounds were in fact Kondo lattice systems, a model first treated by Kasuya in 1956 [Doniach, 1977; Kasuya, 1956]. A Kondo lattice system is described as a dense Kondo impurity system with the local impurity moments residing on a periodic lattice. Resistivity measurements of Kondo lattice systems show a minimum at low temperatures similar to Kondo impurity materials. Specific heat and magnetic susceptibility measurements of heavy fermions also show a likewise similar behavior to the impurity model.

However, having dense, regularly spaced moments leads to several departures from the single impurity Kondo model. First, below the Kondo temperature, the coupled electrons begin to scatter coherently off of the periodic screened impurity sites causing a marked decrease in resistivity. This coherent scattering leads to Landau Fermi liquid behavior at base temperatures, with the heavy electrons acting as the Fermi-liquid (FL) quasiparticles. The large $T^2$ coefficient of the resistivity points to a greatly enhanced quasiparticle mass.

Furthermore, in a periodic Kondo lattice, the proximity of the polarized screening cloud to the neighboring local moment can allow information to be passed between the two local moments indirectly. This indirect exchange interaction can cause long range magnetic ordering and is mediated by what is known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

In RKKY interactions, the local moment, screened by the conduction electrons, induces Freidel-like oscillations in the spin density. If the local moments are close enough, as can be the case for a dense Kondo lattice, the Freidel oscillations couple the neighboring moments, via the screening cloud. This allows spin interactions between the two remote moments and induces long range order to stabilize
In 1977, Doniach schematically outlined the transition from the Kondo state to the RKKY mediated magnetically ordered state as a competition between their energy scales. In the Kondo state, $T_K \sim \exp[-1/2JN(E_F)]$ and $T_{RKKY} \sim J^2N(E_F)$ for the RKKY ordered state, where $N(E_F)$ is the density of electronic states. Doniach did not propose a mechanism for why these states transform from one to the other, however, many heavy fermion materials to some degree follow Doniach’s phase diagram, Figure 2.3 [Coleman, 2007].

Doniach’s phase diagram also highlights the existence of the Fermi liquid state in the Kondo regime. This $T^2$-resistivity becomes a useful feature to track so as to approximate where the Kondo ground state might disappear. As the system moves away from the Kondo ground state, non-Fermi liquid behavior is likely to be seen, accompanied by RKKY mediated magnetic ordering. This also serves as a starting point for understanding pressure, field, and substitution induced quantum criticality.
2.3 Density Waves

Charge and spin density waves are spatial fluctuations of charge and spin, respectively, that break translational symmetry. Cr is a classical example of a material exhibiting a spin density wave [Overhauser, 1962]. As an elemental transition metal, Cr has a less than full outer shell of 3d electrons that become the itinerant conduction electrons. The rest of its shells are full and therefore have no local magnetic moment. Thus it was curious that Cr as well as a few other elemental transition metals, exhibit magnetic ordering. In the case of Fe, Co, and Ni, their ferromagnetism was explained by the Stoner model, which describes a mechanism for itinerant ferromagnetic ordering. In 1962, Overhauser described the case of spin density waves in materials and explained the itinerant antiferromagnetic ordering seen in Cr as a consequence of having parts of the electron and hole Fermi surface nested [Overhauser, 1962; Fawcett, 1988]. Figure 2.4 shows the Fermi surface of the (100) plane and the nesting wavevectors $\tilde{Q}_-$ and $\tilde{Q}_+$.  

We will see in the following description why Fermi surface nesting is integral to the formation of density waves.

Consider that in a crystalline metal, the atomic ions are screened by the electrons. The
Lindhard response function describes how this screening mechanism causes electrons to redistribute in response to an external perturbation, whatever it may be. This is expressed as [Grüner, 2000]:

\[
\chi(\mathbf{q}) = \int \frac{d\mathbf{k}}{(2\pi)^d} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}}
\]

where \(d\) is the dimension of the system and \(f_k\) is the Fermi function. In the cases of charge density waves (CDW) and spin density waves (SDW), the response to the perturbation is achieved by redistributing the charge density or spin density, respectively [Brown and Grüner, 1994]. However, this redistribution also instigates an increase in the energy of the system as now in the case of CDWs and SDWs, electron-phonon and electron-electron interactions need to be considered. Figure 2.5 illustrates the differences between a normal metal, CDW and SDW in real space.

![Figure 2.5](image_url)

Figure 2.5 Comparison of a normal metal, CDW and SDW considering the spin up and down electron density, the total charge density and the spin density as it is visualized in real space [Brown and Grüner, 1994].

For CDWs, the density of electrons is spatially modulated and in doing so, causes periodic distortions of the lattice (via the electron-phonon interaction). This distortion is directly related to the periodicity of the CDW and opens up a gap in the electron band at the associated wavevector. The opening up of the gap decreases the energy of the system as this lowers the
energies of the states below the gap (occupied states) and increases it above the gap (unoccupied states). This becomes energetically advantageous when the gap is opened up at the Fermi level, at $k_F$. However, the distortion of the lattice causes an increase in the system’s elastic energy. For the case where this increase in energy is less than the decrease caused by the opening of the gap, a CDW forms. A diagram of this is shown in Figure 2.6 where the periodicity of the CDW is twice the lattice periodicity.

Figure 2.6 Diagram showing how a CDW changes the Fermi level if the band is half filled. (a) Normal metal with uniform charge density across the lattice. The first Brillouin zone is denoted as $k = \pi/a$. (b) The charge density wave with double the periodicity of the underlying lattice causes a dimerization of neighboring atoms. Note: the distortions shown are greatly exaggerated. The new periodicity creates a gap in the band at the $k$ associated with the new periodicity, in this case, at $k = \pi/2a$ which at half-band filling is also $k_F$ [Grüner, 2000].

In the case of spin density waves, the redistribution of the electrons is according to their spins. As Figure 2.5 shows, while there is a spin modulation in space, the charge density
remains essentially the same everywhere. For spin density waves, the lowering of the energy by creating a spin modulation in space is countered by the electron-electron interaction. This is due to the increased density of a particular spin at a particular location which causes an increase in Coulomb energy. Just as in the case of the CDW, if this increase in energy is less than the lowering of energy from the opening of the gap, a SDW forms. A diagram of this is shown in Figure 2.7 [Grüner, 2000].

![Diagram](image)

Figure 2.7  (a) Diagram showing the gap opening in the band at $k_F$ for SDWs. (b) Real space density modulations of the spin up and spin down electrons [Grüner, 2000].

In real materials, CDW and SDW are much more often seen in lower dimensional systems. This is because it is easier to have Fermi surface nesting in lower dimensions. This Fermi surface nesting is essential for density wave formation and we can see why when we look closer at the Lindhard response function, $\chi(\mathbf{q})$. Figure 2.8 shows the Lindhard response function for a free electron gas in one, two and three dimensions [Grüner, 2000].

When Fermi surface nesting occurs, there are large regions of the Fermi surface that can be mapped onto each other by one momentum vector, $\mathbf{k}$. This then opens up a gap on these
Figure 2.8  (a) A plot of the Lindhard response function for a free electron gas in one, two and three dimensions at $T = 0$. At $2k_F$, indicated by the dashed line, the susceptibility diverges for one dimension and for two dimensions has a sharp corner. For three dimensions, there are no sharp features and changes smoothly [Grüner, 2000]. These correspond to Fermi surface topology in three dimensional materials that manifest pseudo (b) one, (c) two, and (d) three dimensions. The red arrows are wavevectors of $2k_F$ going from one Fermi surface to another and indicate an occupied and unoccupied state.
Fermi surface regions, splitting the electron band. The energy of the band gap can be related to the temperature of this phase transition by the relation $2\Delta = 3.5k_B T_c$, the same as that for a weakly-coupled, BCS, superconducting ground state. The spatially varying charge distribution is expressed as:

$$\rho(x) = \rho_0 \left[ 1 + \frac{\Delta}{\hbar v_F k_F \lambda} \cos(2k_F x + \phi) \right]$$

where $\rho_0$ is the metallic state electron density, $v_F$ and $k_F$ are the Fermi velocity and momentum respectively, $\lambda$ is the dimensionless electron-phonon coupling constant, and $\phi$ is the phase of the density wave. Likewise for the SDW, $\vec{S}(x) = 2\vec{S} \cos(2k_F x + \phi)$.

When the gap opening occurs, in lower dimensional systems, this can cause the system to become insulating, as the band below the gap is filled and above it empty. When a CDW is the cause of this metal to insulator transition, this is called a Peierls transition. However, with higher dimensional systems, the Fermi surfaces tend to have varied structures and so even with having a region that is nested, the material still remains metallic.

### 2.4 Metal to Insulator Transitions

**Band Insulator**

The success of the band theory for materials comes from the simplicity in describing whether a system is a metal or a non-metal [Ashcroft and Mermin, 1976]. Simply put, for a given material, there are bands of allowed energy states for the electrons. If the Fermi level goes through one of these bands then it is filled with electrons only up to that level. The electrons have many other states to move to within the band above the Fermi level and thus it is a metal. If the Fermi level lies somewhere in between two bands, then a band is completely filled below it and completely empty above. For the electrons, the only available states to move to are in the band above the gap. For conduction to occur, the electrons must have enough energy to traverse the gap between the bands. Otherwise, the electrons are restricted and the material is an insulator. Figure 2.9 is a depiction of band theory for an insulator and a metal.

Stemming from this, we can understand how charge and spin density waves can induce a metal to insulator (MI) transition. When a CDW or SDW stabilizes, it opens up a gap at the
Figure 2.9 Depending on where the Fermi level is in relation to the allowed energy bands, the material can be described as an insulator (left) or a metal (right). For the insulator, the Fermi level (shown as the dashed line) is within the gap and so the electrons are restricted to the lower band. In order for electrons to conduct, the electrons must gain enough energy to traverse the gap into the upper band. For the metal, the Fermi level intersects the upper band and so any electrons there can easily move to higher states within that band.

$k$-value associated with the periodicity of the density wave. If this happens to occur at the Fermi level, then by definition at low temperatures, all states below this level are filled and states above the energy gap in the upper band are empty. Thus the system is an insulator.

On the other hand, there exists other systems which exhibit a MI transition associated with structural changes, but a simple mechanism of this transition is still an ongoing discussion (e.g. VO$_2$).

Simple band theory breaks down for materials like NiO or CoO, which have partially filled $d$ states, but shows insulating behavior. We will see that it becomes important to consider electron-electron correlations to shed light on the source of this curious behavior.

**Mott-Hubbard Transition**

Consider a crystalline array of atoms each with one electron and separated by a distance $a$. For very large $a$, with such a large distance to traverse to the next atom, each electron remains on their respective atom, creating a neutral insulating system. Now consider that from this
extreme distance, $a$ is decreased so that at some point, the system becomes metallic. This occurs when at some distance $a$, the attractive potential of the neighboring atom is greater than that due to the screening cloud of the intra-atomic electrons. Effectively, the bandwidth $t$ is tuned via $a$. In Mott’s early works, the Thomas Fermi screened potential was used. This method showed that the MI transition would be discontinuous, with an abruptly changing number of conduction electrons [Mott, 1949, 1968, 1990].

In the Hubbard model, only the intra-atomic electron-electron Coulomb interaction was taken into account, neglecting any long range Coulomb forces. For a simple system with one narrow band with bandwidth, $t$, and Hubbard interaction $U$, the Hamiltonian is:

$$H = t \sum_{j,l} \sum_{\sigma} (c_{j\sigma}^\dagger c_{l\sigma} + c_{l\sigma}^\dagger c_{j\sigma}) + U \sum_{j} n_{j\uparrow} n_{j\downarrow}$$

The first term is the kinetic energy and the second term is the on-site Coulomb repulsion energy between two electrons. The Hubbard intra-atomic energy $U$ is given by:

$$U = \int \int \left( \frac{e^2}{r_{12}} \right) |\phi(r_1)|^2 |\phi(r_1)|^2 dr_1 dr_2$$

where $e$ is the electron charge, $r_{12}$ is the distance between the two electrons, and $\phi(r)$ is the electron wavefunction. For narrow bands $t$ and finite $U$, the electron band splits in two creating an upper and lower Hubbard band. For a system where the number of electrons is equal to the number of atoms, the lower Hubbard band is filled. In this way, if the widths of the individual bands are smaller than the separation between the two bands (called the Hubbard gap), then the system is an insulator. When $U$ is decreased or $t$ is increased, eventually, the two bands overlap and the material becomes a metal, (Figure 2.10). This is the Mott-Hubbard transition. In the Hubbard model, the transition from a metal to an insulator is not abrupt. At the critical $U$, the subbands retain their form and there is a finite density of states at the Fermi level. This gradual transition into a metallic state indicate that this is a second order transition. In the case of the Mott-transition, the Thomas Fermi screening must be overcome in order for the metallic state to stabilize, however, this results in a discontinuous first order transition. Whereas the Hubbard model is concerned with intra-atomic Coulomb forces, the Mott-transition takes into account long-range Coulomb forces [Fazekas, 1999].
When pressure is applied to a Mott-Hubbard insulator, the bandwidth widens as electron-wavefunction overlap increases due to the lattice shrinking. As in the example of the Mott insulator, the bandwidth $t$ is tuned by the interatomic distance $a$. In this manner, the MI transition can be suppressed, thus stabilizing a metallic ground state.

In many cases, an antiferromagnetic transition accompanies this MI transition, for example $V_2O_3$ or MnO. Even in the insulating state the neighboring electron wavefunctions overlap and it becomes energetically favorable for the electron on the neighboring atoms to order antiferromagnetically [Mott, 1990]. In the insulating state, an electron residing on an atom may momentarily visit a nearest neighbor atom. This is made possible when the two electrons have opposite magnetic spins [Blundell, 2001].

There are other mechanisms for MI transitions, such as charge density waves and spin density waves (which are second order transitions in one dimension). These density waves open up an energy gap at the Fermi level, and with all states below occupied and those above the gap, empty, an insulating state stabilizes. In the case of CDW’s, this effect is called a Peierls transition. There are other systems that show a MI transition with structural changes, such as VO$_2$, but a simple description of the mechanism for the MI transition is still open.
2.5 Superconductivity

Superconducting materials show two remarkable properties, zero resistivity [Onnes, 1911] and complete expulsion of an applied magnetic field [Meissner and Ochsenfeld, 1933]. What sets these materials apart from a perfect metal, is the latter characteristic. For both a perfect metal and a superconductor below its critical temperature, if an external magnetic field is applied, both will respond with perfect diamagnetism, expelling all field within themselves. However, consider the case where the field is turned on above the superconducting critical temperature and the two materials are slowly cooled. The perfect metal remains unresponsive whereas the superconductor still expels the field (see Figure 2.11). This effect was discovered by Meissner and Ochsenfeld in 1933 and is known as the Meissner effect [Meissner and Ochsenfeld, 1933].

![Figure 2.11 Illustration of the Meissner effect](Wikipedia, 2013). The blue sphere is the superconductor and $H$ is the applied magnetic field. For a superconductor, if a magnetic field is applied above $T_c$ (left figure) and the system is cooled down to below $T_c$, the magnetic field will be expelled by the superconductor (right figure).

Shortly after, in 1935, the London brothers developed a phenomenological theory to explain the electrodynamics of this new state of matter and introduced a new parameter, called the
London penetration depth, $\lambda_L$ [London and London, 1935; Tinkham, 2004]. In their results, it was found that time-independent magnetic fields are screened out of the superconductor and that the applied magnetic field penetrates the superconducting material, with the magnitude falling off exponentially from the surface inward. The length of this depth is characterized by the penetration depth. An example of this is shown for a cylindrically shaped superconductor in Figure 2.12.

![Penetration Depth Diagram](image-url)

Figure 2.12 Illustration of the penetration depth for a cylindrical superconductor showing the extent of the magnetic field $H$ penetration where $\lambda_L \ll R$ [Poole et al., 2010].

In a further improvement on the London results, the Ginzburg-Landau theory expanded the free energy of the system in terms of a complex order parameter, $\psi(r) = |\psi(r)|e^{i\phi}$, which describes the wave function of the superconducting electrons [Ginzburg and Landau, 1950; Tinkham, 2004]. From these derivations, a correlation length, $\xi$, naturally arises and describes the characteristic length of the variation of $\psi(r)$ in real space. This subsequently led to a correct prediction of the existence of type II superconductors [Abrikosov, 1957; Tinkham, 2004].

Two different types of superconductors are revealed when they are subjected to an applied magnetic field. In the type I superconductors, as field is increased, there exists a critical field where superconductivity is destroyed. In type II superconductors, at some critical field, $H_{c1}$, instead of destroying the superconductivity, magnetic flux vortices, called fluxoids, penetrate the superconductor. Above a second critical field, $H_{c2}$, the superconducting state is completely destroyed (see Figure 2.13). Whether the material falls into one category or the other is
determined by the ratio of the penetration depth to the correlation length:

$$\kappa < \frac{1}{\sqrt{2}}$$  for Type I  \\
$$\kappa > \frac{1}{\sqrt{2}}$$  for Type II

where

$$\kappa \equiv \frac{\lambda_L}{\xi}$$

Figure 2.13  Diamagnetic response for type I and II superconductors.

These phenomenological theories provided a good understanding of how superconductors behave but a description of the underlying mechanism for superconductivity was still needed.

In 1950 and 1951, the superconducting transition temperatures, $T_c$, of several isotopes of Hg were measured to have different values [Maxwell, 1950; Reynolds et al., 1951]. Specific heat measurements of these isotopes showed that whereas the electronic contribution, $\gamma$, did not change, the lattice contribution, $\beta$, showed a small shift in value, which could be directly related to the change in the isotopic mass, $M$. The implication was that the phonons were involved in the mechanism for superconductivity. Taking this into consideration, Bardeen, Cooper, and Schrieffer (BCS) in 1957 published a paper titled “Microscopic Theory of Superconductivity” [Bardeen et al., 1957]. The initial assumption was that the electron-phonon interaction causes a small attractive potential between electrons. The source of this small attraction is the electron-phonon attractive interaction that screens the Coulomb repulsion of the electrons. The theory states that in the presence of a small attractive interaction, electrons pairs of opposite momentum $\vec{k}$ and spin $\vec{\sigma}$ create correlated states called Cooper pairs.
Consider a system where two electrons are introduced to the Fermi sea where they are allowed to interact with each other, but not with the background Fermi sea. In order to minimize the total energy, these electrons should have opposite momenta, \( \vec{k} \) (since we are concerned with only electrons near the Fermi surface). Furthermore, as a consequence of the Pauli exclusion principle, electrons of opposite spin, \( \vec{\sigma} \) have a higher probability of being near each other. Using these parameters, a wave function for the paired electrons, the Cooper pairs, can be constructed with quantum numbers \( L = 0 \) and \( S = 0 \). This wavefunction is applied to the Schrödinger’s equation which includes the electron-phonon interaction potential, \( V \), in order to determine the energy eigenstates, \( E \), of the Cooper pairs. A simplification is made by assuming that the Fermi surface is a sphere and that \( V \) is constant over a range, \( \hbar \omega_D \) about the Fermi energy, where \( \hbar \) is Plank’s constant and \( \omega_D \) is the Debye frequency. \( \omega_D \) is considered the cutoff frequency signifying that \( V \) is zero for energies above \( \hbar \omega_D \).

A detailed derivation is not given here and instead only the results are shown in the following. The quasiparticle (an electron participating in the pairing) excitation energy is given by

\[
E = \sqrt{\varepsilon_k^2 + \Delta^2}
\]

where \( \varepsilon_k = \epsilon_k - E_F \) describes the electron energy relative to the Fermi energy and \( \Delta \) is the gap function (related to the Cooper pairing) and is independent of \( k \). The gap function emerges as the order parameter for superconductivity.

Assuming that the density of states, \( D \), near the Fermi surface is constant, \( N(E_F) \) [Tinkham, 2004; Poole et al., 2010],

\[
\frac{1}{VN(E_F)} = \int_0^{\hbar \omega_D} \frac{\tanh \left[ (\varepsilon_k^2 + \Delta^2)^{1/2} / 2k_B T_c \right]}{(\varepsilon_k^2 + \Delta^2)^{1/2}} d\varepsilon
\]

At \( T = 0 \),

\[
\Delta = \frac{\hbar \omega_D}{\sinh[1/VN(E_F)]}
\]

and in the weak-coupling limit where \( VN(E_F) \ll 1 \),

\[
\Delta \approx 2\hbar \omega_D e^{-1/VN(E_F)}
\]
or in the strong-coupling limit $VN(E_F) \gg 1$,

$$\Delta \approx 2\hbar \omega_D VN(E_F)$$

As the temperature of the system approaches $T_c$, $\Delta$ goes to zero and so in the weak coupling limit,

$$k_B T_c = \frac{2e^\gamma}{\pi} \hbar \omega_D e^{-1/VN(E_F)}$$

where $\gamma = 0.577$ is Euler’s constant. In the strong coupling limit, $T_c = \omega_D VN(E_F)/2$

Pressure studies on superconducting systems can show initial suppressions or increases of $T_c$. The above expression for $T_c$ according to BCS theory depends on three parameters which can be modified by pressure to varying degrees: $\omega_D$, $N(E_F)$, and $V$. Under pressure $\omega_D$ typically increases as a result of hardening of the phonons. Any decrease in $T_c$ would then be attributed to $N(E_F)$ or $V$. For an isotropic Fermi surface, the density of states at the surface is expected to decrease as the bandwidth is increased with pressure and for $V$, we have thus far assumed it was constant, and so we assume it has a negligible pressure dependence [Lorenz and Chu, 2005].

The Eliashberg extension of the BCS theory [Eliashberg, 1960] defines the electron-phonon coupling constant, $\lambda$ where

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

Note that in BCS theory, $\lambda = VN(E_F)$. $\alpha^2(\omega)$ is the strength of the electron-phonon interaction, $F(\omega)$ is the phonon density of states and [McMillan, 1968]. $\alpha^2(\omega) F(\omega)$ is the electron-phonon spectral density which can be determined via band theory calculations or estimated by results from inelastic neutron scattering experiments.

Later work by McMillan and Dynes expanded on the Eliashberg theory [McMillan, 1968; Dynes, 1972]. The following are the results of these works [McMillan, 1968; Dynes, 1972; Lorenz and Chu, 2005; Bennemann and Ketterson, 2008; Poole et al., 2010]. The superconducting transition temperature is expressed as

$$k_B T_c = \frac{\hbar \omega_0}{1.20} \exp \left[ - \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]$$
where $\omega_0$ is the upper cutoff phonon frequency and

$$\mu^* = \frac{N(0)V_c}{1 + N(0)V_c \ln(D/\omega_0)}$$

where $\mu^*$ is the screened Coulomb pseudopotential, $N(0)$ is the average phonon energy, $V_c$ is the Coulomb interaction averaged over the Fermi surface, and $D$ is the electronic bandwidth.

The pressure dependence of $T_c$ on $\mu^*$ and $\langle g^2 \rangle$ are generally neglected and similar to the BCS results, focus is given to the pressure dependence of the average phonon frequency and density of states at the Fermi surface.

The effects of pressure on elemental superconductors have been extensively studied over the years [Garfinkel and Mapother, 1961; Hansen et al., 1973; Eiling and Schilling, 1981; Bireckoven and Wittig, 1988; Thomasson et al., 1990; Suressh and Tallon, 2007] and consequently, in the case of lead (Pb) and tin (Sn), the well known response of $T_c$ to pressure is used as a manometer in many pressure cells. For Pb, $T_c$ is suppressed linearly at a rate of -0.364 to -0.386 K/GPa [Smith and Chu, 1967; Eiling and Schilling, 1981; Bireckoven and Wittig, 1988] up to 2.5 GPa. This rather large change with pressure allows accurate determination of pressure within the sample space. Higher pressure studies have thoroughly tabulated the pressure dependence of $T_c$ [Eiling and Schilling, 1981; Bireckoven and Wittig, 1988; Thomasson et al., 1990] with some results suggesting a precision of 0.2 GPa in highly hydrostatic pressure environments and 0.5 GPa for moderately hydrostatic pressures up to about 14 GPa [Thomasson et al., 1990].

In contrast to the elemental superconductors, exotic superconductors have shown superconductivity often occurring in competition with a different nearby state. For example, a MI transition may be preferred over superconductivity when the phonon coupling is large enough to create a CDW. Another possibility is the stabilization of magnetic ordering which inhibits superconductivity. With pressure, these competing states can sometimes be suppressed and reveal or even enhance superconductivity. For example, in CeIn$_3$ the low temperature antiferromagnetic ordering temperature is fully suppressed with pressure by 2.65 GPa where a superconducting ground state emerges [Grosche et al., 2001; Knebel et al., 2001a]. Additional examples include members of the high-$T_c$ cuprates where pressure enhances $T_c$ [Chu et al., 1987; Gao et al., 1993; Chu et al., 1993] and more recently, the high-$T_c$ iron pnictide com-
pounds where for the non-superconducting parent compound BaFe$_2$As$_2$, pressure suppresses AFM ordering and induces superconductivity [Colombier et al., 2009b; Duncan et al., 2010; Paglione and Greene, 2010].

2.6 Quantum Phase Transitions

Phase transitions describe the changing of a system from one state of matter to another. Two of the most commonly observable phase transitions are that of water freezing or boiling, as the liquid changes to a solid or a vapor, respectively. This type of phase change is what is described as a first order phase transition, so named because in the analysis of the first derivative of the free energy across this transition, there exists a discontinuity. In second order phase transitions, the discontinuity occurs in the second derivative of the free energy but is continuous in the first derivative.

When a second order phase transition occurs, the system undergoes a spontaneous symmetry breaking with the emergence of an order parameter. The order parameter is a property of the system that is zero in the high symmetry state and non-zero in the low symmetry state. For example, when spontaneous magnetic ordering occurs, say ferromagnetism in Fe, the ordering parameter is the zero field magnetization. With the magnetic moments aligned, the spin degrees of freedom are reduced, breaking rotational symmetry.

Quantum phase transitions occur when at $T=0$, a non-thermal parameter such as pressure, doping, or magnetic field drives the system (continuously) through a phase change from a disordered state to an ordered state. The point where this occurs is called a quantum critical point (QCP). For real measurements, $T=0$ is inaccessible, but we find that at low but finite temperatures in the quantum critical region, the QCP still dictates the behavior of the system. This can then be used to trace back to the $T=0$ QCP [Sachdev, 2001].

Classical systems are characterized by thermal fluctuations of the order parameter that have a diverging correlation length as the phase transition is approached. However at $T=0$, these thermal fluctuations can no longer exist and so quantum fluctuations, beyond zero point motion, dominate the system’s behavior. Quantum fluctuations occur due to the Heisenberg uncertainty principle, which introduces time varying fluctuations, and like their classical counterpart, the
Table 2.1  Critical exponents for magnetically ordered systems. The order parameter as stated before is the magnetization, \( m \), with the magnetic field \( H \) as the conjugate field. \( t \) is the proximity to the quantum critical point and \( d \) is the spatial dimensionality of the system [Vojta, 2003].

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<thead>
<tr>
<th>Exponent</th>
<th>Definition</th>
<th>Conditions</th>
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<tr>
<td>Specific heat</td>
<td>( C \propto</td>
<td>t</td>
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<tr>
<td>Order parameter</td>
<td>( m \propto (-t)^{-\beta} )</td>
<td>( t \to 0 ) from below, ( H = 0 )</td>
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<tr>
<td>Susceptibility</td>
<td>( \chi \propto</td>
<td>t</td>
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<td>Critical isotherm</td>
<td>( \chi \propto</td>
<td>m</td>
</tr>
<tr>
<td>Correlation length</td>
<td>( \xi \propto</td>
<td>t</td>
</tr>
<tr>
<td>Correlation function</td>
<td>( G(r) \propto</td>
<td>r</td>
</tr>
<tr>
<td>Dynamic</td>
<td>( \tau \propto \xi^{\zeta} )</td>
<td>( t \to 0, H = 0 )</td>
</tr>
</tbody>
</table>

correlation length, \( \xi \), of these fluctuations diverge at the quantum critical point described by \( \xi \propto t^{-\nu} \) where \( t \) is the proximity to the critical point and \( \nu \) is a critical exponent [Sachdev, 2001; Vojta, 2003]. When the QCP is approached via a parameter \( g, t = |g - g_c|/g_c \), where \( g_c \) is the critical value of the parameter. The time for the system to equilibrate after a perturbation is described as \( \tau \propto \xi^{\zeta} \) where \( \zeta \) is the dynamic exponent and this also diverges as the QCP is approached. \( \nu \) and \( \zeta \) are two of several critical exponents, see Table 2.1, which are related to each other by the scaling relations \( 2 - \alpha = 2\beta + \gamma \) and \( 2 - \alpha = \beta(\delta + 1) \) and the hyperscaling relations \( 2 - \alpha = d\nu \) and \( \gamma = (2 - \eta)\nu \) [Vojta, 2003].

In general, the power law behavior near a QCP depends only on the symmetry of the order parameter, the spatial dimensionality and the correlation length of the system and is independent of other microscopic details.

For transitions that occur in the quantum critical region, where \( \hbar \omega > k_B T \), fluctuations take place in both space and time, with an effective dimensionality of \( d + z \) where \( d \) is the spatial dimensionality. The dynamic exponent \( z \) is the effective spatial dimensionality that corresponds to the time dimensionality \( \tau \propto \xi^{\zeta} \) [Stewart, 2001; Si and Steglich, 2010].

For the case of AFM or ferromagnetically ordered states, by using renormalization-group theory Hertz and Millis were able to make several predictions for the power law behavior for several measurable properties near a QCP, categorized by the spatial dimension and the dynamic exponent of the system [Hertz, 1976; Millis, 1993; Stewart, 2001]. As an approximation
Table 2.2 Temperature dependence of non-Fermi liquid behavior according to spin fluctuation theories by Hertz, Millis, and Moriya [Hertz, 1976; Millis, 1993; Moriya and Takimoto, 1995; Stewart, 2001].

<table>
<thead>
<tr>
<th></th>
<th>Hertz-Millis</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AFM $z = 2$</td>
<td>AFM $z = 2$</td>
<td>FM $z = 3$</td>
<td>FM $z = 3$</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>$d = 3$</td>
<td>$d = 2$</td>
<td>$d = 3$</td>
<td>$d = 2$</td>
<td></td>
</tr>
<tr>
<td>$C/T$</td>
<td>$\gamma - a\sqrt{T}$</td>
<td>$c\log(T_0/T)$</td>
<td>$c\log(T_0/T)$</td>
<td>$T^{-1/3}$</td>
<td></td>
</tr>
<tr>
<td>$\Delta\chi$</td>
<td>$T^{3/2}$</td>
<td>$\chi_0 - dT$</td>
<td>$T^{3/2}$</td>
<td>$T$</td>
<td></td>
</tr>
<tr>
<td>$\Delta\rho$</td>
<td>$T^{3/2}$</td>
<td>$T$</td>
<td>$T$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{N/C}$</td>
<td>$(g_c - g)^{2/3}$</td>
<td>$(g_c - g)$</td>
<td>$(g_c - g)^{3/4}$</td>
<td>$(g_c - g)$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Moriya</th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>AFM</td>
<td>AFM</td>
<td>FM</td>
<td>FM</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>$d = 3$</td>
<td>$d = 2$</td>
<td>$d = 3$</td>
<td>$d = 2$</td>
<td></td>
</tr>
<tr>
<td>$C_m/T$</td>
<td>$\gamma_0 - a\sqrt{T}$</td>
<td>$-\log T$</td>
<td>$-\log T$</td>
<td>$T^{-1/3}$</td>
<td></td>
</tr>
<tr>
<td>$\Delta\chi_Q$</td>
<td>$T^{-3/2}$</td>
<td>$-(\log T)/T$</td>
<td>$T^{-4/3}$</td>
<td>$-T^{-1}\log T$</td>
<td></td>
</tr>
<tr>
<td>$\Delta\rho$</td>
<td>$T^{3/2}$</td>
<td>$T$</td>
<td>$T^{5/3}$</td>
<td>$T^{4/3}$</td>
<td></td>
</tr>
</tbody>
</table>

to this theory, the self-consistent renormalization theory by Moriya also makes power law predictions, however the limited success of these predictions for heavy fermion systems suggest that this model might be more applicable to 3$d$ transition metal compounds [Moriya and Takimoto, 1995; Stewart, 2001]. The temperature dependence of measurable properties near a QCP according to these spin fluctuation theories are tabulated in Table 2.2.

To an extent, these predictions adequately describe the spin density wave AFM seen in several heavy fermion compounds where the Kondo temperature remains finite across the QCP. It is that the Kondo screening breaks down at the QCP, creating locally critical behavior.

Pressure is a useful tool for inducing non-Fermi liquid behavior across a QCP. It introduces perturbations to the system without introducing disorder as in the case with doping. Furthermore, the exact $T = 0$ QCP can be approached with pressure, whereas in undoped systems, the QCP might only be close to its composition. Several heavy fermion compounds have been studied under pressure to drive the magnetic ordering to zero and expose the nFL behavior across the QCP (e.g. $CeRu_2Ge_2$ and $Ce_7Ni_3$ [Wilhelm et al., 1999; Umeo et al., 1996]). An example of this is CeVSb$_3$ where the ferromagnetic transition temperature $T_C$ was driven up then down with pressure [Colombier et al., 2011], consistent with moving from left
to right on the Doniach phase diagram for Kondo systems. As $T_C$ is suppressed with pressure, nFL behavior is encountered, with $n < 2$ power law behavior for $\rho = \rho_0 + AT^n$ as the critical pressure is approached and reaching a minimum at $P_c$. For Yb-based heavy fermion systems, according to the Doniach phase diagram, pressure should drive the system from the right side, the non-magnetically ordered state, to the left through a QCP (or even possibly a quantum critical region) and into the RKKY mediated magnetically ordered state. In some cases, superconducting ground states have been discovered (e.g. $CeCu_2Si_2$, $CeCu_2Ge_2$, and $CeIn_3$ [Stockert et al., 2011; Jaccard et al., 1992; Knebel et al., 2001a]) with pressure.
CHAPTER 3. EXPERIMENTAL METHODS

The following is an overview of the experimental methods for pressure related measurements, focusing on resistivity measurements. An extensive and thorough description of the preparation of the mBAC is given in Appendix A. First, a description of the piston cylinder cell and the diamond anvil cell are given to provide a means of comparison to the capabilities of the Bridgman anvil cell. The bulk of the experimental results presented in this thesis are from measurements of temperature dependent electrical resistivity in a modified Bridgman Anvil cell (mBAC), which can generate pressures up to 8.4 GPa. The following chapters include any additional experimental details that are specific to that study.

3.1 Pressure Cells

3.1.1 Piston Cylinder and Diamond Anvil Cells

Over the years, there have been several key advancements in the tools available for transport measurements under pressure. Early Bridgman Anvil pressure cells (BAC) proved quite useful for this, however the necessary use of solid pressure media created highly non-hydrostatic environments within the sample space. This inhomogeneity can lead to several consequences: broadening of otherwise sharp features in the data, unavoidable uniaxial pressures, and pressure gradients than can break samples. For better hydrostaticity, pressure cells utilizing liquid media were developed. The most common ones in use now are the self-clamping piston cylinder cells (PCC) which can generate and sustain pressures up to 3 GPa and the diamond anvil cells (DAC) with a maximum pressure in the range of hundreds of GPa (for measurements without the need for electrical contacts). These cells are self-clamping in the sense that the pressure is locked in by the cell so that it can be removed from the press and measured elsewhere.
Self-clamping cells are popular due to their ease of use and the variety of measurements that can be done with them, such as resistivity, susceptibility, thermopower, specific heat, Nuclear Magnetic Resonance, x-ray scattering (for DAC only), to name a few. Like any experimental setup, there are advantages and drawbacks for using either PCC or DAC. In some cases, as will be outlined below, the BAC is a prudent and practical alternative.

The piston cylinder cell, as the name suggests, uses a piston to compress a Teflon cup that houses the liquid medium, sample and other components. A diagram of a typical PCC can be seen in Figure 3.1. The body of the cell is typically made of a non-magnetic, hard alloy, such as BeCu and this is reinforced by a hard core liner such as NiCrAl or WC. Pressure is increased by applying a load to the piston. Then the pressure is locked into place by tightening the upper locking nut. The anti-extrusion rings, made out of steel (hardened or unhardened for the desired pressure range) or BeCu, are placed above and below the Teflon cup. While under pressure, this prevents the Teflon from flowing through the interstices and causing breaks in the liquid-tight seal. The feed-through provides access for the electrical leads that connect the sample and other components within the sample space to the outside. The feedthrough is sealed with black Stycast (2850FT) to secure against high pressures.

The use of the Teflon cup allows liquids to be used as a pressure transmitting medium and the large volume can house relatively large samples with average longest dimension $\sim$1-2 mm in length. One of the limiting factors for the PCC is that at higher pressures, the lip of the Teflon cup can extrude through the interstices of the components, even with the use of anti-extrusion rings. Other limiting factors at high pressure are the breaking of the feedthrough, distortion of the body, and cold-welding of the threads. For the PCC, the maximum pressure is typically less than 3 GPa.

For higher pressures, a diamond anvil cell (DAC) can be useful for transport measurements. A diagram of a DAC setup for transport measurements can be seen in Figure 3.2. The DAC uses two opposing diamond anvils embedded in an appropriate hard metal such as stainless steel or BeCu to sustain the high pressures. The anvils are separated by a metal gasket with a central bore that serves as the space for the sample, sample leads, and rubies (for determining pressure inside the cell). Thus for resistivity measurements that inevitably need to extend out
of the sample space, generally only pressures up to 40 GPa can be achieved [Garg et al., 2004]. However, for all other experiments without the need for wires, maximum pressure can be as high as hundreds of GPa [Eremets, 1996].

Very high pressures can be reached with a DAC, however, these cells greatly restrict the size of the samples that can be measured. For anvils with a culet diameter of 700 \( \mu \text{m} \), the central bore can have a diameter of roughly 350 \( \mu \text{m} \). Then the maximum length of the sample can be about 150 \( \mu \text{m} \). The thickness of the sample is also restricted by the thickness of the gasket, which can be as thin as 100 \( \mu \text{m} \). Table 3.1 shows the dimensions of the sample space for the PCC, DAC, and mBAC. (Given the roughly four orders of magnitude between the sample volume of a PCC and DAC, there is a clear need for an intermediate cell.) For resistivity measurements, four electrical leads must be attached to the sample and this further decreases the maximum thickness of the sample. It is preferred to attach these leads onto samples by spot welding very thin (12.5 \( \mu \text{m} \) diameter) gold wires onto the surface. The need to spot weld the electrical leads also puts another restriction on the type of samples that can be measured.
Figure 3.2 (a) Diagram of a Diamond Anvil cell [Jayaraman, 1983]. (b) Picture of a sample assembled on a DAC for resistivity measurements and three pieces of ruby placed in the sample space as a manometer. In this case, culet size is 1 mm in diameter.

Table 3.1 Dimensions of the sample space for the piston cylinder, diamond anvil, and modified Bridgman anvil cells

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Diameter (mm)</th>
<th>Height (mm)</th>
<th>Volume (mm$^3$)</th>
<th>Max. Pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piston Cylinder</td>
<td>4</td>
<td>11</td>
<td>120</td>
<td>3</td>
</tr>
<tr>
<td>Modified Bridgman Anvil</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Diamond Anvil</td>
<td>0.35</td>
<td>0.1</td>
<td>0.01</td>
<td>$\sim$40 (Transport)</td>
</tr>
</tbody>
</table>

in a DAC. Insulators, semiconductors and poor metals cannot be readily spot welded to due to their poor electrical conductivity. Instead, for these types of materials, conductive paints and epoxies need to be used to attach the leads which make their overall thickness too large for a DAC. Alternatively, the Bridgman anvil cell can be used to measure these samples up to moderately high pressures $\sim$9 GPa.

3.1.2 Bridgman Anvil Cells

The Bridgman cell received its moniker from the creator of the original reinforced anvil setup by P. W. Bridgman [Bridgman, 1941]. In his proof of concept, a tungsten-carbon (WC) anvil was press fitted into a sleeve of steel. When pressed against another anvil, likewise seated
in steel, this arrangement sustained higher loads than for the WC anvils alone. This was used with great success to measure a number of materials under pressure [Bridgman, 1952].

![Original Bridgman anvil cell design](image1)

(a) Original Bridgman anvil cell design used to test the maximum achievable load [Bridgman, 1941]. (b) Slightly modified design used by Bridgman to measure the resistivity of numerous metals under pressure [Bridgman, 1952]. A and B indicate the WC anvils and C and D indicate the steel rings shrunk onto the anvils.

Over the years, innumerable iterations of these types of pressure cells have been created to increase the upper limit of pressure. Likewise, modifications have been made to improve the hydrostaticity of the pressurized environment. Early on soft solids like talc, steatite, or NaCl were used as a solid pressure medium, but despite their softness, these materials still caused highly non-hydrostatic pressure within the sample space. (It should be noted that some groups still use these solid pressure media, even now, and simply ignore or work around the consequences of non-hydrostaticity.) This use of solid media made the BAC a curious intermediate cell, with the PCC and DAC being the liquid media based lower and higher pressure options. The next obvious choice for pressure mediums are liquids. However, a difficulty arises in sealing the sample space of the BAC so as to prevent leaks of the medium, especially during initial pressurization.

Several methods were developed to use liquid media within a BAC. For example, G. Fasol measured the electric and magnetic properties of materials under hydrostatic liquid pressure [Fasol and Schilling, 1978]. In this setup, a metallic gasket, made of BeCu or steel, with a central bore was placed between two WC anvils and filled with a 4:1 methanol : ethanol mixture as the
liquid pressure medium. Electrical contact leads were laid in shallow grooves in the metallic gasket, which was filled with an epoxy resin for electrical insulation. This also served to seal in the liquid medium under pressure.

In order to utilize the advancements in cryogenic systems that allow for lower temperature measurements and at high fields, such as the dilution refrigerator, a smaller pressure cell body was needed to fit inside the cryostat. Figure 3.4(a) shows a more recent incarnation of the Bridgman cell as it was designed by Nakanishi et al. [Nakanishi et al., 2002]. A Teflon capsule was used to prevent leaking of the liquid pressure medium. A further improvement on this method was made by Colombier et al. (Figure 3.4(b)) where the Teflon capsule was replaced by two Teflon rings [Colombier and Braithwaite, 2007]. This latter design simplified the components considerably and thus reduced the preparation time. The bulk of the measurements presented in this thesis were done using such a modified Bridgman anvil cell (mBAC) (as taught to me by E. Colombier during her post-doctoral appointment at Ames Laboratory and Iowa State University from 2008 to 2011).

The mBAC is useful for measurements between 2 and 9 GPa. A diagram of a typical Bridgman anvil cell can be seen in Figure 3.4. For a detailed description of the modified Bridgman anvil cell and the setup process, see Appendix 1.

3.2 Hydrostaticity

The theoretical ideal for pressure measurements is to have as hydrostatic an environment as possible for the sample so that changes can be modelled as simply as possible. In addition to problems with modelling, non-hydrostaticity causes varying pressures over the sample which can even broaden out otherwise sharp transitions. In some cases, stresses and strains on the sample can induce parts of it to undergo a phase change as was the case with SrFe$_2$As$_2$ where strain induced filamentary superconductivity was seen at low temperatures [Torikachvili et al., 2008a; Saha et al., 2009].

A key component for ensuring hydrostaticity is selecting the proper pressure medium. The desire is to have a medium with a combination of low shear yield strength and low compressibility. Solid pressure mediums such as NaCl and steatite are soft and are easy to use, however,
Figure 3.4  Diagrams of a modified Bridgman Anvil Cell (a) using a Teflon cup (b) and a closer view [Nakanishi et al., 2002]. 1-Top anvil, 2-Bottom anvil, 3-Stainless steel, 4-Au foil, 5-Au wire, 6-sample, 7-Teflon capsule, 8-pressure medium, 9-epoxy resin, 10-pyrophyllite gasket, 11-stycast, and 12-electrical leads. (c) Using Teflon rings (d) and a closer view with a picture of two samples within the sample space [Colombier and Braithwaite, 2007]. With the diameter of the sample space at 1.4 mm, the volume is 0.31 mm$^3$. 
the shear strength is still too high for our desired hydrostaticity. Ideally, an inert noble element such as helium, or argon in liquid form should be used. However, with a mBAC, it is technically difficult to fill the sample space with these liquids and to lock in the first pressure. Therefore, for simplicity, liquid pressure media which can be used at ambient temperature and pressure were used for all our measurements.

Liquid pressure media are not without their own problems. The main problem we contend with is the vitrification/solidification of the liquid medium with low temperature and/or applied pressure. When applying pressure to a Bridgman anvil cell, the load is applied uniaxially. If the pressure medium is still a liquid during this process, hydrostaticity is retained. However, if the medium has solidified, then when we apply a load, the sample experiences a more uniaxial increase in pressure. When the pressure medium undergoes a vitrification/solidification, this phase transition is marked by decreased hydrostaticity that leads to poorly controlled, anisotropic pressure gradients on the sample. We call the vitrification/solidification pressure the hydrostatic limit. Many measurements have been done to determine the hydrostatic limit for several liquid media [Gelles, 1968; Piermarini et al., 1973; Sundqvist, 1987; Fukazawa et al., 2007; Klotz et al., 2009].

A pressure study of the Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ system, a system which is highly sensitive to strain, allowed us to measure both the pressure and temperature dependence of two different liquid pressure media. Using the modified Bridgman anvil cell, two main liquid pressure media were used. One was a 1:1 mixture of Fluorinert 70 to 770 (FC70:FC770) and the other was a 1:1 n-pentane : iso-pentane mixture. Past studies of Fluorinert mixtures as a liquid pressure medium used Fluorinert 77, but unfortunately, it is no longer in production. Instead, 3M has created Fluorinert 770 as its equivalent. Subsequent pressure measurements using Fluorinert 770 showed no noticeable differences between it and its predecessor. The hydrostatic limit for Fluorinert 70:770 was found to be near 1 GPa.

The hydrostatic limit for the 1:1 n-pentane : iso-pentane mixture is higher at 6.5 GPa, but it suffers in terms of compressibility. Lower maximum pressures were reached with the 1:1 n-pentane : iso-pentane mixture than with FC70:FC770. Therefore, in some cases, the 1:1 n-pentane : iso-pentane mixture was used for measurements up to ~6.5 GPa and for higher
pressure measurements, the less hydrostatic but also less compressible FC70:FC770 mixture was used.

Liquid media consisting of any of the alcohols were avoided because they dissolved the epoxies that are used to create and define the sample space (see Appendix A for details).

3.3 Components of the modified Bridgman Anvil Cell

The assembled mBAC is shown in Figure 3.5(a). The BeCu body is mounted onto a puck used with the Quantum Design Physical Properties Measurement System (PPMS). This cell was specifically designed to be used with the PPMS. The disassembled cell is shown in Figure 3.5(b).

![Image of mBAC components](image)

Figure 3.5 (a) The modified BAC, assembled and attached to a PPMS puck. The small profile of this pressure cell has been specifically designed for use with a PPMS. (b) The disassembled BAC.

The bottom anvil and sample space is shown in Figure 3.6. Within the sample space, a sample and a lead manometer are placed inside (see Figure 3.4(d) and 3.7). The effects of pressure on the superconducting temperature of lead and several other elements have been well studied over the years [Hake et al., 1958; Eiling and Schilling, 1981; Bireckoven and Wittig, 1988; Suresh and Tallon, 2007] allowing us to use the suppression of \( T_c \) as a manometer (pressure
Values from a study by Bireckoven and Wittig 1988 were used to determine the pressure for all studies in this thesis. Both the lead and the sample have four gold wires (12.5 \( \mu \)m in diameter) attached to them by either spot welding or with silver paint (DuPont 4929N).

![Soldering Pad, Pyrophyllite Gasket, Wire leading through the BeCu down to the PPMS Puck, PPMS Puck]

Figure 3.6 Bottom anvil and sample space of the Bridgman anvil cell. The outer diameter of the grey pyrophyllite gasket is 3.2 mm. Platinum wires connect the outer soldering pads to the sample space inside the gasket. Black square electrical tape holds down the platinum wires.

These gold wires are mechanically connected to platinum (or gold) wires that go through the slits in the pyrophyllite gasket. Figure 3.7 shows the Pb and sample placed within the sample space. The platinum wires are then connected to soldering pads on the circumference outside the anvil face which themselves are connected to the PPMS puck on the bottom of the cell. A more detailed description follows in Appendix A.

### 3.4 Resistivity Measurements

Samples for resistivity measurements were polished (with 2400 grit paper) or cleaved (with a sharp razor) into the desired bar shape. The typical size for the samples used in the mBAC was 700 \( \times \) 150 \( \times \) 30 \( \mu \)m\(^3\). Four gold wires with diameter 12.5 \( \mu \)m were used as electrical leads to the sample. For metallic samples, these wires were attached using a spot welder to directly
weld the gold wires onto the sample. In other cases where spot-welding did not work, silver paint (DuPont 4292N) was used to create the electrical and mechanical connection.

Resistance was measured in a four-wire arrangement (see Figure 3.8) where current is passed through the outer two wires and voltage is measured across the inner two wires. This arrangement ensures that the contact resistance of the electrical wires on the sample are not measured. Even so, efforts were made to reduce the contact resistances as they can heat the sample when current is passed through them and which we want to minimize at very low temperatures. Typically, on metallic samples, pairs of contact resistances were usually near 1 Ω or less. On samples where spot-welding was not possible, the contact resistances were between 10 and 20 Ω and possibly less.

In order to determine the resistivity of the samples \( R = \rho \frac{l}{A} \) where \( R \) is the resistance, \( A \) is the cross section, and \( l \) is the distance between the two inner wires), the dimensions were measured to within a precision of about 6 µm which is half the distance between ticks on a microscope (set to the highest magnification) used to measure these dimensions. Even so, the minute size of the sample dimensions lead to an error of up to 50% for the absolute resistivity. Other factors that contribute to the large error is the width of the silver paint or epoxy used.

Figure 3.7 Sample space of the modified Bridgman anvil cell. The upper bar is the lead manometer and the lower bar is a sample of \( V_7O_{13} \). The top lead sample has gold wires spot welded onto it and the bottom \( V_7O_{13} \) sample has gold wires attached using silver paint (DuPont 4292N)
to make the electrical contacts between the wire and sample as illustrated in Figure 3.8 which causes a large error in $l$. Another factor is the difficulty in polishing or cleaving samples to have perfectly straight edges, thus creating large errors in $th$ and $h$.

Temperature dependent resistance from 2 to 300 K was measured using a PPMS. The AC Transport option was used with a frequency of 17 Hz and a current of 1 mA, unless otherwise stated. In order to measure at even lower temperatures, down to 320 mK, a CRYO Industries of America $^3$He system was used. Resistance measurements in this case were taken using a Lakeshore LS370 resistance bridge with an ac current of 316 $\mu$A and a frequency of 13.7 Hz. The resistance data points are the average of several measurements, sometimes 10 to 300 measurements.

Although both cooling and warming data were taken, only warming data are shown in the figures unless otherwise stated. As the cell is cooled or warmed, there is a small thermal lag between the outer and inner part of the cell. To minimize this in the temperature range of interest, the cell was warmed at a rate of 0.1 to 0.2 K/min (with the PPMS) and even slower with the $^3$He system. At 0.2 K/min we can expect a temperature lag of at most 100 mK.

Further experimental details specific to each of the studies in the following chapters are addressed at the beginning of those chapters.
CHAPTER 4. COMBINED EFFECTS OF PRESSURE AND Ru SUBSTITUTION ON BaFe$_2$As$_2$

4.1 Motivation

Many studies have investigated the effects of electron, hole, and isovalent substitutions in the AEFe$_2$As$_2$ (AE = Alkaline Earth Ca, Sr, Ba) system [Canfield and Bud’ko, 2010; Rotter et al., 2008a, 2010; Kasahara et al., 2010; Kim et al., 2010; Ni et al., 2008, 2010; Sefat et al., 2008, 2009; Chu et al., 2009; Thaler et al., 2010; Ni and Budko, 2011]. For BaFe$_2$As$_2$, in some cases this substitution causes the suppression of the structural/magnetic transition temperature ($T_{sm}$) and the emergence of superconductivity [Canfield and Bud’ko, 2010; Ni et al., 2008, 2010; Rotter et al., 2008a, 2010; Kasahara et al., 2010; Kim et al., 2010]. In other cases, such as substitution of Cr or Mn for Fe, $T_{sm}$ is suppressed without superconductivity ever stabilizing [Kim et al., 2010; Sefat et al., 2009]. For the case of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$, increasing the concentration of isovalent Ru [Thaler et al., 2010], reveals behavior grossly similar to Co substitution [Ni et al., 2008], but for much higher Ru substitution levels and without formally introducing additional charge carriers into the system [Thaler et al., 2010; Rullier-Albenque et al., 2010]. Pressure has also been used as an isoelectronic tuning mechanism [Colombier et al., 2009b; Matsubayashi et al., 2009a; Ishikawa et al., 2009; Duncan et al., 2010; Yamazaki et al., 2010; Torikachvili et al., 2008a,b; Alireza et al., 2009; Kotegawa et al., 2009]. As pressure is applied to these systems, $T_{sm}$ is suppressed gradually and disappears at a critical pressure, $P_c$. The superconducting temperature ($T_c$) reaches its maximum value and the transition width is narrowest near $P_c$ [Colombier et al., 2009b, 2010].

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Although Ru substitution for Fe gives rise to an increase of the unit cell volume, the c-lattice parameter and the ratio of the c-lattice parameter to the a-lattice parameter (c/a) both decrease with increasing Ru concentration [Thaler et al., 2010]. Using pressure dependent crystallographic data for BaFe$_2$As$_2$ [Kimber et al., 2009], it was shown by Thaler et al. [Thaler et al., 2010] that the ambient pressure T – x phase diagram for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ and T – P phase diagram for BaFe$_2$As$_2$ manifest similar features and can be scaled to each other [Thaler et al., 2010], by creating a T versus c/a phase diagram. This scaling is not universal, though: for BaFe$_2$(As$_{1-x}$P$_x$)$_2$, $T_{sm}$ and $T_c$ scale better with changes in c than with changes in c/a [Thaler et al., 2010]. In order to better quantify and understand the similarities between the effects of Ru substitution and pressure, we have determined the T – P phase diagrams for multiple Ru substitution levels and explored the possibility of a universal scaling between these isoelectronic tuning mechanisms.

In addition, it is well known that the behavior of BaFe$_2$As$_2$ is sensitive to pressure conditions [Colombier et al., 2009b; Matsubayashi et al., 2009a; Ishikawa et al., 2009; Duncan et al., 2010]. Pressure inhomogeneities (uniaxial in the Bridgman pressure cells) associated with non-hydrostatic conditions tend to decrease the pressure needed to suppress $T_{sm}$ and induce superconductivity. This sensitivity causes discrepancies in the construction of the T – P phase diagram. Therefore, conditions as close to hydrostatic as possible are necessary for consistent results. In this study, a piston-cylinder cell and a modified Bridgman cell with appropriate liquid media were used to measure the resistivity of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ samples under pressure. A maximum pressure of 7.4 GPa was achieved. Although parent BaFe$_2$As$_2$ has already been measured several times under various pressure conditions [Colombier et al., 2009b; Matsubayashi et al., 2009a; Ishikawa et al., 2009; Duncan et al., 2010; Yamazaki et al., 2010], it was measured again under the same conditions as the Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ samples in order to allow for more reliable comparisons as well as to gauge the level of hydrostaticity of the liquid medium. We find a remarkably simple scaling between pressure and Ru substitution: 3 GPa of applied pressure affects the phase diagram in a manner similar to 10% Ru substitution for Fe.
4.2 Experimental methods

All Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ single crystals measured in this study were grown out of self flux using the method described by Thaler, *et al.* [Thaler et al., 2010].

Due to the small dimensions of the samples used in the modified Bridgman anvil cell, resistivity values can have errors of up to 50%. Furthermore, the micaceous nature of the crystals makes them prone to exfoliation, a tendency which is compounded by the inevitable damage inflicted by the cleaving and cutting done to shape them into the appropriate dimensions. Great care was taken to choose samples with as few of these defects as possible, but it is possible that under pressure, the layers could be compressed or further distorted, leading to changes in the strains in the sample resulting in small jumps or changes in resistivity values. So as to provide a better view of the evolution of the sample behavior with pressure, the piston cylinder cell data (collected by Professor Milton Torikachvili) were normalized so that the ambient temperature and pressure resistivity value matched that of the corresponding mBAC sample.

Figure 4.1 shows the $T - x$ phase diagram for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ [Thaler et al., 2010]. The open symbols and arrows indicate the Ru concentrations that were chosen for this study in order to explore the low-$x$ and optimal-$x$ regions of the phase diagram. The criteria for $T_c$ are shown in Figure 4.2(b). The onset $T_c$ was taken as the intersection of the extrapolated lines seen in the inset of Figure 4.2(b). The temperature at which the resistivity reaches zero as seen in Figure 4.2(b) is denoted as $T_{c,\rho=0}$.

Strain induced, granular/filamentary superconductivity is known to occur in many of the AEFe$_2$As$_2$ systems [Torikachvili et al., 2008b; Kogawa et al., 2009; Saha et al., 2009; Hu et al., 2011]. To gauge the impact of this effect on the superconducting phase transition, current dependent resistivity measurements were done at various pressures. Figure 4.3 shows two such measurements. At 3.64 GPa (Figure 4.3(a)) only the onset of the superconducting transition is seen and there is a definite dependence on the applied current which suggests that granular/filamentary superconductivity is responsible for the resistance decrease. At 6.21 GPa (Figure 4.3(b)) this current dependent behavior is less prominent, but still seen during the superconducting transition. The difference in the zero resistivity temperature of the super-
conducting transition between 0.01 mA and 1 mA of applied current is $\sim 3$ K. Based on the assumption that the effects of filamentary superconductivity will be suppressed by higher current densities (partially due to heating of the sample), a 1 mA current was used for all measurements.

### 4.3 Results

#### 4.3.1 BaFe$_2$As$_2$

Previous pressure measurements of BaFe$_2$As$_2$ with a modified Bridgman cell have been reported [Colombier et al., 2009b; Ishikawa et al., 2009] using a mixture of 1:1 Fluorinert 70 : Fluorinert 77 as the liquid pressure-transmitting medium. The hydrostatic limit for this medium is $\sim 1$ GPa [Sakai et al., 1999], thus an additional, poorly-controlled, small, uniaxial stress component along the samples’ c-axis is likely at higher pressures. Due to the sensitivity of BaFe$_2$As$_2$ to uniaxial stress, a different liquid medium, a mixture of 1:1 n-pentane : iso-pentane, with a higher hydrostatic limit of 6.0 GPa (see Appendix A) was used in this study.
Figure 4.2 Temperature dependence of the resistivity of BaFe$_2$As$_2$ for pressures up to 5.32 GPa measured using the modified Bridgman cell. (a) Measurements are shown for temperatures up to 300 K. Inset shows criteria used for the determination of $T_{sm}$. (b) Same measurements shown for temperatures up to 70 K with criterion used for $T_{c,\rho=0}$. Inset shows the criterion used for $T_{c,onset}$. [Kim et al., 2011]
Two samples of BaFe$_2$As$_2$ were measured using the Bridgman cell: one measured up to 5.32 GPa (Figure 4.2) and the other up to 6.71 GPa (not shown). The ambient pressure resistivity of BaFe$_2$As$_2$ decreases on cooling. At $\sim 134$ K, the sample undergoes a structural/magnetic transition where it converts from a high temperature tetragonal, paramagnet to a low temperature, orthorhombic, antiferromagnet. As pressure is applied, the resistivity decreases and the structural/magnetic transition moves to lower temperatures and at high enough pressures, broadens. In addition, a small downturn arises at low temperature as a precursor to the superconducting transition. This increasingly kink-like feature is reminiscent of the pressure induced, granular/filamentary, superconducting behavior of SrFe$_2$As$_2$ [Colombier et al., 2009b] and CaFe$_2$As$_2$ [Torikachvili et al., 2008b]. A current dependent resistivity measurement at 3.64 GPa (Figure 4.3(a)) suggests that superconductivity in a small fraction of the sample, most likely due to internal strains, precedes the occurrence of a more robust superconducting state, when $\rho(T)$ is much less sensitive to the excitation current, as shown in Figure 4.3(b).

The resistive feature associated with the structural/magnetic transition is suppressed with pressure but still persists at the maximum pressure of 6.4 GPa even with the emergence of a finite $T_{c,\rho=0}$ at $\sim 5$ GPa. The structural/magnetic transition temperatures for BaFe$_2$As$_2$ were taken as the maximum of the derivative of the resistivity shown in the inset of Figure 4.2(a). The general form of the phase diagram is not very dependent on the hydrostaticity of the pressure, however, the features in the phase diagram shift towards higher pressure as hydrostaticity is improved [Colombier et al., 2009b; Matsubayashi et al., 2009a; Ishikawa et al., 2009; Duncan et al., 2010; Yamazaki et al., 2010]. The phase diagram for pure BaFe$_2$As$_2$ using the 1:1 n-pentane : iso-pentane mixture is shown in Figure 4.4 and show qualitatively similar behavior with a quantitative shift of about 1.5 GPa in the transition temperatures at the highest pressures for Run 2. Unfortunately, it is these last three, highest pressure, data points that are associated with manometer inconsistencies that may be associated with over estimating the actual pressure experienced by the sample. The phase diagram presented in Figure 4.4 is in qualitative agreement with previous measurements of BaFe$_2$As$_2$ under pressure in a Bridgman cell using the 1:1 FC70 : FC770 mixture [Colombier et al., 2010], but with all transition temperatures shifted to higher pressures for the 1:1 n-pentane : iso-pentane mixture.
Figure 4.3 Resistivity measurements of BaFe$_2$As$_2$ with applied currents of 0.01, 0.1, and 1 mA at (a) 3.64 GPa and (b) 6.21 GPa. [Kim et al., 2011]
4.3.2 \textbf{Ba(Fe_{0.91}Ru_{0.09})_2As_2}

As shown in Figure 4.4, for pure BaFe\textsubscript{2}As\textsubscript{2}, superconductivity is just being stabilized in the $P \sim 5$ GPa range, while the resistive signature of the structural/magnetic transition remains visible up to our highest measured pressures. For the first Ru concentration in this study, we chose $x = 0.09$ which has no bulk superconductivity and an approximately 35 K suppression of $T_{sm}$ ($\sim 98$ K) from that of parent BaFe\textsubscript{2}As\textsubscript{2} ($T_{sm} = 134$ K).

Two samples of Ba(Fe$_{0.91}$Ru$_{0.09}$)$_2$As$_2$ were measured: one with the piston cylinder cell up to 1.83 GPa and another with the Bridgman cell up to 4.94 GPa (Figure 4.5). Figure 4.5 shows the effects of pressure on the resistivity of Ba(Fe$_{0.91}$Ru$_{0.09}$)$_2$As$_2$ samples.

With increasing pressure, $T_{sm}$ is gradually suppressed to lower temperatures and granular/filamentary superconductivity develops and gradually shorts out more of the sample. When zero resistivity is achieved, with 3.16 GPa of pressure, a small feature due to the structural/magnetic transition can still be observed, suggesting that the suppression of the structural/magnetic transition is not complete. Further pressure increase almost completely
suppressed the structural/magnetic transition and increased $T_{c,\rho=0}$ to a value of 25.7 K at $P_c = 4.94$ GPa. The superconducting transition width also decreased with pressure. At this critical pressure, there is no measurable current dependence of the resistivity curve, suggesting the development of bulk superconductivity. As will be seen for higher Ru substitutions, these features are consistent with $P_c \approx 5$ GPa for this sample.

A phase diagram constructed from these measurements can be seen in Figure 4.6. For all Ru substituted samples that were measured, $T_{sm}$ was taken as the minimum of the resistivity derivative. Error bars were taken as the full width at half maximum where possible, typically when the structural/magnetic transition was far removed from the superconducting transition. When $T_c \lesssim T_{sm}$ and effectively truncates the lower-temperature part of the $d\rho/dT$ curve, twice the half width at half maximum was used. An example of these criteria can be seen in Figure 4.5(c) and 4.5(d). As $T_{sm}$ is suppressed, the minimum of $d\rho/dT$, which was used to determine $T_{sm}$ becomes broader and, near $P_c$, becomes indistinguishable from the onset of $T_c$. The phase diagram shows a consistent qualitative behavior with $T_{sm}$ decreasing with pressure and a superconducting $T_c$ dome arising at higher pressures; the addition of $x = 0.09$ Ru simply shifts $P_c$ and the superconducting dome to lower pressures.

### 4.3.3 Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$

Measurements of $\rho(T,P)$ were carried out on three samples of Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$: one with the piston cylinder cell up to 2.30 GPa and two with the Bridgman cell with maximum pressures of 1.57 GPa and 4.97 GPa. As shown in Figure 4.1, Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$ also resides on the low-$x$ side of the $T - x$ phase diagram, but with a further reduction of the structural/magnetic phase transition and much closer proximity to the superconducting dome. Ambient pressure resistivity measurement (Figure 4.7) of Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$ shows both the structural/magnetic transition as well as the onset of superconductivity. Added pressure decreases $T_{sm}$ and a finite $T_{c,\rho=0}$ is achieved with 1.57 GPa of pressure. A maximum $T_{c,\rho=0}$ of 23 K is achieved with 3.57 GPa and the narrowest superconducting transition width is realized at 4.09 GPa with a $T_{c,\rho=0}$ of 22.9 K and width of $\Delta T_c \sim 0.4$ K. At 4.09 GPa, the structural/magnetic transition has all but disappeared. Further pressure increase causes the
Figure 4.5  Temperature dependence of the resistivity of Ba(Fe$_{0.91}$Ru$_{0.09}$)$_2$As$_2$ up to 1.83 GPa and 4.94 GPa using a piston cylinder cell and a Bridgman cell, respectively. (a) Shown for temperatures up to 300 K. The 0.66, 1.50, and 1.83 GPa measurements have been shifted down by 0.035, 0.045, and 0.06 mΩ cm, respectively, for clarity. (b) Shown for temperatures up to 35 K. (c) and (d) Criteria used to determine $T_{sm}$ and their corresponding error bars. [Kim et al., 2011]
structural/magnetic transition to disappear completely, a decrease in $T_{c,i}$, and a broadening of the superconducting transition.

For the low pressure, piston cylinder cell measurements, the structural/magnetic transition at 0.5 GPa is broader than at 0.9 GPa and $T_{c,onset}$ is also higher. One possible cause of this is that the first pressurization could have caused strains in the sample due to a small increase in pressure from constrictions and contractions of the cell from the first cooling and warming of the cell. Of greater concern is the fact that there are noticeable differences between measurements done in the piston cylinder and the Bridgman cell. For the 1.53 GPa and 2.30 GPa measurements from the piston-cylinder cell and 1.57 and 2.41 GPa measurements from the Bridgman cell, the corresponding sets of the temperature dependent resistivity data overlap well from room temperature down to $\sim 150$ K, below which the resistivity of the sample in the Bridgman cell is suppressed much faster. Furthermore, in this pressure range, the Bridgman cell measurements manifest a sharp superconducting transition whereas, for the piston cylinder cell, the transition is wider and does not reach $\rho = 0$ even at the base temperature of 1.8 K. In addition,
Figure 4.7  Temperature dependence of the resistivity of Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$ up to 2.30 and 4.97 GPa measured using the piston cylinder cell and the modified Bridgman cell, respectively. (a) Shown for temperatures up to 300 K. (b) Shown for temperatures up to 30 K. [Kim et al., 2011]
the $T_{c,\text{onset}}$ values are consistently lower in the piston cylinder cell than in the Bridgman cell and the rate of suppression of $T_{sm}$ is smaller in the piston cylinder cell. These differences suggest a slight disparity in the degree of hydrostaticity between the piston cylinder cell with the 4:6 mineral oil:n-pentane mixture and the Bridgman cell, using the 1:1 n-pentane : iso-pentane mixture. At 2 GPa, it is expected that the vitrification/solidification temperature for the 4:6 mineral oil:n-pentane mixture is near 227 K and for the 1:1 n-pentane : iso-pentane mixture, near 169 K (see Appendix A) which is both above $T_{sm}$. In the $x = 0.09$ Ru measurements, these differences were also seen, although smaller. Despite these discrepancies, the combined phase diagram shown in Figure 4.8 demonstrates rather good agreement between measurements taken with these two cells. Another possibility is that there might be a marginal sample to sample discrepancy within this batch of materials, however, the nearly similar $T_{sm}$ and $T_c$ suggest that this is a small difference.

Figure 4.8  $T – P$ Phase Diagram for measurements of Ba(Fe$_{0.84}$Ru$_{0.16}$)$_2$As$_2$. Open and solid symbols indicate measurements using the piston cylinder cell and the modified Bridgman cell, respectively. [Kim et al., 2011]
4.3.4 \( \text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_{2}\text{As}_{2} \)

\( \text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_{2}\text{As}_{2} \) is very close to the optimal Ru concentration (see Figure 4.1). At higher Ru concentrations, the homogeneity of the Ru substitution starts to vary within the batch of samples, as reported by Thaler, et al. [Thaler et al., 2010]. Figure 4.9 shows the results of resistivity measurements for the samples used in the piston cylinder cell and the Bridgman cell for pressures up to 1.12 and 7.39 GPa, respectively, both using the 1:1 n-pentane : isopentane mixture. At ambient pressure, \( \text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_{2}\text{As}_{2} \) samples show a coexistence of both the structural/magnetic transition and superconductivity. The ambient pressure \( T_{c} \) for the two samples used in the cells differ by \( \sim 1 \) K. A maximum \( T_{c,\rho=0} \) of 20.3 K was achieved with only 2.27 GPa and also has the narrowest transition width at this pressure. Further pressure increases causes the suppression of \( T_{c} \) and a widening of the transition width.

The phase diagram for \( \text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_{2}\text{As}_{2} \) is shown in Figure 4.10. \( T_{sm} \) in the piston cylinder cell \( (P < 1.2 \text{ GPa}) \) is only weakly affected by pressure, whereas by \( P = 2.27 \text{ GPa} \) (the first finite pressure in the Bridgman cell) \( T_{sm} \) was significantly decreased. As with other substitution levels, \( T_{c}(P) \) forms a dome-like region with the highest and sharpest \( T_{c} \) found near \( P_{c} = 3.28 \text{ GPa} \).

4.3.5 \( \text{Ba(Fe}_{0.72}\text{Ru}_{0.28})_{2}\text{As}_{2} \)

\( \text{Ba(Fe}_{0.72}\text{Ru}_{0.28})_{2}\text{As}_{2} \), having optimal Ru concentration, shows no structural/magnetic transition at ambient pressure and the superconducting transition is relatively sharp with \( T_{c} \sim 16 \text{ K} \) and the transition width \( \Delta T_{c} \sim 0.7 \text{ K} \). Added pressure marginally increases \( T_{c,\text{onset}} \) and in fact widens the transition width with \( T_{c,\rho=0} \) decreasing as shown in Figures 4.11 and 4.12. The superconducting onset and zero resistivity temperatures show very little scatter compared to low pressure measurements on the other Ru substituted samples.

4.4 Discussion

Previous pressure studies have shown that \( \text{BaFe}_{2}\text{As}_{2} \) and related compounds are sensitive to the degree of non-hydrostaticity of the pressurized environment [Colombier et al., 2009b;
Figure 4.9  Temperature dependence of the resistivity of \( \text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_2\text{As}_2 \) up to 1.12 and 7.39 GPa measured using the piston cylinder cell and the modified Bridgman cell, respectively. (a) Shown for temperatures up to 300 K. (b) Shown for temperatures up to 30 K. [Kim et al., 2011]
Figure 4.10  $T - P$ Phase Diagram for measurements of $\text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_2\text{As}_2$. Open and solid symbols indicate measurements using the piston cylinder cell and the modified Bridgman cell, respectively. [Kim et al., 2011]

Matsubayashi et al., 2009a; Ishikawa et al., 2009; Duncan et al., 2010; Yamazaki et al., 2010]. Empirically, increasingly hydrostatic environments move $T_{sm}$ and $T_c$ to higher pressures on the $T - P$ phase diagram. Having the pressure-transmitting medium still be a liquid at room temperature when pressure is increased reduces the degree of uniaxial stress on the sample. In such cases any non-hydrostaticity is caused on cooling and warming by the differential thermal contractions of the various components of the cell below the vitrification/solidification temperature (the temperature below which the liquid medium changes into a glass or solid).

For measurements taken with the piston cylinder cell using the 4:6 light mineral oil : n-pentane mixture, the superconducting onsets were broader and more rounded than those taken with the Bridgman cell using the 1:1 n-pentane : iso-pentane mixture. This is expected since the samples for the piston cylinder cell were typically twice as long as those for the Bridgman cell. Longer samples are more vulnerable to pressure inhomogeneities due to the larger region across which strain gradients can occur and may be the likely the cause of the broader superconducting transitions and rounded features.
Figure 4.11  Temperature dependence of the resistivity of $\text{Ba}$(Fe$_{0.72}$Ru$_{0.28}$)$_2$As$_2$ up to 2.22 GPa measured using the piston cylinder cell (a) Shown for temperatures up to 300 K. (b) Shown for temperatures up to 20 K. [Kim et al., 2011]
Figure 4.12  $T - P$ Phase Diagram for measurements of Ba(Fe$_{0.72}$Ru$_{0.28}$)$_2$As$_2$ using the piston cylinder cell.

Figure 4.13  Combined phase diagram for all Ru concentrations. Open and closed symbols are transitions temperatures from measurements using the piston cylinder cell and Bridgman cell, respectively. Lines are guides for the eyes. [Kim et al., 2011]
The effect of strain gradients and or internal crystallographic strain [Saha et al., 2009] (associated with dislocation and other mechanically induced defects) on the samples can also be invoked to explain the relatively low pressure sensitivity of the $T_{c,\text{onset}}$ line in the phase diagrams. Given that $T_{c,\rho=0}$ forms a fairly well defined, pressure dependent dome-like region, $T_{c,\text{onset}}$ can be understood in terms of an effective internal strain gradient over some region of the sample, equivalent to several GPa. With such a gradient, a wide distribution of the $T_c$ values could exist leading to a fairly pressure insensitive $T_{c,\text{onset}} \sim T_{c,\text{max}}$. This is precisely what is seen here as well as in SrFe$_2$As$_2$ [Saha et al., 2009] and inferred by Nakashima, et al. [Nakashima et al., 2010]. Based on this premise, we pay far greater attention to $T_{c,\rho=0}(P)$.

All of the $T – P$ phase diagrams for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ are shown together in Figure 4.13. Although the suppression of $T_{sm}$ with increasing Ru concentration and pressure is clear, as is the stabilizing of the superconducting region, this plot does not clearly reveal any other unifying trends.

In the earlier study of Ru substitution in BaFe$_2$As$_2$ [Thaler et al., 2010], a comparison was made between the $T – x$ phase diagram and the $T – P$ phase diagram of the parent compound. We make the same comparison here, in Figure 4.14, with measurements taken with the 1:1 n-pentane : iso-pentane. Although the full superconducting dome was not determined under pressure for pure BaFe$_2$As$_2$, by overlapping the $T_{sm}$ suppression curve, it is readily seen that 3 GPa is grossly comparable to $x = 0.10$ Ru substitution for these pressure conditions. It should be noted that for the Fluorinert 70 : Fluorinert 77 pressure medium used in the Bridgman cell used in previous studies [Thaler et al., 2010; Colombier et al., 2009b], this relation was close to 2 GPa to $x = 0.10$ Ru. Clearly this relationship depends on multiple factors, most likely associated with non-hydrostatic pressure components due to the freezing of the liquid medium.

Using this relation between pure BaFe$_2$As$_2$ under pressure and Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ at ambient pressure, a more revealing, composite phase diagram can be created by shifting the $T – P$ phase diagrams for the various Ru concentrations according to the ratio 3 GPa:$x = 0.10$ Ru. When this is done (see Figure 4.15), the data form a much more consistent picture with $T_{sm}$ and $T_c$ manifolds lying roughly on top of each other. It is important to point out that although the pressure:Ru concentration ratio was based on $T_{sm}$ normalization, the $T_{c,\rho=0}$ data fall onto
Figure 4.14 Comparison of the $T - x$ phase diagram for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ from a previous study [Thaler et al., 2010] and $T - P$ phase diagram of BaFe$_2$As$_2$ with a ratio of 3 GPa to $x = 0.10$ Ru relating the two horizontal axes. The $T_{c,offset}$ for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ was determined from the maximum slope of the superconducting transition in the resistivity data. [Kim et al., 2011] a fairly consistent manifold as well. Figure 4.15 demonstrates that for all Ru concentrations that were studied, only a single scaling, 3 GPa for $x = 0.10$ Ru, is necessary to line up the phase diagrams. This means that the effects of pressure and Ru substitution on BaFe$_2$As$_2$ are additive in a simple manner across the whole phase diagram. It must be emphasized, though, that this scaling value, 3 GPa $\sim 0.1 \times$ Ru, is associated with a specific pressure media; for the 1:1 FC70 : FC770 mixture used by Colombier, et al. [Colombier et al., 2009b], the scaling is 2.2 GPa$\sim 0.1 \times$ Ru, and, using data from Yamazaki et al. [Yamazaki et al., 2010], a scaling of 5 GPa$\sim 0.1 \times$ Ru can be inferred.

Whereas both pressure and Ru substitution are nominally isoelectronic, a similar composite phase diagram can be assembled from $T - x - P$ data collected on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ samples [Colombier et al., 2010]. In this non-isoelectronic case, a scaling of 0.8 GPa:$x = 0.01$ Co gives the best collapse of the data onto single $T_{sm}$ and $T_c$ manifolds. This result implies that the additive nature of doping and pressure may not be limited to isoelectronic substitutions.
Figure 4.15 Phase diagram of all Ru concentrations each shifted by 3 GPa for every $x = 0.10$ Ru substitution. Open and closed symbols are transitions temperatures from measurements using the piston cylinder cell and Bridgman cell, respectively. [Kim et al., 2011]

Another way of seeing the effect of pressure on the Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ system, is to plot the maximum $T_{c, \rho=0}$ on the ambient pressure $T - x$ phase diagram, (Figure 4.16). Because $P_c$ was not reached with parent BaFe$_2$As$_2$, with this pressure medium, we use the maximum value reported by Colombier, et al. as an estimate [Colombier et al., 2009b]. For the lower-than-optimal Ru substituted samples, as pressure suppresses the structural/magnetic transition, $T_c$ dramatically increases, as was the case for Co substituted BaFe$_2$As$_2$ [Colombier et al., 2010]. On the other hand, if $T_{sm}$ has already been suppressed, by either Co or Ru substitution, pressure no longer increases $T_c$, but rather suppresses it. This is consistent with the idea that long range structural/magnetic ordering is detrimental for superconductivity and is the primary reason $T_c$ is low or absent in sub-optimally substituted samples.

Figures 4.15 and 4.16 bring up an interesting question, perhaps a key one: Do Ru sub-
Figure 4.16  Comparison of $T - x$ phase diagram and the maximum $T_{c,\rho=0}$ achieved with pressure at various Ru concentrations. Solid stars are $T_{c,\text{max}}$ values from this study. The open star is the $T_{c,\text{max}}$ reported by Colombier, et al. [Colombier et al., 2009b]. [Kim et al., 2011]

Substitution and pressure produce similar phase diagrams via similar or different mechanisms? At a gross level the reason for the similarity is the same: suppression of $T_{sm}$ leads to an increase in $T_c$, as has been observed for a wide range of transition metal substitutions [Canfield and Bud’ko, 2010]. Both Ru substitution and pressure suppress $T_{sm}$. The question becomes whether this is accomplished via similar or different mechanisms. Whereas it is fairly certain that pressure can only change details of the band structure (such as nesting or density of states near the Fermi surface), the effects of Ru substitution are harder to predict. Although there was an initial claim that Ru substitution may change the band structure [Rullier-Albenque et al., 2010], more recent work indicates that this is not the case [Dhaka et al., 2011]. Instead, it seems more likely that Ru substitution may suppress the magnetic transition temperature by replacing Fe with a far less magnetic Ru ion. Angle-resolved photoemission study [Dhaka et al., 2011] of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ for $x$ up to 0.55 indicated very little change in the Fermi surface and density of states at the Fermi level for different Ru concentrations. The implication
is that the nested property of the Fermi surface may be retained and that another mechanism is causing the suppression of the AFM order. In a simple Stoner picture, the magnetic moment can depend on a product of density of states and on-site repulsion. Ru seems the change the latter whereas pressure will not significantly change the on-site term for Fe. In this light, Ru substitution is likely a less dramatic example of substituting Y or Lu for \( R = \text{Gd-Tm} \) in a rare earth intermetallic compound [Wiener et al., 2000], perhaps involving Stoner enhancement, rather than local moments.

### 4.5 Conclusion

Pressure measurements have been carried out on the \( \text{Ba(Fe}_{1-x}\text{Ru}_x)\text{As}_2 \) system. The resulting phase diagrams show a suppression of \( T_{sm} \) and an enhancement of \( T_c \) up to \( P_c \) where we see the narrowest superconducting transition, \( T_{c,max} \), and the disappearance of \( T_{sm} \) by the addition of pressure for under-doped compounds. For the optimal Ru concentrations, further pressure increases beyond \( P_c \) lowers \( T_c \) and broadens the superconducting transition. Comparisons between the \( \text{Ba(Fe}_{1-x}\text{Ru}_x)\text{As}_2 \) \( T - x \) phase diagrams indicate an additive correlation between physical pressure and Ru substitution of 3 GPa to \( x = 0.10 \) Ru concentration. A comparison between \( T_{c,max} \) and the \( T - x \) phase diagram indicate that suppression of the structural/magnetic transition is necessary for superconductivity to reach its maximum \( T_c \) values.
CHAPTER 5. EVOLUTION OF THE ELECTRONIC TRANSPORT PROPERTIES OF V$_6$O$_{11}$ and V$_7$O$_{13}$ UNDER PRESSURE$^1$

5.1 Motivation

As discussed in Chapter 1, V$_2$O$_3$ and VO$_2$ are classic manifestations of materials with metal to insulator transitions. In these and other systems with MI transitions, pressure is used to tune the system, often suppressing $T_{MI}$. For V$_2$O$_3$, with an ambient pressure $T_{MI} = 176$ K on warming, applied pressure causes a decrease in $T_{MI}$, with it being fully suppressed by 2.6 GPa [McWhan and Rice, 1969]. For $P \geq 2.6$ GPa, quadratic behavior is seen in the low temperature resistivity. On the other hand, VO$_2$ has a MI transition at $T_{MI} = 340$ K and no magnetic ordering was observed down to low temperatures [Berghlund and Guggenheim, 1969; Mott, 1990; Kachi et al., 1973]. With applied pressure, the $T_{MI}$ was seen to increase linearly at 0.82 K/GPa [Berghlund and Jayaraman, 1969].

Combining the structural and pressure tuning, the effect of pressure on several of the Magnéli series compounds (which are series of transition metal oxides with a stoichiometric ratio of TM$_n$O$_{2n-1}$ [Magnéli, 1948; Schwingenschlögl and Eyert, 2004]) have already been studied [Ásbrink and Malinowski, 1987; Canfield et al., 1990b,a; Canfield, 1990; Ueda et al., 2003; Sidorov et al., 2003; Perucchi et al., 2008]. Systematic studies by Canfield et al. [Canfield et al., 1990b,a; Canfield, 1990] measured the transport properties of V$_n$O$_{2n-1}$ ($n = 4 - 8$) for pressures $P < 2$ GPa. $T_{MI}$ was found to decrease with pressure to varying degrees for $n = 4, 5, 6$, and 8. For V$_7$O$_{13}$ the $T_N$ also decreased with increasing pressure at a rate of -7.5 K/GPa [Canfield et al., 1990b]. Particularly interesting was V$_8$O$_{15}$ where $T_{MI}$ could be fully suppressed.

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by these modest pressures, revealing the same resistive antiferromagnetic (AFM) signature that was seen in V_7O_{13}. This discovery suggested that the spin density wave-like order in V_7O_{13} was not anomalous, but was in fact a general feature of the V_nO_{2n-1} system.

Pressure studies of V_7O_{13} that were initially performed up to 2 GPa [Canfield et al., 1990b,a; Canfield, 1990] and later extended up to 3.5 GPa [Ueda et al., 2003] have shown that the AFM transition temperature steadily decreases with applied pressure until, near 3.4 GPa, it disappears in measurements down to 1.7 K. Near this critical pressure (P^c_{AFM}), Ueda et al. [Ueda et al., 2003] found a T^{3/2} dependence for resistivity at base temperatures, indicating non-Fermi Liquid behavior near a quantum critical point (QCP). V_8O_{15}, also measured under pressure up to 3.5 GPa, showed a suppression of its MI transition with pressure until at 1.34 GPa, where the MI transition disappeared and revealed a feature associated with AFM ordering. Further increase of pressure suppressed this feature until at P^c_{AFM} = 3.4 GPa, where it is driven to T = 0. For V_8O_{15}, continued T^2 dependence was seen at low temperatures near the AFM critical pressure [Ueda et al., 2003].

In order to further study the effects of pressure on the V_nO_{2n-1} series, in this work we present high pressure (P < 8 GPa) measurements of the electrical resistivity of V_6O_{11} and V_7O_{13} for 0.3 < T < 300 K. For V_6O_{11} we find that the MI transition can be suppressed to zero by P \approx 3.8 GPa and that the behavior of \rho(T,P) is consistent with the suppression of a first order phase transition to zero rather than a second order one. As T_{MI} is suppressed, though, no features associated with AFM ordering were seen to emerge. For V_7O_{13}, the spin density wave-like transition can be suppressed to zero by P^c_{AFM} \sim 3.5 GPa and the behavior of \rho is consistent with a second order transition being driven to zero, with the coefficient A, of \rho \propto AT^2, diverging at P^c_{AFM}. Finally we can create a composite phase diagram for V_6O_{11}, V_7O_{13}, and V_8O_{15} that provides some rationalization for why V_6O_{11} does not manifest the SDW-like state seen in V_7O_{13} and V_8O_{15}.

5.2 Experimental methods

The V_6O_{11} and V_7O_{13} single crystals were prepared in a two step process. First, stoichiometric mixtures of powdered V_2O_3 and VO_2 were reacted to form polycrystalline V_6O_{11} or
V$_7$O$_{13}$. Then the polycrystalline material was ground and mixed with a few tens of mg of TeCl$_4$ and sealed in an evacuated quartz tube. The tube was placed horizontally in a thermal gradient furnace where the end of the tube with starting material is kept near 1050 °C and the other side set to be near 950 °C. Several weeks were needed to grow the single crystals [Nagasawa et al., 1969; Canfield, 1990].

Given the subtle differences in the powder x-ray diffraction spectra of the large unit cells of triclinic V$_6$O$_{11}$ and V$_7$O$_{13}$, and given the distinct ordering temperatures and phase transitions of the various V$_n$O$_{2n-1}$ members [Okinaka et al., 1970; Keer et al., 1977; Kosuge et al., 1972; Canfield, 1990; Canfield et al., 1990b], temperature dependent resistance and magnetization were used to confirm the characteristic features of the V$_6$O$_{11}$ and V$_7$O$_{13}$ samples. These measurements were conducted in a Quantum Design Physical Properties Measurement System (PPMS) and a Magnetic Properties Measurement System (MPMS) respectively.

Two sets of pressure measurements were done, one with a 1:1 mixture of Fluorinert 70 and Fluorinert 770 (FC70 : FC770) serving as the liquid pressure medium and the other with a 1:1 mixture of n-pentane and iso-pentane. For V$_7$O$_{13}$, the 1:1 n-pentane : iso-pentane mixture was used to see if the degree of hydrostaticity of the medium had measurable effects.

When measuring V$_6$O$_{11}$, the ambient pressure structural transition at 170 K often destroyed the samples, making them unusable for further measurements. This is most likely caused by the strains associated with changing V-V bond lengths as the MI transition occurs. Of the V$_n$O$_{2n-1}$ family, V$_6$O$_{11}$ exhibits the largest such change with a V-V bond length expanding by $\sim$ 0.5 Å on cooling through $T_{\text{MI}}$ [Canfield, 1990]. Fortuitously, even a small amount of hydrostatic pressure seems to prevent the sample from irreversibly cracking during the structural transition, allowing for measurements under pressure [Canfield, 1990]. In order to work around this structural degradation at ambient pressure, a V$_6$O$_{11}$ crystal was polished into a long rectangular rod and separated into several pieces, one of which was used for a preliminary resistance measurement. As a result of this, for V$_6$O$_{11}$, the ambient pressure resistivity curve could not be measured beforehand for all sets of pressure measurements (each set denoted as cell 1, 2, and so on). However, for cell 1 after several pressure measurements, the V$_6$O$_{11}$ sample survived the depressurization process and was then used to measure the ambient pressure, temperature
dependent resistivity. This provided the only full temperature range measurement of \(V_6O_{11}\) at ambient pressure that could be compared to higher pressure measurements. \(V_6O_{11}\) samples from all other pressure measurements were lost when the sample space was depressurized. For \(P \gtrsim 3\) GPa, the suppression rate of the ambient temperature resistivity values with respect to pressure were fairly consistent, at close to \(-6 \times 10^{-6}\) Ω cm GPa\(^{-1}\). Thus, all \(V_6O_{11}\) measurements were normalized to cell 1. This was done by having the ambient temperature resistivity of the initial pressure measurement of each cell normalized to a linear interpolation of the same value from the pressure measurements of cell 1. For the few \(P < 3\) GPa measurements, these curves were also normalized to cell 1 in a similar manner, except the rate of suppression of the resistivity value for cell 1 was only defined by two points, one at ambient pressure and one at 3.52 GPa.

For resistivity measurements of \(V_6O_{11}\) at \(P = 0.84\) and 1.64 GPa, at least one of the contacts on the sample was electrically connected to the pressure cell itself. This likely contributed to the measured negative slope of \(\rho(T)\) of the sample for these two pressures. However, at these low pressures, only \(T_{MI}\) was determined from these data.

\(V_7O_{13}\) remains metallic and avoids the structural phase transition associated with the MI transitions found for the rest of the series, thus allowing for ambient pressure resistivity measurements for all samples. A comparison of the \(R/R(300\ \text{K})\) for all the samples at ambient pressure shows the curves very nearly lying on top of each other. Therefore, all sets of \(V_7O_{13}\) measurements were normalized to that of one set by having the ambient pressure and temperature resistivity of each cell multiplicatively normalized to that of one cell and this normalization factor was propagated to the resistivity measurements under pressure.

5.3 Results

5.3.1 \(V_6O_{11}\)

The ambient pressure, temperature dependent resistivity for \(V_6O_{11}\) can be seen in Figure 5.1(a) for cooling and warming. This measurement was taken using a sample that was retrieved after being measured under several pressures up to 5.44 GPa. A comparison of cool-
ing and warming data shows the hysteresis (inset of Figure 5.1(a)) of the 1st order MI transition near 170 K. Erratic jumps in the resistivity at low temperatures are attributed to cracks in the sample due to the structural transition that accompanies the MI transition. The hysteretic behavior of the MI transition exists for all resistivity measurements for $0 \leq P \leq 3.52$ GPa. For clarity, only warming data for selected resistivity curves from four sets of pressure cell measurements are shown for $V_6O_{11}$ in Figure 5.1(b) and 5.1(c).

Temperature dependent resistivity for pressures up to 2.86 and 7.5 GPa are shown in Figure 5.1(b) and 5.1(c), respectively. At ambient pressure, the jump in the resistivity at $T_{MI}$ is very sharp. For resistivity measurements at 0.84 and 1.64 GPa, the higher temperature ($T > T_{MI}$) resistivity decreases with increasing temperature. This was likely caused by the electrical connection between the sample and the cell, mentioned above. Subsequent measurements with other cells without such electrical connections had more metal-like $\rho(T)$ behavior with the high temperature resistivity increasing with increasing temperature consistent with the behavior seen at ambient pressure. For $0 < P < 3.92$ GPa, the MI transition temperature was taken as the intersection of the extrapolated lines seen in Figure 5.1(c) on the $P = 2.86$ GPa resistivity curve.

For $V_6O_{11}$, the 1:1 FC70 : FC770 mixture was used as the liquid pressure medium. Near 10 K at ambient pressure, the resistivity in the insulating state reaches a maximum and decreases with further lowering of temperature. As pressure is applied, $T_{MI}$ is gradually suppressed and the insulating state maxima are reduced in magnitude and shifted to higher temperatures. By 3.52 GPa, there is only a small discontinuous jump in the resistivity near 46 K, which is likely a remnant signature of the MI transition. The upper inset of Figure 5.1(c) shows both the cooling and warming data for this pressure confirming the presence of the hysteresis at pressures close to $P_{c}^{MI}$. The width of the hysteresis is $\sim 6$ K which is considerably larger than the temperature lag (less than 1 K) from cooling and warming of the cell. At the next higher pressure (3.92 GPa), where the MI transition has disappeared, there is virtually no hysteresis between the cooling and warming data. Above $P_{c}^{MI}$, the resistivity shows no MI transition and instead declines smoothly and faster at low temperatures revealing $T^2$ dependence near base temperatures.
Figure 5.1  Resistivity curves for V$_6$O$_{11}$ under pressure. For clarity, not all data sets are shown. (a) Ambient pressure resistivity for cooling and warming data. The arrow indicates the MI transition temperature. The inset shows the hysteresis of the MI transition near 170 K. (b) Resistivity measurements at $P = 0.84, 1.64, \text{ and } 2.86 \text{ GPa}$ show suppression of $T_{\text{MI}}$ (indicated by the arrows) with applied pressure. (c) Resistivity measurements for $P = 2.86, 3.52, 3.92, 5.98, \text{ and } 7.52 \text{ GPa}$ are shown on a $\mu\Omega \text{ cm}$ scale. The criterion used for determining the MI transition is illustrated on the $P = 2.86 \text{ GPa}$ curve. The upper inset shows the hysteresis of the MI transition at 3.52 GPa with arrows indicating the cooling and warming data. The lower inset shows resistivity versus $T^2$ data down to 0.47 K at 3.87 GPa and a fit to the low temperature data. The arrow indicates the onset of low temperature Fermi Liquid-like, $\rho \propto T^2$, behavior. [Kim et al., 2013]
Resistivity measurements just above $P_{c}^{\text{MI}}$ were done under a pressure of 3.87 GPa down to 0.47 K (lower inset of Figure 5.1(c)). There were no indications of any low temperature phase transitions (e.g. superconductivity) and instead FL behavior was seen up to 2.1 K. Further pressure increases up to 7.52 GPa caused a systematic reduction of the resistivity across the measured temperature range and an increase of the temperature region of FL behavior to 6.8 K.

### 5.3.2 $V_7O_{13}$

Resistivity measurements for $V_7O_{13}$ at several pressures are shown in Figure 5.2 for measurements using 1:1 FC70 : FC770 as the liquid pressure medium. At ambient pressure, the resistivity remains metallic down to 2 K. At $\sim$43.5 K, there is a clear resistive anomaly as was seen in previous studies [Griffing et al., 1982; Canfield et al., 1990b,a; Ueda et al., 2003]. This anomaly had been associated with the AFM transition seen in susceptibility measurements [Griffing et al., 1982; Canfield et al., 1990b,a]. The AFM transition temperature, $T_N$, was inferred from the minimum of the derivative of the resistivity, shown in the inset of Figure 5.2(a). Upon lowering the temperature below $T_N$, there is a rapid decrease of resistivity with $T^2$ behavior emerging at low temperatures. As pressure is increased, the resistive anomaly shifts to lower temperatures, and disappears at a pressure between 2.99 and 4.0 GPa. Pressure increases beyond $P_{c}^{\text{AFM}}$ expand the $T^2$ region and the $T^2$ coefficient of resistivity, $A$, decreases rapidly.

For measurements with improved hydrostaticity, a 1:1 n-pentane : iso-pentane mix was used for several pressure measurements. Results are shown in Figure 5.3. Pressures closer to $P_{c}^{\text{AFM}}$ were reached (3.11, 3.25 GPa, and 3.83 in Figure 5.3(b) and the low temperature resistivity data for $P = 3.11$ and 3.25 GPa show a noticeable change in slope. This feature is better seen in the temperature derivative of the resistivity (inset of Figure 5.3(b)) and appears to be related to the feature that has been associated with AFM order which is suppressed at a higher pressure. Above 3.25 GPa, the resistivity curves remain smooth down to base temperature with a widening range of $T^2$ behavior (as pressure increases) at low temperatures. The critical pressure is inferred to be between 3.25 and 3.83 GPa. Measurements of $V_7O_{13}$ at 3.22 and 3.83 GPa down to 0.32 K showed no indications of a low temperature phase transitions. An example of a fit to $T^2$ behavior is shown in the inset of Figure 5.3(a) for 3.22 GPa.
Figure 5.2 Resistivity measurements under pressure for $V_7O_{13}$ where the 1:1 FC70 : FC770 mix was used as the pressure medium. Only a few selected resistivity curves are shown for clarity. (a) Full temperature range of measurements show metallic behavior of $V_7O_{13}$. Inset shows $d\rho/dT$ and the criterion used for determining the AFM transition temperature. (b) Low temperature resistivity data with arrows indicating the AFM transition temperature. [Kim et al., 2013]
Figure 5.3  Resistivity measurements under pressure using the more hydrostatic 1:1 n-pentane : iso-pentane mixture as the pressure medium. (a) The full temperature range is shown with selected curves from two different sets of measurements. Inset shows the low temperature $T^2$ fit for 3.22 GPa measured down to 0.32 K. (b) The low temperature resistivity data is shown, with the kink-like feature in the 3.11 and 3.25 GPa measurements that is likely a remnant signature of AFM ordering. The arrows the AFM transition temperature. The inset shows $d\rho/dT$ for $P = 3.11$ GPa that where the feature is more noticeable and $T_N$ determined. [Kim et al., 2013]
5.4 Analysis and Discussion

Figure 5.4(a) presents temperature-pressure data that form a phase diagram of the MI transition for $V_6O_{11}$ and the progression of the range of low temperature, $\rho \propto T^2$, FL behavior. The $T_{MI}$ data overlap those from a previous study by Canfield et al. where measurements up to 1.87 GPa showed a linear decrease in $T_{MI}$ with pressure [Canfield, 1990], but, as shown in Figure 5.4(a), the new data show a somewhat larger $dT_{MI}/dP$ value and clear, non-linear suppression of $T_{MI}$ with pressure until $T_{MI}$ disappears between 3.52 and 3.87 GPa. The suppression of $T_{MI}$ indicates the occurrence of a quantum phase transition driven by a nonthermal parameter, in this case, pressure. At 3.87 GPa, just above $P_{cMI}$, the low temperature resistivity measurements down to 0.47 K showed $\rho \propto T^2$ behavior for $T < 2.1$ K (inset of Figure 5.1(c)). As pressure increases beyond $P_{cMI}$, $T_{FL}$ increases monotonically (Figure 5.4(b)) and the coefficient $A$ decreases (Figure 5.4(c)). The pressure dependence of both $T_{FL}$ and $A$ are not consistent with divergent behavior at $P_{cMI}$ but rather seem to manifest a low pressure truncation below $P_{cMI}$. This is not too surprising given that the transition being suppressed maintains its first order nature (as evidenced by the hysteretic behavior of the MI transition close to $P_{cMI}$ shown in the upper inset of Figure 5.1(c)) down to the lowest detectable values of $T_{MI}$. Therefore, the divergence of $A$ associated with $T_{FL}$ going to zero at a QCP is not seen in $V_6O_{11}$.

For $V_7O_{13}$, the suppression of the second order AFM transition temperature with pressure can be seen in Figure 5.5(a), with data from past studies using different liquid media included for comparison. The data match well for the liquid media with lower hydrostatic limits, namely 1:1 FC70 : FC770 and the Daphne 7373 mixtures with hydrostatic limits of 1 and 2.2 GPa respectively [Sidorov and Sadykov, 2005; Yokogawa et al., 2007]. The evolution of $T_N$ with pressure shows a small dependence on the choice of pressure medium. This is not unexpected, as it has been seen before that the choice of pressure medium can affect the pressure dependence of a magnetic transition temperature [Colombier et al., 2011]. For the measurements with the 1:1 n-pentane : iso-pentane media, with a higher hydrostatic limit of 6.5 GPa [Kim et al., 2011], the AFM transition temperatures tend to be lower at a given pressure. In our measurements, despite the minute difference in $T_N$ suppression rates due to the choice of liquid medium, an
Figure 5.4  (a) Phase diagram of $V_6O_{11}$ illustrating the salient features as they progress with pressure. Triangles denote the MI transition temperature ($T_{MI}$) and the open stars with the central dot denote the upper limit of FL behavior ($T_{FL}$). The open red triangles are data from a study by Canfield et al. [Canfield et al., 1990a; Canfield, 1990]. The red dashed line is a guide to the eye. (b) The range of the Fermi Liquid behavior, that the $V_6O_{11}$ $\rho(T)$ data can be fit when it is metallic throughout the full temperature range. (c) $T^2$ coefficient of the resistivity versus pressure phase diagram. The black dashed vertical line indicates the first pressure where the MI transition has been fully suppressed. [Kim et al., 2013]
extrapolation of $T_N$ shows that the critical pressure of $P_{c}^{AFM} = 3.5$ GPa is very nearly the same and may at most, differ by 0.2 GPa for different liquid media.

$\rho \propto T^2$ fits to the low temperature resistivity data for $V_7O_{13}$ were used to infer $T_{FL}$ as shown in the phase diagrams Figure 5.5(a) and 5.5(b).

There is a large region of Fermi Liquid behavior at ambient pressure, up to 8.6 K, and this region diminishes as pressure is increased to $P_{c}^{AFM}$. For two pressures close to $P_{c}^{AFM}$, 3.22 and 3.83 GPa, measurements down to 0.32 K revealed quadratic behavior at very low temperatures. For 3.22 GPa, this quadratic behavior persisted up to 0.9 K with the highest $T^2$ coefficient found, $A = 3.7 \times 10^{-6}$ $\Omega$ cm K$^{-2}$. For 3.83 GPa, the quadratic behavior is seen up to 1.2 K ($T^2 = 1.4$ K). Above $P_{c}^{AFM}$ for $V_7O_{13}$, the $T^2$ coefficient decreases (roughly inversely with $P - P_{c}^{AFM}$) and the temperature region of Fermi Liquid behavior increases rapidly to nearly 4 K. The contributions to the scattering due to the magnetic excitations (below $T_N$) and fluctuations (above $T_N$) may have different prefactors, but the data clearly shows $T^2$ resistivity at low temperatures on both sides of $P_{c}^{AFM}$.

A hallmark feature of a QCP is the divergent behavior of the $T^2$ coefficient near the critical point. The divergence has been fit to $A \propto |P - P_{c}^{AFM}|^{-1}$ on either side of $P_{c}^{AFM} = 3.5$ GPa in Figure 5.6(a) (shown as the solid red line). Another indication of a QCP is a sharp drop of $\rho_0$ at the critical pressure. A phase diagram of $\rho_0$ vs. pressure is shown in Figure 5.6(b) showing a modest rise as pressure is increased up to $P_{c}^{AFM}$ and a sharp drop at pressures just above.

A past study [Ueda et al., 2003] down to $T = 1.7$ K showed a $T^{3/2}$ dependence at $P_{c}^{AFM} = 3.4$ GPa at base temperatures, consistent with self-consistent renormalization theory for spin fluctuations near a QCP for a three-dimensional AFM [Moriya and Ueda, 2003]. Unfortunately, in our body of work, measurements closer to 3.4 GPa were not taken due to the difficulty of controlling the increase of pressure by anything less than 0.5 GPa. Measurements with the PPMS at 3.28 GPa do show a $T^{3/2}$ dependence from 2 to 2.3 K. However, upon closer inspection of lower temperature measurements down to 0.32 K at $P_{c}^{AFM} = 3.22$ GPa, the resistivity shows $T^2$ dependence up to 0.9 K (Figure 5.7). This behavior is not unexpected near a QCP where the Fermi Liquid behavior has been significantly suppressed. The fact that FL behavior only exists at low temperatures indicates that at 3.22 GPa, we are close to the QCP.
Figure 5.5  Phase diagrams for V$_7$O$_{13}$. (a) $T_N$ as it is suppressed by pressure. The blue dashed line is a guide for the eye. (b) Expanded, low temperature region showing $T_{FL}$ (range of Fermi Liquid behavior), the blue dashed line shows the extrapolation of the $T_N(P)$ line. [Kim et al., 2013]
Figure 5.6 Phase diagrams for $V_7O_{13}$. (a) $T^2$ coefficient as it evolves with pressure. The red lines are fits of the results from measurements with the 1:1 n-pentane : iso-pentane and 1:1 FC70 : FC770 mixtures with the form of $A \propto |P - P_{c}^{AFM}|^{-1}$ where $P_{c}^{AFM} = 3.5$ GPa is denoted as the dashed vertical black line. Open and closed symbols are for measurements with 1:1 FC70 : FC770 and 1:1 n-pentane : iso-pentane media, respectively. For comparison, results from previous studies [Canfield et al., 1990b; Canfield, 1990; Ueda et al., 2003] are also plotted and can be seen as the crossed symbols. (b) $\rho_0$ inferred from $T^2$ fits. [Kim et al., 2013]
Figure 5.7 Resistivity plotted versus $T^2$ showing the low temperature FL behavior up to $\sim$1 K. [Kim et al., 2013]

Measuring with a more hydrostatic medium (the 1:1 n-pentane : iso-pentane mix), shows that the divergence of $A$ at $P_{c}^{\text{AFM}}$ is stronger than was seen when using the less hydrostatic 1:1 FC70 : FC770 mix. This might be the cause of the reduced divergent behavior of $A$ near $P_{c}^{\text{AFM}}$ seen in previous measurements of $V_7O_{13}$ [Ueda et al., 2003] where Daphne Oil 7373 was used as the liquid pressure medium. With a room temperature solidification pressure of 2.2 GPa [Yokogawa et al., 2007], Daphne Oil 7373 has better hydrostaticity than the 1:1 FC70 : FC770 mixture which solidifies near 1 GPa but is still less hydrostatic than the 1:1 n-pentane : iso-pentane mixture which has a solidification pressure of 6.5 GPa [Sidorov and Sadykov, 2005; Kim et al., 2011]. Improved hydrostaticity decreases the pressure gradients across the sample and improves its homogeneity, which is essential when studying the narrow pressure region where quantum fluctuations can drive a magnetic quantum phase transition.

A composite phase diagram for $V_6O_{11}$, $V_7O_{13}$, and $V_8O_{15}$, is shown in Figure 5.8(a) with data from past pressure measurements included for comparison [Canfield et al., 1990b; Canfield, 1990]. The pressure dependence of $T_N$ for $V_7O_{13}$ is remarkably consistent for measurements using different liquid media. Even more surprising is a comparison of $T_N(P)$ for $V_7O_{13}$ to $V_8O_{15}$. 
For $V_8O_{15}$, pressure suppresses the MI transition fast enough to reveal the low temperature AFM transition in the resistivity. The pressure dependence of this AFM transition for $V_8O_{15}$ directly maps onto the same for $V_7O_{13}$ without any shifts in pressure or normalizations to $T_N$. $T_N(P)$ is virtually identical for $V_7O_{13}$ and $V_8O_{15}$, giving rise to the possibility that it is a universal feature of the low temperature metallic state of the Magnéli series.

The composite phase diagram shown in Figure 5.8(a) helps explain several of the features that emerge in the $V_6O_{11}$ data set. First of all, the fact that signatures of an antiferromagnetic phase transition, similar to those seen for $V_7O_{13}$ and $V_8O_{15}$, are missing in $V_6O_{11}$ at any measured pressure can be understood by noting that the $T_N(P)$ line goes to zero before the critical pressure for the complete suppression of the MI transition in $V_6O_{11}$. This means that, for $V_6O_{11}$, we cannot directly access a QCP associated with antiferromagnetic order. This being said, though, Figure 5.8(a) does show that, as the pressure applied to $V_6O_{11}$ is decreased from the high pressure side (i.e. as we progress from 7 GPa toward 4 GPa) the sample, at low temperatures is approaching not only the quantum phase transition associated with the end point of the $T_{MI}(P)$ line, but also may be approaching a hidden QCP associated with the potential antiferromagnetic ordering seen for $V_7O_{13}$ and $V_8O_{15}$. This possibility is explored more fully in Figures 5.8(b) and 5.8(c) where the pressure dependences of $T_{FL}$ and $A$ as a function of $P$ are plotted for both $V_7O_{13}$ and $V_6O_{11}$. For $V_6O_{11}$, the evolution of $T_{FL}$ with pressure is consistent with the possibility that the FL behavior is associated with the antiferromagnetic fluctuations that gradually weaken with the increase of pressure. The $A(P)$ data is similar for $P > 5$ GPa, but for $3.8 < P < 5$ GPa the $A$ values for $V_6O_{11}$ are significantly smaller than those for $V_7O_{13}$. This may, of course, be due to the fact that whereas for $V_7O_{13}$ we can experimentally pass through the critical pressure for the QCP, we cannot approach the QCP so closely for $V_6O_{11}$ given the higher pressure $T_{MI}(P)$ line.

Consequently, it is of interest to study other members of $V_nO_{2n-1}$ that have a lower MI transition at ambient pressure. $V_9O_{17}$ which has a MI transition at 79 K would be a natural choice as its $T_{MI}$ is slightly higher than that of $V_8O_{15}$ [Kuwamoto et al., 1981]. Another possible candidate for pressure measurements is $V_5O_9$ with $T_{MI} \sim 130$ K [Kachi et al., 1973; Nagata et al., 79; Inglis et al., 1984; Canfield, 1990]. Previous studies of $V_5O_9$ with pressure measurements
Figure 5.8  (a) Composite phase diagram of $V_6O_{11}$, $V_7O_{13}$, and $V_8O_{15}$ with the latter data from work by Canfield et al. [Canfield et al., 1990b,a; Canfield, 1990]. The AFM transition of $V_7O_{13}$ and $V_8O_{15}$ overlap, however, the MI transition of $V_6O_{11}$ persists near the AFM critical pressure, negating any possibility of seeing a splitting of the MI and AFM transition as in $V_8O_{15}$. The dashed lines are guides for the eye.  (b) Combined phase diagram of $T_{FL}$ for $V_6O_{11}$ (shown as green open stars with a central dot) and $V_7O_{13}$ (shown as orange open and blue closed stars). The solid red line is a fit to the $V_7O_{13}$ data as described before.  (c) Combined phase diagram of $T^2$ coefficient for $V_6O_{11}$ (shown as green circles with a central dot) and $V_7O_{13}$ (shown as orange open and blue closed circles indicating the use of 1:1 FC70 : FC770 and 1:1 n-pentane : iso-pentane liquid media, respectively). The black dashed line indicates $P_c^{AFM}$ for $V_7O_{13}$ and the green solid line indicates $P_c^{MI}$ for $V_6O_{11}$. [Kim et al., 2013]
up to 0.85 and 1.73 GPa show a linear suppression of $T_{\text{MI}}$ at a rate of about 9 K/GPa [Terukov et al., 1979; Canfield, 1990]. Such a low suppression rate would consign it to the same fate as $V_6O_{11}$ where the MI transition is too robust for the region $P < 3.5$ GPa. However, if this rate increases with pressure, as it did for $V_6O_{11}$ and $V_8O_{15}$, then combined with its somewhat low $T_{\text{MI}}$, it may be possible to suppress $T_{\text{MI}}$ sufficiently to see the AFM feature emerge in the low temperature metallic state, or possibly even reveal a different ground state.

5.5 Conclusion

The electrical transport properties of $V_6O_{11}$ and $V_7O_{13}$ have been measured under pressures up to 7.52 and 6.40 GPa, respectively. The MI transition in $V_6O_{11}$ was fully suppressed by 3.87 GPa which overshoots the AFM critical pressure for $V_7O_{13}$ where $P_c^{\text{AFM}} = 3.5$ GPa. The suppression of the AFM temperature in $V_7O_{13}$ with pressure maps directly to the same seen in $V_8O_{15}$ suggesting that this is a universal characteristic of the members of this Magnéli series. However, the robust MI transition in $V_6O_{11}$ is not fully suppressed until after the AFM critical pressure in $V_7O_{13}$. Therefore, no AFM ordering was seen for $V_6O_{11}$.

Resistivity measurements under pressure for $V_7O_{13}$ show that the AFM transition temperature is gradually suppressed with pressure until it is gone by 3.83 GPa. The divergent behavior of the $T^2$ coefficient with $P_c^{\text{AFM}} = 3.5$ GPa indicates proximity to a quantum critical point. A previously reported region of $T^{3/2}$ behavior was found to be in fact a crossover region to FL behavior at even lower temperatures below 0.9 K.

Although the $P-T$ phase diagram for $V_6O_{11}$ does not show any long range magnetic order (of the kind found in $V_7O_{13}$), there is clear Fermi liquid behavior at low temperatures, above $P_c^{\text{MI}}$ with the $T_{\text{FL}}$ value diminishing as $P_c^{\text{MI}}$ was approached from higher pressures. These data suggest that there might well be a hidden QCP in $V_6O_{11}$ that can only be inferred from the extrapolation of high pressure $T_{\text{FL}}$ results.
CHAPTER 6. SEARCH FOR PRESSURE INDUCED QUANTUM CRITICALITY IN YbFe$_2$Zn$_{20}$

6.1 Motivation

Strongly correlated electron systems manifest a rich variety of electronic and magnetic properties that have fascinated scientists for decades; Mott insulators [Mott, 1990], exotic superconductors [Bennemann and Ketterson, 2008; Norman, 2011], and heavy fermions [Stewart, 1984, 2001, 2006] continue to be topics of intense study. Heavy fermions are a subset of materials known as Kondo lattices. In a Kondo lattice system, near the characteristic Kondo temperature, $T_K$, the moment bearing ions in the lattice each act as a Kondo impurity, with which the conduction electrons hybridize and create a screening cloud of dynamically polarized electrons. At lower temperatures, the conduction electrons become coherent and manifest Fermi-liquid (FL) behavior. This leads to a myriad of novel features in measurements of the Kondo lattice’s thermodynamic and transport properties at and below $T_K$: the susceptibility, which has a local moment-like, paramagnetic behavior at high temperatures, shows a loss of local moment behavior below $T_K$; in measurements of specific heat, a large Sommerfeld coefficient for $T < T_K$ points to a large effective electron mass; resistivity measurements for $T \ll T_K$ are Fermi-liquid-like and are consistent with a large electronic density of states at the Fermi energy.

The YbTM$_2$Zn$_{20}$ (TM = Fe, Co, Ru, Rh, Os, and Ir) compounds form a family of Yb-based heavy fermions where subtle changes in the hybridization of the Yb local moment with the conduction electrons can be achieved by changing the transition metal (TM) element.

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1This chapter is based on a submitted article: Kim, S. K., Torikachvili, M. S., Jia, S., Bud’ko, S. L., and Canfield, P. C., “Search for Pressure Induced Quantum Criticality in YbFe$_2$Zn$_{20}$” submitted to Phys. Rev. B Apr. 2013
These materials show classical heavy fermion behavior in their physical properties [Torikachvili et al., 2007; Canfield et al., 2008; Jia et al., 2009; Jia, 2008; Mun et al., 2012]. Of this series, YbCo$_2$Zn$_{20}$ seems to be an outlier with $T_K$ much lower than those of the other five members ($T_K = 33, 30, 16, 20, \text{ and } 21 \text{ K for TM = Fe, Ru, Rh, Os, and Ir, respectively, and } T_K = 1.5 \text{ K for TM = Co}$) [Torikachvili et al., 2007]. Specific heat measurements yielded large Sommerfeld constants ($\gamma = 520, 580, 740, 580, 540 \text{ mJ/mol K}^2 \text{ for TM = Fe, Ru, Rh, Os, and Ir, respectively, and an exceptionally large value of } 7200 \text{ mJ/mol K}^2 \text{ for YbCo}_2\text{Zn}_{20}$) [Torikachvili et al., 2007]. Magnetic susceptibility measurements show Curie-Weiss behavior at high temperatures and a broad maximum at low temperatures, signalling a Kondo screened local moment. When the magnetic component of the resistivity is isolated by subtracting from it the resistivity of the non-magnetic counterpart LuTM$_2$Zn$_{20}$, the resistivities of all members of the YbTM$_2$Zn$_{20}$ series show a local maximum near $T_K$. Below $T_K$, the coherent scattering of electrons decreases the resistivity until at very low temperatures, a wide temperature range of $T^2$ behavior signals the onset of Fermi-liquid behavior [Coleman, 2007].

Although no indication of low temperature, local moment order was found for any of the YbTM$_2$Zn$_{20}$ compounds [Torikachvili et al., 2007; Canfield et al., 2008; Jia et al., 2009; Jia, 2008; Mun et al., 2012], by combining the idea of the basic Doniach model [Doniach, 1977] with simple steric arguments, it is anticipated that the application of pressure will stabilize local-moment-like states in Yb-based Kondo lattic systems. Indeed under pressure, indications of a magnetic instability were seen in YbCo$_2$Zn$_{20}$. When a modest pressure of $\sim 1 \text{ GPa}$ was applied, the resistivity measurement showed an anomaly, possibly magnetic in origin, at $\sim 0.15 \text{ K}$ [Saiga et al., 2008; Matsubayashi et al., 2010]. Given the drastic difference in Kondo temperatures between YbCo$_2$Zn$_{20}$ and YbFe$_2$Zn$_{20}$ a significantly larger amount of pressure is expected to be needed to drive the YbFe$_2$Zn$_{20}$ system to a magnetically ordered state at low temperature. For YbCo$_2$Zn$_{20}$, at the critical pressure needed to induce an ordered state, the temperature of the local maximum of the magnetic component of the resistivity ($T_{max}$), was at its minimum value. A similar minimum was also seen in pressure measurements on YbRh$_2$Zn$_{20}$ and YbIr$_2$Zn$_{20}$ at $\sim 3 \text{ GPa}$ [Matsubayashi et al., 2010, 2009b], however, no features signalling magnetic ordering were seen down to 2 K for these compounds. This is not surprising consid-
ering the magnetic ordering temperature for YbCo$_2$Zn$_{20}$ was, at most, ∼0.5 K at 2.37 GPa. If indeed both YbRh$_2$Zn$_{20}$ and YbIr$_2$Zn$_{20}$ with $T_K = 16$ and 21 K, respectively, have critical pressures near 3 GPa, then it is expected that for YbFe$_2$Zn$_{20}$, which has a higher Kondo temperature of $T_K = 33$ K [Torikachvili et al., 2007], the critical pressure for a pressure induced QCP will be $P_c > 3$ GPa. On the other hand, YbFe$_2$Zn$_{20}$ may well manifest a higher magnetic ordering temperature than YbCo$_2$Zn$_{20}$. A comparison of the relative ordering temperatures of GdCo$_2$Zn$_{20}$ and GdFe$_2$Zn$_{20}$ [Jia et al., 2007, 2009] combined with de Gennes scaling suggests that if an RKKY interaction induces a magnetically ordered state for the Yb system, a magnetic transition temperature, as high as ∼1 K may be found for YbFe$_2$Zn$_{20}$ under pressure. Moreover, other members of the family of RFe$_2$Zn$_{20}$, namely R = Gd-Tm manifest ferromagnetic ordering which suggests that the ordered state in YbFe$_2$Zn$_{20}$, if it can be stabilized, may be more complex than simple AFM order.

### 6.2 Experimental methods

Starting with a high temperature melt of stoichiometry: Yb:Fe:Zn = 2:4:94, single crystals of YbFe$_2$Zn$_{20}$ were grown out of excess Zn. A detailed description of this process is described elsewhere [Torikachvili et al., 2007; Jia et al., 2007; Canfield et al., 2008; Jia et al., 2009; Canfield, 2010].

For resistivity measurements, the single crystals were polished down to appropriate dimensions for the two types of pressure cells used: 1.6 × 0.5 × 0.4 mm$^3$ for the piston cylinder cell ($P \lesssim 2$ GPa) [Torikachvili et al., 2008a, 2009] and typically 700 × 150 × 30 μm$^3$ for the modified Bridgman anvil cells (mBAC) (2.85 ≤ $P$ ≤ 8.23 GPa) [Colombier and Braithwaite, 2007]. The small sizes of the samples used in these pressure cells lead to relatively large geometric errors in the resistivity values. Therefore, all resistivity measurements were normalized to that of a single measurement on a large sample which was used in a previous study on the transport properties of Yb-based heavy fermions [Jia, 2008; Jia et al., 2009]. The normalization was done by multiplicatively matching the resistivity at ambient pressure and at 298 K, then applying the same multiplicative value to the rest of the resistivity measurements under pressure. Given that these materials have cubic unit cells [Torikachvili et al., 2007; Jia et al., 2007; Canfield
et al., 2008; Jia, 2008; Jia et al., 2009], this normalization procedure is considered to be quite reliable.

A modified Bridgman anvil cell was used for resistivity measurements at pressures up to about 8.2 GPa. For this study, two pressure media were used with the mBAC: a mixture of 1:1 n-pentane : iso-pentane and a mixture of 1 : 1 Fluorinert 70 : Fluorinert 770 (1:1 FC70 : FC770) [Piermarini et al., 1973; Klotz et al., 2009; Varga et al., 2003; Sidorov and Sadykov, 2005]. Despite the the lower pressure of solidification at room temperature of the latter liquid medium, its lower compressibility allowed higher pressures to be more readily achieved.

At ambient pressure, YbFe$_2$Zn$_{20}$ samples had residual resistivity ratios that varied from 18 to 38. The low-temperature resistivity follows $\rho(T) = \rho_0 + AT^2$ with the value of $A$ having an average of $7.0 \pm 0.3 \times 10^{-10}$ Ω cm K$^2$ and the crossover temperature, $T_{FL}$, below which this form fits the data, has an average value of $11.4 \pm 0.8$ K. With two different pressure cells and three different liquid media, there are clear, albeit small, differences between the various pressure dependent data sets, that may (in part) be attributed to cell to cell and/or sample to sample differences but these are small compared to the much larger changes due to pressure (see Figure 6.8 below and associated discussion).

For most pressure cells, one cycle of cooling and warming causes a pressure cell to thermally contract and expand. One subtlety of pressure measurements with the mBAC is that this thermal cycling can induce a modest pressure increase within the pressure cell. This is the origin of the slight pressure differences between subsequent measurements with the PPMS (used for measurements down to 2 K) and the $^3$He system (used for measurements down to nearly 0.3 K). An example of this effect is seen below in Figure 6.3.

### 6.3 Results

Temperature dependent resistivity measurements of YbFe$_2$Zn$_{20}$, at ambient pressure and under pressures up to 2.03 GPa, are shown in Figure 6.1. These measurements were taken using a piston cylinder cell. As temperature is decreased from 300 K (inset of Figure 6.1) the resistivity decreases in a near-linear manner until, near 30 K, a broad shoulder-like drop appears. Below this shoulder, the resistivity decreases rapidly with temperature and at the
lowest temperatures manifests $T^2$ behavior. As the applied pressure is increased, the shoulder
shifts to lower temperatures and the resistivity data for temperatures just above the shoulder
flattens.

Figure 6.1  Temperature dependent resistivity measurement of YbFe$_2$Zn$_{20}$ under pressure us-
ing a piston cylinder cell are shown up to 50 K for pressures up to 2.03 GPa. Inset: Full temperature range of the resistivity at ambient pressure and 2.03 GPa. The high temperature region shows typical metallic behavior with a near-linear
dependence on temperature. [Kim et al., 2013]

For measurements at higher pressures, the mBAC was used with both the 1:1 n-pentane : iso-
pentane mixture and the 1:1 FC70 : FC770 mixture. Figure 6.2 shows resistivity measurements
with an mBAC for pressures up to 5.14 GPa using 1:1 n-pentane : iso-pentane as the liquid
pressure medium. As pressure is applied, a local maximum in the resistivity above the shoulder
grows as the shoulder itself shifts to lower temperatures.

The $\rho(T) = \rho_0 + AT^2$ behavior that persisted up to about 11 K at ambient pressure
is diminished to a lower temperature range and the upward curvature becomes steeper as
pressure is increased. Measurements with the PPMS down to 2 K show quadratic behavior
up to ~ 3.3 K at 4.58 GPa (Figure 6.3). $T_{FL}$ was defined as the temperature at which the
Figure 6.2  Low temperature resistivity measurements under pressure using a modified Bridgman anvil cell with 1:1 n-pentane : iso-pentane as the liquid pressure medium, reaching a maximum pressure of 5.14 GPa. Inset: Resistivity curves for the full temperature range up to 300 K for pressures at 0, 2.85, and 5.14 GPa. [Kim et al., 2013]

difference between experimental resistivity data, $\rho_{\text{exp}}$, and linear fits to the $\rho_{\text{exp}}$ versus $T^2$ data, $\rho_{\text{fit}}$, became greater than 0.01 $\mu\Omega$ cm. For pressures where $T^2$ behavior was still observable above 2 K, $T_{\text{FL}}$ was determined from measurements with the PPMS. For $T_{\text{FL}}$ lower than 2 K, $^3$He data were used for the quadratic fits.

In order to explore the possibility of magnetic ordering at lower temperatures, measurements of resistivity down to nearly 0.3 K for 4.20 and 4.73 GPa were taken using a $^3$He cryostat, shown in Figure 6.3. These measurements revealed no resistive anomalies down to almost 0.3 K and confirmed that $T^2$ behavior persists down to our lowest temperatures.

In order to achieve higher pressures, the 1:1 FC70 : FC770 liquid medium was used with the mBAC. Figure 6.4 shows selected resistivity curves for pressures up to 8.23 GPa from two different packings of the pressure cell (each using one half of the same crystal as a sample). The resistivity in the high temperature region, between 30 and 300 K, continues to decrease
Figure 6.3  $T^2$ dependence of resistivity at low temperatures for measurements with the PPMS at 3.90 and 4.58 GPa shown as the closed squares and circles, respectively, as well as measurements with the $^3$He cryostat at 4.20 and 4.73 GPa denoted by the open squares and circles, respectively. The black dashed lines are linear fits to the low temperature data taken with the PPMS. The arrows indicate the temperature limit of $T^2$ behavior, $T_{FL}$, from PPMS data. Inset: $\rho_{exp} - \rho_{fit}$ for both 3.90 and 4.58 GPa versus $T^2$. The black dotted line indicates a difference of $-0.01 \, \mu\Omega\, cm$ used to determine $T_{FL}$. [Kim et al., 2013]

with temperature (inset of Figure 6.4) in a near-linear fashion. The broad shoulder once again changes into a broad maximum with pressure and further increases up to 8.23 GPa reveal this maximum sharpening.

Measurements down to nearly 0.3 K were also conducted with 1:1 FC70 : FC770 as the liquid medium in the mBAC (Figure 6.5). No features associated with magnetic ordering were seen in the data for pressures up to 8.23 GPa. Above 5 GPa, the range of $T^2$ behavior is suppressed to below 2 K. This decrease in $T_{FL}$ continues with pressure and, at 8.23 GPa, the $T^2$ behavior is found only up to $T \sim 0.6$ K ($T^2 \sim 0.3$ K$^2$).
Figure 6.4 Low temperature resistivity data of YbFe$_2$Zn$_{20}$ at pressures up to 8.23 GPa using 1:1 FC70 : FC770 as the liquid medium. Selected curves are shown ($P = 0, 3.62, 4.95, 5.62, 7.68, \text{ and } 8.23$ GPa) from two separate sets of measurements. Inset: Resistivity curves up to 300 K for $P = 0, 3.62, \text{ and } 8.23$ GPa. [Kim et al., 2013]

6.4 Discussion

Applying pressure to Yb-based heavy fermion systems can shift the systems from being dominated by the Kondo effect and manifesting low-temperature FL behavior, to being more local-moment like and even, in some cases, to manifesting long-range order [Alami-Yadri et al., 1998; Knebel et al., 2001b; Trovarelli et al., 2002; Winkelmann et al., 1998]. In resistivity measurements of a Kondo lattice system, the logarithmic rise of resistivity due to the Kondo effect is countered by the coherent scattering of the electrons at lower temperatures, creating a local maximum in the resistivity. Since the Kondo temperature, $T_K$, sets an energy scale for a crossover from a local moment to a Kondo-screened moment state and is not associated with any sharp features in physical measurements, it becomes necessary to isolate the magnetic contribution from the resistivity data in order to determine, or set limits on, $T_K$. The position of this local maximum is expected to scale with $T_K$ [Yoshimori and Kasai, 1983; Coleman, 1987; Bauer et al., 1993].
Figure 6.5  \(T^2\) dependence of resistivity at pressures of 5.71, 6.79, 7.68, 8.01, and 8.23 GPa. At maximum pressure, the \(T^2\) region has greatly diminished. The black arrows indicate \(T_{\text{FL}}\) values that were determined as shown in the inset of Figure 6.3. [Kim et al., 2013]

The total resistivity of YbFe\(_2\)Zn\(_{20}\) can be described as a combination of non-correlated, normal metal resistivity and a magnetic contribution to the resistivity. The normal metal resistivity, can be approximated by the temperature-dependent resistivity of LuFe\(_2\)Zn\(_{20}\), which, with a full 4\(f\) shell, is a non-magnetic analogue to YbFe\(_2\)Zn\(_{20}\). Both Yb and Lu curves are shown in the inset of Figure 6.6. By taking the difference, \(\rho_{\text{mag}} = (\rho - \rho_0)_{\text{Yb}} - (\rho - \rho_0)_{\text{Lu}}\), the partially filled 4\(f\) shell contribution to the resistivity can be effectively isolated. This is shown for several measurements under pressure in Figure 6.6. For the subtraction, only the ambient pressure resistivity values of LuFe\(_2\)Zn\(_{20}\) were used and is the likely cause of the negative \(\rho_{\text{mag}}\) values at higher temperatures.

It is apparent that the low temperature maximum in the magnetic component of the resistivity decreases with pressure. For Kondo lattice systems, the electrons participating in the spin-dependent screening in the region of the Kondo temperature are intimately related to the Fermi-liquid quasiparticles at low temperatures. With previous results for YbCo\(_2\)Zn\(_{20}\) having shown indications of a magnetic transition when \(T_{\text{FL}}\) was suppressed [Saiga et al., 2008; Mat-
Figure 6.6 The magnetic contribution, $\rho_{mag} = (\rho - \rho_0)_{Yb} - (\rho - \rho_0)_{Lu}$, to the total resistivity for various pressures are shown on a semi-log scale. The inset shows the ambient pressure curves for YbFe$_2$Zn$_{20}$ and its non-magnetic analogue LuFe$_2$Zn$_{20}$. [Kim et al., 2013]

subayashi et al., 2010], it is expected that a quantum critical point will also be reached when $T_{FL}$ in YbFe$_2$Zn$_{20}$ has been driven to zero.

The suppressions of $T_{max}$ and $T_{FL}$ with pressure for YbFe$_2$Zn$_{20}$ are shown in Figure 6.7. If the minimum of $T_{max}$ is indeed an indicator that the system will manifest magnetic ordering [Matsubayashi et al., 2010], then for YbFe$_2$Zn$_{20}$, the critical pressure may well be at a slightly higher pressure than the maximum achieved in this study. Furthermore, the Fermi-liquid state is almost completely suppressed by 8.23 GPa, another indicator that the system should be near its critical pressure value.

The influence of pressure on the Fermi-liquid behavior of YbFe$_2$Zn$_{20}$ is shown more clearly in Figure 6.8. In Figure 6.8(a), the spread of $T_{FL}$ values seen at ambient pressure is small compared to the overall change in $T_{FL}$ over the 8 GPa pressure range. Although $T_{FL}$ has not been driven to zero by our maximum pressure, extrapolation of $T_{FL}(P)$ suggests that this will occur at higher pressures in the range of 9-10 GPa. The plot of the $T^2$ coefficient, $A$, as a
Figure 6.7 $T_{max}$ and $T_{FL}$ as they evolve with pressure. The dashed lines are guides for the eye. [Kim et al., 2013]

function of pressure (Figure 6.8(b)) shows divergent behavior with pressure, consistent with the diminishing $T_{FL}$ and closeness to a quantum critical point.

The divergence of $A(P)$ is very clearly quantified in Figure 6.8(c) where the progression of $A^{-1/2}$ with pressure is shown. A linear fit to the data, denoted by the black dashed line, shows that $A^{-1/2}$ will go to zero (indicating an infinitely large $A$ value) at $\sim$ 9.8 GPa. These data indicates that $A \propto (P - P_c)^{-2}$ with $P_c \simeq$ 9.8 GPa. It should be noted that data for $\rho_0(P)$ (not shown) does gradually increase from $P = 0$ to 8.23 GPa, effectively doubling in value from ambient to highest pressure.

At our highest pressures, $A$ increases rapidly indicating a proximity to a quantum critical point near $P_c = 9.8$ GPa. As pressure increases from atmospheric pressure to $\sim$ 8 GPa, we anticipate that the low temperature electronic specific heat, $\gamma$, increases. By using the Kadowaki-Woods plot in Figure 4 of Ref. Torikachvili et al. [2007], we can predict an increase in $\gamma$ from 520 mJ/mol K$^2$ to $\sim$ 2000 mJ/mol K$^2$ or greater at 8.23 GPa depending on whether all crystalline electric field split levels are comparable or lower than $T_K$. 
Figure 6.8 (a) Evolution of $T_{FL}$ as pressure is applied. By 8.23 GPa, $T_{FL}$ is only as high as \sim 0.6 K. Crossed, closed, and open symbols are results from the piston cylinder cell, the mBAC with the 1:1 n-pentane : iso-pentane mixture and mBAC with the 1:1 FC70 : FC770 mixture, respectively. (b) $T^2$ coefficient ($\rho(T) = \rho_0 + AT^2$) which diverges as pressure is increased. (c) $A^{-1/2}$ as it progresses with pressure. The dashed line is a linear fit to the data with $A^{-1/2}$ reaching zero near 9.8 GPa. [Kim et al., 2013]
For $P > P_c \sim 9.8$ GPa, long-range magnetic ordering is expected. Such behavior was speculated to be seen with YbCo$_2$Zn$_{20}$, where at $P_c \approx 1.0$ GPa, a small anomaly in the resistivity appeared near 0.15 K [Saiga et al., 2008]. The large difference in the pressure needed to drive these systems to a quantum critical point is attributed to their large difference in ambient pressure Kondo temperatures ($T_K = 1.5$ K for YbCo$_2$Zn$_{20}$ and $T_K = 33$ K for YbFe$_2$Zn$_{20}$) [Torikachvili et al., 2007; Matsubayashi et al., 2009b]. This is also reflected in the value of $P_c$ for YbRh$_2$Zn$_{20}$ and YbIr$_2$Zn$_{20}$ which is suggested to be 3 GPa, where $T_K = 16$ and 21 K, respectively [Torikachvili et al., 2007; Matsubayashi et al., 2009b]. To estimate the hypothetical magnetic ordering temperature for trivalent Yb in YbFe$_2$Zn$_{20}$ and YbCo$_2$Zn$_{20}$, the ordering temperature for the Gd counterparts, GdFe$_2$Zn$_{20}$ and GdCo$_2$Zn$_{20}$, can be scaled by the de Gennes factor. The de Gennes factor correlates the magnetic ordering temperature with the strength of the interaction between the local rare earth moment and the polarized conduction electrons [Jia et al., 2007, 2009]. Using this method, YbFe$_2$Zn$_{20}$ and YbCo$_2$Zn$_{20}$ would be expected to order at 1.75 and 0.12 K, respectively. For YbCo$_2$Zn$_{20}$, this is relatively close to the value of 0.15 K measured under pressure [Saiga et al., 2008], suggesting that magnetic ordering in YbFe$_2$Zn$_{20}$ might be found as high as $\sim 1$ K for $P \gtrsim 9.8$ GPa.

Furthermore, RFe$_2$Zn$_{20}$ compounds, for R = Gd-Tm, manifest ferromagnetic ordering with the Curie temperature, $T_C$, for Gd as high as 86 K [Jia et al., 2007, 2009]. The enhanced $T_C$'s of these compounds are thought to be associated with the near Stoner nature of YFe$_2$Zn$_{20}$ and LuFe$_2$Zn$_{20}$ [Jia et al., 2007; Jia, 2008; Jia et al., 2009]. This then raises the possibility that the magnetic ordering that evolves with pressure from the Fermi-liquid state of YbFe$_2$Zn$_{20}$ might be more complex than simple antiferromagnetic order.

To further investigate the possibility that a QCP is being approached, an analysis of the progression of the power law behavior at low temperatures and high pressures was done. Figure 6.9 shows the results for pressures where measurements down to $\sim 0.3 - 0.4$ K were taken. Data from base temperature to 3 K are results from measurements in the $^3$He cryostat and above 3 K, results from measurements in the PPMS. In this analysis, the lowest temperature $\rho_0$ from a $T^2$ fit was used for both sets of measurements.

As expected, low pressure measurements show $n = 2$ at base temperatures across a decade of
Figure 6.9  Power law behavior for selected resistivity curves on a semilog scale. Data for \( T < 3 \) K are from measurements with a \( ^3 \)He cryostat and data for \( T > 3 \) K are from measurements with the PPMS. The black dotted line is a guide for the eye and indicates a power of \( n = 2 \) for \( \rho(T) = \rho_0 + AT^n \). [Kim et al., 2013]

temperature. The large noise in the low temperature data for 3.90 and 4.58 GPa is restricted to one particular packing of the pressure cell (with higher noise) as the higher pressure \( n \) values (from different pressure cell packings) do not suffer from such large noise. For pressures above 4.58 GPa, \( n = 2 \) for a short range at low temperatures then gradually decreases as temperature increases. For the highest pressures where \( P \geq 5.71 \) GPa, \( n = 2 \) for only the lowest temperatures and instead shows \( n \) close to 1.5 for a significant temperature range. Since at our highest pressure, 8.23 GPa, is still below the expected \( P_c \approx 9.8 \) GPa, it is still possible that by 9.8 GPa, the system will manifest an \( n = 1.5 \) power law behavior over a wider temperature range. If AFM order does arise at the critical pressure, this would be consistent with the results for spin fluctuation theories by Hertz and Millis as well as Moriya [Hertz, 1976; Millis, 1993; Moriya and Takimoto, 1995] where an \( n = 1.5 \) power law is predicted for
a 3D AFM system. On the other hand, if ferromagnetic ordering occurs, $n \approx 1.33$ or 1.67 is predicted by Moriya [Moriya and Takimoto, 1995] for 2D or 3D systems, respectively.

Another possibility is that instead of a QCP, we may be approaching a quantum critical region where neither Fermi-liquid behavior nor magnetic ordering exists and instead another exotic ground state may stabilize which is then followed by, at higher pressure, a magnetically ordered state [Bud’ko et al., 2004, 2005a,b; Custers et al., 2010; Schmiedeshoff et al., 2011; Mun et al., 2013]. It is evident that higher pressure measurements are necessary to further explore these possibilities.

### 6.5 Conclusion

The resistivity of YbFe$_2$Zn$_{20}$ was measured under pressure up to 8.23 GPa and down to temperatures of almost 0.3 K. Increasing pressure drives the characteristic Kondo temperature, $T_K$, to lower temperatures and diminishes the range of Fermi-liquid behavior. The dramatic enhancement of $A$ as pressure increases to 8.23 GPa suggests a close proximity of YbFe$_2$Zn$_{20}$, at our highest pressure, to a quantum critical point where the system may develop a new magnetic ground state. Although not reached in this study, the critical pressure for YbFe$_2$Zn$_{20}$ can be inferred from $A(P) \propto (P - P_c)^{-2}$ to be $P_c \simeq 9.8$ GPa.
CHAPTER 7. CONCLUSIONS

Pressure has many uses in the sciences. For us, it provides a “clean” parameter with which to probe the electronic properties of materials. We mean “clean” in the sense that it does not add disorder to a system in the way that elemental substitution does. Under pressure, the materials properties can change dramatically as a consequence of the strain on the lattice. As we have seen, the pressure on the lattice can cause changes to the Fermi surface, density of states, electronic bandwidth, and structural stability, all of which can affect the electron-electron interactions that dictate the behavior of the material. Ultimately, this helps us to understand which mechanism is driving the systems’ behavior and how the mechanism works.

The recently discovered Fe-based superconductors provided fertile ground for pressure studies of high temperature superconductors. Pressure measurements of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ confirmed the need to suppress the antiferromagnetic (AFM) ordering for superconductivity to arise. It was apparent from this and multitudes of measurements on other related compounds that these two ground states are competing with each other. For substitution of Ru for Fe in BaFe$_2$As$_2$, the lattice experiences a decrease in the $c$ lattice parameter and an increase in both $a$ and $b$ lattice parameters, leading to an overall increase in volume [Thaler et al., 2010]. Unlike other transition metal substitutions, Ru does not add an electron or hole to the system. One possible reason for the suppression of AFM order was that the change in lattice parameters or the disorder caused by the Ru ions could alter the nesting property of the Fermi surface and thus destroy the spin density wave AFM ordering. Another possibility was that the Ru ion, in some sense was diluting the magnetism of the Fe moments by changing the bandwidth of the conduction electrons. More recently, angle resolved photoemission studies (ARPES) on Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ for $0 < x < 0.55$ indicated no appreciable change in the Fermi surface across the series, implying that the nesting property was unchanged thus pointing to magnetic
dilution as the likely cause of the suppression of magnetic ordering [Dhaka et al., 2011]. In our studies, it was hoped to make a connection between the behavior of the parent $\text{BaFe}_2\text{As}_2$ and several Ru substituted compounds in their response to pressure. It was revealed that there was a simple relationship between pressure and Ru substitution, mainly that 3 GPa of pressure was akin to a $x = 0.10$ Ru concentration. The response of the Ru substituted systems to pressure is very like the response of the parent compound, except shifted in value to account for the fact that in $\text{Ba(Fe}_{1-x}\text{Ru}_x)\text{As}_2$, the AFM is already suppressed to some degree. Under pressure, whatever mechanism that is suppressing the AFM ordering in $\text{BaFe}_2\text{As}_2$ seems to affect $\text{Ba(Fe}_{1-x}\text{Ru}_x)\text{As}_2$ in the same manner.

Within the last 30 years, there has been a resurgence in interest in materials exhibiting metal-to-insulator transitions which can be attributed to discovery of the CuO based high temperature superconductors. In undoped parent compounds, these materials are characterized as Mott-insulators, where Coulomb repulsion leads to localization of electrons on the atomic sites and causes insulating behavior. Earlier examples of Mott insulators, $\text{V}_2\text{O}_3$ and $\text{VO}_2$ showed signs of a highly correlated ground state. The Magnéli series, $\text{V}_n\text{O}_{2n-1}$, that bridges these two compounds shed light on this highly correlated state and may perhaps elucidate the mechanism for their difference in behavior. All but one of this Magnéli series ($\text{V}_7\text{O}_{13}$) undergoes a MI transition and makes it a curious outlier. In order to reconcile its disparate behavior and hopefully provide a unifying trend for the entire series, $\text{V}_6\text{O}_{11}$ and $\text{V}_7\text{O}_{13}$ were measured under pressure. It was revealed that the MI transition in $\text{V}_6\text{O}_{11}$ could be fully suppressed by 3.87 GPa and the AFM transition in metallic $\text{V}_7\text{O}_{13}$ is suppressed by 3.5 GPa, nearly the same as that found in a previous study [Ueda et al., 2003]. A comparison of the $T_N$ and $T_{MI}$ versus $P$ phase diagrams of $\text{V}_6\text{O}_{11}$, $\text{V}_7\text{O}_{13}$, and $\text{V}_8\text{O}_{15}$ reveal that there might be an underlying AFM ordering in the metallic state of these materials. The metallic state $T_N$ versus $P$ phase diagram for $\text{V}_7\text{O}_{13}$ and $\text{V}_8\text{O}_{15}$ map directly onto each other without any other normalization. However, the insulating state of $\text{V}_6\text{O}_{11}$ is found to be too robust, in that it persists beyond the AFM critical pressure for $\text{V}_7\text{O}_{13}$. Another property that we probed was the Fermi liquid state of $\text{V}_7\text{O}_{13}$ near the critical pressure. A past measurement of $\text{V}_7\text{O}_{13}$ under pressure down to 1.7 K [Ueda et al., 2003] indicated non-Fermi liquid (nFL) behavior at the
critical pressure, indicating a possible proximity to a quantum critical point. Measurements in this thesis reveal that this nFL behavior was instead, a crossover region to FL behavior at even lower temperatures. However, the small temperature range where FL behavior is seen suggests that the quantum critical point may be close by in pressure. As stated before, high pressure and low temperature measurements of V$_3$O$_9$ and the other vanadium Magnéli series members could provide more insight into the correlated electron ground state in their metallic phases.

Quantum criticality is the phase transition that occurs due to quantum fluctuations in the absence of thermal fluctuations. Necessarily, this should occur at $T = 0$ however, these quantum fluctuations still have reverberating effects at temperatures close to zero [Sachdev, 2001]. If the phase transition is not driven by temperature, then it can be driven by other non-thermal parameters. For heavy fermion systems, this is reflected in the Doniach phase diagram which outlines the competition of interaction energies (Kondo effect or Ruderman-Kittel-Kasuya-Yosida mediated magnetic ordering) as they are driven by a perturbative, non-thermal parameter [Doniach, 1977]. In our case, the non-thermal parameter was the application of pressure. In the YbFe$_2$Zn$_{20}$ heavy fermion system, the Kondo effect was well established as the dominant electronic state [Torikachvili et al., 2007; Canfield et al., 2008; Jia et al., 2009]. Under pressure, the system approached a quantum critical point, seen as the dramatically reduced temperature range of the low temperature Fermi liquid behavior and the divergence of $A$ (the Fermi liquid coefficient) in $\rho = \rho_0 + AT^2$. A large $A$ indicates a large effective electron mass. Although magnetic ordering was not seen down to 0.320 K and up to 8.23 GPa, the $A$ versus pressure phase diagram indicated that the quantum critical point that bring about magnetic ordering, is just above our pressure capabilities. Higher pressure measurements with a diamond anvil cell should be done to pursue the nearby QCP. Furthermore, pressure measurements of the other members of the Yb-based heavy fermion family can help is understand how changing the TM in YbTM$_2$Zn$_{20}$ affects the interaction energies of the correlated electrons.
APPENDIX A. THE MODIFIED BRIDGMAN ANVIL CELL (mBAC)

A.1 Introduction

As has been shown, the modified Bridgman Anvil Cell is useful for a variety of measurements. Its improved hydrostaticity with the use of a liquid medium makes it an ideal pressure cell for transport measurements at intermediate pressures between the working pressure ranges of the piston cylinder cell and the diamond anvil cell. The following sections describe in detail the construction of a modified Bridgman Anvil Cell, going over the essential components (BeCu body, gasket, anvils, and manometers), and the process of setting up a working pressure cell.

A.2 Components of a Modified Bridgman Cell

A.2.1 BeCu

The body and several other components of the mBAC are made of beryllium copper (BeCu) C17200, which is an alloy of copper with 1.8-2.00% Beryllium by weight with less than a 1% of Cobalt, Nickel, and Iron. The hardness, on the Hardness Rockwell Scale C (HRC), of BeCu ranges from 38-44. For reference, hard steels have a hardness in the range of HRC 55-66 [Wikipedia, 2012]. After being machined to the desired dimensions, the BeCu is further hardened using a process called age hardening. This was done by heat treating the alloy at 320°C for 3 hours to improve its yield strength. For high pressure applications, it is necessary for the body to retain enough plasticity while under pressure and also during cooling to very low temperatures. Contrary to expectations, the plasticity of BeCu actually increases slightly upon cooling [Eremets, 1996]. The lack of embrittlement of the BeCu with cooling makes it a safe material to use for high pressure and low temperature measurements. Schematics of the dimensions of the Bridgman Cell are shown in Figures A.1 and A.2.
Figure A.1  Schematics of the modified Bridgman Anvil Cell by Daniel Jones
A.2.2 Gasket

Pyrophyllite is a naturally formed material made up of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ that can be found near hydrothermal vents all across the world [Carte, 1955; Chao and Ruoff, 1970]. It is also known as Wonderstone, G-stone, or Koranna. Pyrophyllite is used as the gasket for the pressure cells because it is an insulating material that is easy to machine and polish, with a Mohs hardness between 1 to 2. Furthermore and more importantly, its yield strength increases under pressure [Eremets, 1996]. For reference, indium, tin, and lead have a Mohs hardness of $\sim$1.5. It can be easily glued to the surface of the anvil using a stiff glue (Sodium Silicate Solution) which prevents it from slipping under high pressures. Pyrophyllite is used as a gasket material because its yield strength increases with pressure from $\approx 0.2$ GPa at ambient pressure to $\approx 1$ GPa at 4 GPa. Under pressure, it compresses without extruding significantly, and also is a good electrical insulator [Eremets, 1996].

Typically, the pyrophyllite gaskets were machined with a lathe to have a 3.5 mm outer diameter (OD) and 2 mm inner diameter (ID); and polished with 1200 grit sandpaper to 0.200 mm in thickness. These dimensions can be multiplicatively sized down for smaller ODs, for example, a gasket with 3.2 mm OD will have a 1.83 mm ID and a thickness of 0.183 mm.

During the summer, when humidity is high, it becomes necessary to dry the gaskets in a furnace at 120°C for about two hours. Then to ensure that good gluing is possible, a gasket is glued to the anvil then the pressure cell was assembled without any other preparation and the gasket is squeezed with 2000 lbs of load. After this process, if the gasket is still affixed to the culet of the anvil, then all the conditions are good for a successful preparation of the cell. However, if the gasket is loose after this process, then either the ambient humidity is too high or the gasket needs to be dried for an extended period of time.

A.2.3 Anvils

For the anvils, we use a tungsten-carbide (WC) anvil machined to our specifications (Figure A.3). Both Ni and Co can be used as a binder for WC fabrication and although WC with Co is stronger and less brittle than with Ni, the latter is less magnetic. It was found that the
level of ferromagnetism seen in the WC depends on the quality control of the manufacturing company. The WC that is used for the anvils have roughly 8% Ni with a minute ferromagnetic component. These were purchased from Ceratizit (CTM160 φ14 mm). The lack of a magnetic signature is important for our setup, especially since the superconducting transition of Pb can be affected by magnetic fields, which then gives an erroneous pressure value. Furthermore, minimizing the magnetism from the WC anvils are also important when field dependent measurements of the sample are necessary. The dimensions of the WC anvils are shown in Figure A.3 for a culet diameter of 3.2 mm. Note the chamfer cut on the bottom edges of the anvil (see below for details). The BeCu bottom screw and top piston that the the WC anvils sit in do not have perfect corners inside the base. Initially, a brass ring was glued to the outside of the WC anvils, to account for the imperfect corners. Later on, a chamfer was cut directly on the WC anvils, diminished the need for the brass rings.

The culet diameter sizes ranged from 3.2 to 3.5 mm in diameter depending on the sample space that was desired.

![Figure A.3 Typical dimensions of the WC anvils used in the pressure cell.](image)

### A.2.4 Manometers

To accurately measure the pressure inside the sample space, several types of manometers can be used. Manganin wire undergoes changes in the resistance as pressure is applied. It is also sensitive to non-hydrostaticity [Sundqvist, 1987]. However, Manganin wire is not used with the Bridgman cell because it requires a larger sample space than is available. Furthermore, it is
less reliable in the non-hydrostatic conditions that can occur when the liquid medium solidifies.

Another method is to use an elemental metal such as tin or lead. These are readily available in high purity form and the pressure dependences of their superconducting transition temperatures have been extensively tabulated and have appropriate \( \frac{dT_c}{d\rho} \) values for the anticipated pressure range (see Figure A.4). For the Bridgman pressure cells, a lead sample was included with the sample for each run, to be used as a manometer. Compared to other elemental superconductors, lead has one of the highest superconducting transition temperatures. Furthermore, lead is malleable and can be shaped and cut into the desired rectangular bars quite easily. In order to spot weld gold wires onto the lead, the surface was polished by brushing it once or twice with a paper tissue and then flattening it again by gently rolling a glass vial over it. This way, spot welding gold wires onto the surface was not difficult. (See Figure 3.7 for an example of a lead sample in the cell.)

![Figure A.4 Pressure dependent \( T_c \) of Pb from Bireckoven and Wittig, 1988.](image)

### A.3 Preparation of the Bridgman Cell

The anvils are cleaned and then placed into the bottom BeCu screw and top piston. Originally, a brass ring was placed around the anvil due to the curved inner corners of the plug and piston. However, later on, a chamfer was made directly on the anvil, negating the need for the brass ring. Once the anvil sits snugly inside its BeCu holder, a thickened epoxy (Blue Araldite)
is gently draped into the interstitial space between the anvil and the BeCu. Thickening the epoxy a priori makes sure that it will not seep all the way down to the bottom and underneath the anvil, which would make the anvil nearly impossible to remove later, at the end of the run. There are often uncertainties associated with the anvils culet size (up to 0.3 mm uncertainty) which are machined by the Ames Lab Machine Shop. It is then important to check the size of the new anvils under the microscope and if one has a slightly bigger diameter (not more than 0.1 mm), it should be preferably used as the top anvil (closer to the loading piston).

Once the epoxy is cured, the anvils are then checked for levelness. For every 1 mm in diameter of the face, the height can differ by not more than 5 µm. A Mitutoyo Absolute Digimatic Indicator (Model # ID-S112E) is used to measure this height difference shown in Fig. A.5. As long as the BeCu components of the pressure cell have been machined to the appropriate precision, with the anvils seated in their respective BeCu parts, their culets should be parallel.

Small square soldering pads are then glued to the top of the bottom BeCu screw using epoxy (see Figure A.6). They should lie flat and should not be higher than the height of the anvil. These soldering pads are made of an insulating G10 layer, covered by a copper layer, and then finally lead solder. These soldering pads provide a contact point for the copper wires that connect to the PPMS puck.

Copper wires of American Wire Gauge (AWG) 34 are twisted in pairs and then encased in plastic tubing. These are then fed through the side holes in the bottom BeCu screw (see Figure A.7). Then the PPMS puck is glued to the bottom of the BeCu using GE varnish, then weighed down with a heavy weight and left overnight to dry. The copper wire is affixed to the holes by applying a small dab of thickened epoxy. Then the copper wires are soldered to the bottom of the puck and also to the soldering pads. This provides the connection between the sample and the puck. In the present case, the connections to the puck are made to be used with the AC Transport option in the PPMS, so the current and voltage wires are appropriately connected.

Pyrophyllite gaskets are machined out of rods of pyrophyllite. It is machined and then polished to the following dimensions: 3.2 mm outer diameter, 1.8 mm inner diameter, and
Figure A.5  A Mitutoyo digital thickness gauge used to check the levelness of the culet of the anvil seated in the BeCu plug.
Figure A.6  Closer view of the soldering pads on the mBAC. In this case, a brass ring was used around the anvil.

Figure A.7  The top left piece is the top plug (closest to the loading piston) with a WC anvil and brass ring glued inside. The top right piece is a PPMS puck which provides the electrical connected to the PPMS. The bottom piece is the bottom plug (furthest from the loading piston) with Cu wires fed through the holes in it its perimeter. The Cu wires provide the electrical connection between the inner chamber of the cell and the PPMS puck.
0.183 mm thickness. For larger anvil faces, the dimensions of the inner diameter and thickness are proportionally scaled up. The outer diameter upper limit of 3.5 mm provides ample space within the gasket (2.0 mm), however, this decreases the maximum pressure that can be achieved due to the larger area to which the load force is applied to. The pyrophyllite gasket is glued to the face of the bottom anvil using Sodium Silicate Solution (SSS). SSS is a stiff glue that fastens the gasket to the anvil so that under pressure, the gasket does not slip. Once the SSS hardens a bit, excess SSS from just outside the gasket, is removed. If the SSS is allowed to hardened for too long, then removing the SSS just outside the gasket risks delaminating the SSS glue underneath the gasket as well. Then the SSS is removed everywhere else on the anvil except directly underneath the gasket.

Teflon rings serves as the liquid barrier within the gasket and are machined from a rod of Teflon. The dimensions of the rings are 1.8 mm OD, 1.3 mm ID, and 0.05 to 0.11 mm in thickness. Although the rings are machined to these dimensions, these values are approximations since Teflon is a soft material. The minute thickness is achieved by polishing with a 2400 grit sandpaper that has already been used to polish the pyrophyllite gasket. This allows for a gentler polishing of the very soft Teflon rings. The desired final thickness of the Teflon rings are determined by stacking both rings within the gasket that has already been glued down with the SSS. With both rings placed, the top one should be flush with the gasket, or preferably just barely above it if the pressure medium is 1:1 n-pentane : iso-pentane. When using 1:1 FC70 : FC770, the Teflon thickness should be just barely below the gasket height. This variation in Teflon thickness with liquid medium is due to the differences in compressibility of the liquid media.

After removing the excess SSS, the rest of the surface of the anvil is coated with epoxy (Blue Araldite); this includes the culet surface within the gasket. The bottom Teflon ring is placed within the gasket and is glued down by the epoxy. This coating ensures that there are no electrical shorts between the wires and the anvil. Furthermore, some glue is draped on the sides of the gasket as shown in Figure A.8 to provide some small support to the pyrophyllite when it extrudes under pressure. The top anvil is also coated with this epoxy everywhere except on the outer ring of the culet, where the gasket will be in contact with the top anvil.
After the epoxy has cured overnight, eight small triangles were cut out of the epoxy surrounding the gasket and a small amount of fast drying epoxy (Red Araldite) was spread within the triangles (see Figure A.9). Then using a homemade blade fashioned from existing straight edge razors (thickness 0.236 mm), narrow slits were carved out of the gasket itself, corresponding to the locations of the triangles. Commercially available scalpel blades were too wide for creating these slits. These slits allow the platinum wires to pass through the gasket to the soldering pads on the outer edge of the anvil. The depth of the slits are determined by the height of the inner Teflon ring to ensure that the platinum wire when placed in the gasket is at the same height as on the Teflon ring. However, despite the height of the lower Teflon ring, the depth of the slits should not be more than 2/3 the gasket thickness.

Platinum wires are annealed to make them more malleable. One end of the wire is flattened (less than 1 mm) by rolling a small glass vial and cutting off any excess length using a straight edge razor. The wires are placed so that the flattened ends are placed within the gasket and passed through the slits and the triangles. Outside of the gasket the wires are fastened to the glue covered anvil with electrical tape (see Figure A.9). The tape prevents the wires from moving as well as preventing electrical shorts with other wires. The ends of these wires are then soldered to the solder pads, thus providing the electrical connection from within the gasket to the PPMS puck glued on the bottom of the cell. For a brief period, 25 µm gold wires were used instead of the platinum wires, however, this led to more breaks in electrical contacts when the cell was pressurized. The prevailing theory is that the gold wires were more inclined to
break between the gasket and the Teflon ring as load is applied. The platinum wire, being thicker, is less susceptible to breaking at this juncture.

Figure A.9 Image of a prepared mBAC before samples are placed.

The sample and lead are placed within the gasket and the flattened ends of the platinum wires are bent to cover the respective gold wires of the samples. This provides a mechanical contact under pressure. Sometimes, to further safeguard this connection, a small amount of silver paint is painted on this connection (see Figure 3.7).

The slits in the gaskets are then filled in with a dense mixture of epoxy and pyrophyllite powder. Increasing amounts of pyrophyllite powder is mixed into the epoxy until it appears very dry. This ensures that the epoxy will not seep into the gasket. Once filled in, the epoxy mixture in the slits is made flush with the surrounding gasket (see Figure 3.7).

The top Teflon ring is precariously affixed by applying a small drop of epoxy on one of the flattened platinum ends away from any gold wires. At this point, the ambient temperature and pressure resistance of both the sample and the lead is measured.
Then the BeCu body is screwed on and the liquid medium is inserted using an eye dropper to pour the liquid along the inside wall. This method prevents the various components within the gasket from shifting as the liquid is filled. For our most hydrostatic measurements, a 1:1 n-pentane : iso-pentane was used. If higher pressures are desired, 1:1 FC70 : FC770 was used. Enough liquid is added so that the liquid level was higher than the top of the gasket, ensuring that the volume within the gasket is completely filled. Then a visual check is made to confirm that the top Teflon ring is still held in its position. For the cells where the 1:1 n-pentane : iso-pentane mixture is used, an extra check was made to ensure that the liquid is no longer bubbling within the gasket. Due to the fast evaporation of the 1:1 n-pentane : iso-pentane mixture, excess liquid is poured in.

The top anvil is then carefully and slowly lowered into the body. Sudden movements during this step have in the past caused the top Teflon to shift and overlay parts of the gasket which under pressure lead to low pressure ruptures (explosions) of the cell. If using the 1:1 n-pentane : iso-pentane mixture, the liquid medium should cover the top piston (up to the BeCu disc) at this point. Then the BeCu disc is place on top and the top plug screwed on slightly. The BeCu disc provides a barrier between the loading piston and the BeCu top piston when the top screw is tightened.

Then a collar, a stand, and a press piston are assembled to the cell. The load is applied using a hydraulic press. A slow, continuous motion should be used to apply the load. It is important to make sure that the initial load be roughly 2000 lbs or greater to ensure proper sealing by the Teflon rings. If not, the liquid medium will leak through causing initially a slow decrease in pressure and then a rapid catastrophic depressurization, or more adequately called an explosion. Once the cell explodes, nothing within the gasket can be recovered and the platinum wires are unusable. The preparation of the cell has to be restarted from the gluing of the gasket.

If a minimum load is reached without explosion, a torque wrench is used to screw the top plug. The typical relationship between the load and the torque wrench setting is $n \times 1000$ lbs load=$n \times 10$ N m. Once the torque wrench locks (it clicks when the designated torque is achieved), the load from the hydraulic press is slowly decreased. After the pressure has been
locked in, there is a relaxation time where the various components of the cell need stabilize. For the less hydrostatic 1:1 FC70 : FC770 mixture, this is usually 8 hours. For the more hydrostatic 1:1 n-pentane : iso-pentane mixture, this can be as little as 3 hours. This relaxation time was determined by measuring the resistance of the lead at ambient temperature over time. Initially, there is a small increase in resistance and then a slow decrease and finally saturates. After the relaxation time, the resistance of the lead sample is again measured. The ratio of the resistance of the lead at pressure to the lead at ambient pressure gives a first estimate of the pressure inside the cell. Figure A.10 shows the approximate relationship between pressure and the ratio of the resistances at ambient and loaded pressure [Balchan and Drickamer, 1961]. More accurate measurements of the pressure, at low temperature, are done with the superconducting temperature of the Pb sample.

![Figure A.10](image_url)

Figure A.10  Resistance ratio versus pressure for Pb at ambient temperature used to estimate the pressure upon loading of the cell [Balchan and Drickamer, 1961].

Although the preparation process seems extensive, once the preliminary components are assembled, only the gasket, Teflon rings, and the circuitry on top of the anvil needs to be changed for each setup. If this is the case, preparation of a cell takes as little as two days. However, if the whole cell needs to be prepared, at least five days are required.
A.4 Solidification of Liquid Media with Pressure and Temperature

Given the importance of hydrostaticity for the measurements of $\rho(T)$ under pressure, we often opted for a pressure medium that solidifies at relatively high pressure at ambient temperature for each pressure cell, thus reducing non-hydrostatic components associated with the pressurization process. As a side product of our studies on FeAs-based materials, we were able to use the sensitivity of Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ to pressure conditions in order to track the melting temperature of the two liquid media we use most commonly at various pressures. We found that on warming, the resistivity data at various pressures and samples showed a small, anomalous, kink-like feature at temperatures well above any phase transition associated with the sample (see Fig. A.11(a)). Because this resistive anomaly consistently appeared at similar temperatures for similar pressures, and was independent of Ru content, it was attributed to a subtle change in the pressure conditions. For the mBAC with the 1:1 n-pentane : iso-pentane mixture, this feature was found to correspond to the melting temperature of the liquid medium [Klotz et al., 2006]. Although this feature is essentially invisible in the $\rho(T)$ plots shown in Chapter 4 and is even difficult to see in the expanded Fig. A.11(a), this feature is readily seen in the derivative of the resistivity, Fig. A.11(b). The minimum of this derivative was taken as the vitrification/solidification temperature of the liquid medium.

The $T - P$ phase diagram inferred from these data is presented in Fig. A.12. When this curve is extrapolated to zero pressure, the melting event occurs at $\sim 85$ K. This is lower than the previously reported freezing temperatures (105 K and 125 K at ambient pressure [Klotz et al., 2006; Sundqvist, 1987]) but this discrepancy is not unexpected given the different criterion used to determine this: Sundqvist, et al. measured the resistivity of a Manganin wire, suspended in this liquid medium and noted the temperature at which the resistivity dramatically diverges from the expected linear behavior, indicating the onset of solidification [Sundqvist, 1987]. On the other hand, Klotz, et al. used the “blocked-capillary method” where a thin capillary inside a temperature-controlled, copper block is filled with the liquid medium [Klotz et al., 2006]. In this case, the reported values are for temperatures where the liquid medium attains a viscosity similar to thick molasses.
Figure A.11  (a) Feature in resistivity data for Ba(Fe$_{0.79}$Ru$_{0.21}$)$_2$As$_2$ at 2.27, 3.28, and 3.99 GPa. Dashed are extrapolations of the lower temperature, linear $\rho(T)$ data. (b) Feature in $d\rho/dT$ indicative of the melting of the liquid medium.
More importantly, it is useful to know the hydrostatic limit of the liquid medium at the temperature when pressure is applied. Usually this is at room temperature ($\sim 300$ K). Measurements where rubies were placed in a diamond anvil cell which was filled with the 1:1 n-pentane : iso-pentane mixture [Piermarini et al., 1973; Klotz et al., 2009] showed that at 7.4 GPa, there was a broadening of the spectral line of rubies. This was correlated to the solidification of the medium. The hardness of rubies makes them less sensitive to pressure gradients, therefore 7.4 GPa can be considered a higher hydrostatic limit of the liquid medium.

In a different approach, Manganin wire was suspended in the liquid medium and the resistivity was measured, however this time, inside a cubic anvil pressure cell [Nomura et al., 1982]. At 283 K, the resistivity of the Manganin wire diverged from the expected linear behavior at 5.6 GPa.

In our study, the anomaly seen in the resistivity curves indicate that the melting event occurs at $\sim 6.0$ GPa at 300 K which is within the range of previously reported values. In fact at $\sim 283$ K, the hydrostatic limit from our study is 6.5 GPa which is only 0.4 GPa higher than the results from [Nomura et al., 1982].
The advantage of this study was that the freezing transition was tracked across a wide range of temperatures and pressures. Previous reports [Klotz et al., 2009, 2006; Piermarini et al., 1973; Nomura et al., 1982] on the vitrification/solidification of the 1:1 n-pentane : iso-pentane mixture were typically studied only at a given temperature or pressure.

In a similar manner, the vitrification/solidification temperature of the mixture of 6:4 n-pentane : mineral oil was determined at several pressures using the piston cylinder cell. The resistivity data for $\text{Ba(Fe}_{0.79}\text{Ru}_{0.21})_2\text{As}_2$ taken on warming with this liquid medium showed a similar anomalous kink the the derivative of the resistivity data showed a clear feature that we took to be the vitrification/solidification event. Figure A.13 shows the $T - P$ phase diagram for this liquid medium. At 300 K, this phase transition is expected to occur at a pressure of roughly 3.5 GPa, thus quantitatively justifying the use of this liquid medium at pressures up to 3 GPa in the past [Bud’ko et al., 1984].

![Figure A.13](image)

**Figure A.13** Phase diagram of the vitrification/solidification of 6:4 n-pentane : mineral oil

In light of these discoveries, it became obvious that $\text{BaFe}_2\text{As}_2$ and related FeAs materials could be used to track the vitrification/solidification temperature of any liquid medium under
pressure. In fact, this method is being used currently by Professor Milton Torikachvili to
determine the hydrostatic limit of a variety of liquid pressure media.

A.5 Explosions, Electrical Shorts and Breaks

Not all prepared pressure cells were successful. The most common failure was a catastrophic
explosion of the gasket upon applying load as seen in Figure A.14. In the past, these explosions
started occurring shortly after the beginning of summer. A systematic search for the cause of
the explosions eventually led to an issue with humidity, the pyrophyllite gasket, and the sodium
silicate solution used to glue it to the anvil.

Figure A.14  (a) Sample space prepared for loading with pressure.  (b) Closer view of the
sample space. (c) Sample space after explosion. (d) Closer view of the exploded
sample space. A considerable section of the gasket has been removed by the
explosion, which indicates that the gasket was not glued adequately to the bottom
of the anvil.
An analysis of the aftermath of the explosions showed whole pieces of the gasket seemed to have become unseated. Typically, explosions are expected only when unloading a working cell and when they occur, only a small section of the gasket is removed, with the rest still firmly attached to the anvil surface. In the catastrophic explosions, whole chunks, at times more than half of the gasket was completely unseated. Therefore, the gasket was not properly glued to the anvil.

Several solutions were pursued to resolve this. One possibility was the type of glue that was used to reinforce the outer wall of the gasket. We currently use Blue Araldite which is an epoxy with a long (∼24 hr) curing time. This was switched to a clear stycast (1266), however, this was completely inadequate. After curing, lots of bubbles formed and stayed in the stycast, see Figure A.15. With the Blue Araldite, the bubbles always disappear when cured. Furthermore, the stycast was not as stiff as the Blue Araldite, and therefore, likely was not a good support for the gasket.

![Figure A.15](image)

Figure A.15 mBAC with clear stycast. (a) Close view showing the bubbles still present after curing. (b) The bubbles are present all over the anvil surface.

Another possibility was the anvil itself. The gasket is glued directly onto the anvil culet using sodium silicate solution, which is a stiff glue. If the gasket was becoming unseated, then it was possible that the glue was not attaching to the anvil culet. To resolve this, the culet was roughened slightly. This did not resolve the explosions.

New sodium silicate solution was purchased and used, suspecting that it might have a short shelf life. This also did not fix the issue.

In the end, everything component was exactly set to the way it was when the cells were
working, but the explosions continued. So the focus went to things that have changed that we did not actively change. Knowing that the gaskets were not exploding when I first started working with them, it was suspected that the summertime humidity was perhaps the issue. Therefore, the gaskets were baked at 120°C for two hours right before being glue to the anvil. At this point, instead of preparing an entire cell to have it explode, a preliminary test was used to determine if the gaskets were being glued well. In this test, the gasket is glued to the anvil culet and then the body assembled and load was applied. If the gasket stayed glued to the anvil, then it was a good day for gluing. If the gasket did not stick to the anvil, then the humidity was too high. Since controlling the humidity of the entire lab was cumbersome, an attempt was made to blow nitrogen gas (directly from a dewar) across the anvil during the gluing process. This made the sodium silicate solution cure much faster and considerably shortened the time available to place the gasket on the glue and anvil. In the end, a small room was converted to a work station for pressure cells where a dehumidifier decreased the summertime humidity to below 60%. In the end, a combination of using relatively new sodium silicate solution, prebaking the gaskets and working in the humidity controlled room led to consistently working pressure cells.

Another show stopping issue that can come up is the occurrence of an electrical short or break in one of the eight contact leads. Tracking down the cause was often made difficult by the fact that opening the cell would inevitably lead to an explosion. Once again, I would have to analyze the remnants of the exploded cell to determine the cause of the electrical failure. Early on, the main cause of the electrical shorts was from the platinum leads embedded in the pyrophyllite gasket. These were sometimes not buried deep enough and so during the loading of pressure, the platinum wire would touch the top anvil. Other times, even though the Pt wire was buried deeply in the gasket, while loading, the exposed platinum wire on the outer perimeter of the gasket got bent and pushed against the upper or lower anvil, causing an electrical short. Despite the use of the insulating Blue Araldite, shorts could still occur under pressure.

Another disconcerting failure were breaks in the electrical leads. There were two main causes for electrical breaks. For one, sometimes, the contact on the sample will fall off under
pressure. This occurs when special care is not taken to ensure a strong mechanical connection. The other common cause of failure was eventually resolved. For a short period, instead of using platinum leads to connect the 12.5 $\mu$m diameter gold leads from the sample to the soldering pads, a 25 $\mu$m gold wire was used (thinner than the platinum wires). This was to try to make the gasket stronger by decreasing the width of the slits. Most likely, the breaks occurred during the loading process. The different compression rates of the Teflon rings and the pyrophyllite gasket shears the gold wire, unlike the platinum wire, which is much thicker and more resilient to the shearing forces. Due to explosions upon opening the cell, this was never directly confirmed, however, upon reverting back to using the platinum wires, these electrical breaks no longer occurred.

There were also many cases where the pressure cell exploded for no obvious reason or contacts were lost after several good measurements. Other times, pressure cells have been accidentally dropped on to the cement floor and survived with no explosions. Figure A.16 shows before and after pictures of a rare case where the gasket did not explode when unloading after several pressure measurements.

![Figure A.16](image_url)

**Figure A.16** Sample space (a) before and (b) after pressure measurements. In this instance, the gasket did not explode when unloading the pressure cell. This was a great opportunity to see how the loading process deforms the various components of the setup. The left sample is the lead bar and on the right is a YbFe$_2$Zn$_{20}$ sample.
It shows all the components have been deformed in the pressurization process, however there seemed to be negligible change to the samples themselves. The lead manometer might have deformed slightly with pressure, but it is a very malleable metal and smaller forces can change its shape. Despite this, we are only concerned with the superconducting transition of the lead sample and not its absolute resistivity.

The maximum load for the two different sized pressure cells we use are 8,000 and 10,000 lbs. However, it is not uncommon to have other failures that prevent us from reaching these upper limits. First, as higher loads are applied, the sample space and the gasket are reduced in height which might cause the wires within to touch the anvil surfaces (despite our efforts to electrically insulate them). Second, the sample or wires might break. Third, the WC anvils might break. When the anvils break, there is a very loud sound, very similar to a hammer hitting a solid surface. When this occurs, the pressure within the cell is reduced, but the seal is not broken. This provides an opportunity to conduct low pressure measurements on a sample after high pressure measurements have already been done.

In order to remove the broken anvil, a removal tool (sturdy metal rod) is used (see Figure A.17).

Despite the iterated troubles, the modified Bridgman anvil cell has proven quite useful. One working cell provides an expansive pressure range of measurements, so the fruits of these labors are in fact, quite plentiful. With the humidity issues resolved, all pressure cells should be able to retain pressure. However, there can still be failures due to electrical shorts and breaks. The failure associated with these will depend on the person preparing the pressure cell. However, electrical shorts are more likely at higher pressures (greater than 6 GPa).
Figure A.17  Broken WC Anvil removed from BeCu.
APPENDIX B. ALBUM OF PREPARED BRIDGMAN ANVIL CELLS
APPENDIX C. HIGH PRESSURE FURNACE OPERATION

C.1 Introduction

The High Pressure Furnace (HPF) shown in Figure C.1 uses a cubic anvil system to generate a maximum pressure of 3.34 GPa and maximum working temperature 1700 °C in our sample space. The Walker system is another anvil system which uses an octahedral configuration and can be used to generate even higher pressures, but the following will only cover the operation of the cubic anvil system.

Figure C.1 Image of the High Pressure Furnace and ancillary devices.
The Pressure Chamber

Figure C.2 shows a side view of the high pressure furnace. Pressure is generated by having a load applied to the pressure chamber from the bottom. A diagram of this is shown in Figure C.3.

![Figure C.2 Closer image of the High Pressure Furnace](image)

Figure C.4 is an image of the four wedges/anvils, the four wedge drivers and the top and bottom anvils. When everything within the pressure chamber is assembled, the load is applied to bottom press plate which in turn puts a load onto the wedge drivers and the top and bottom anvils. The wedge drivers then apply a load onto the wedges, forcing them to move inward. In this manner, load is applied along all six directions of the pyrophyllite cube. The wedge drivers are made of hardened steel and the anvils are made of tungsten carbide (WC).

The following is a description of how to assemble the components for a pressure growth.
Figure C.3 Diagram of the Pressure Chamber
C.2 Operation

Packing a Crucible

When packing a crucible, the necessary elements are weighed out keeping in mind that the sample space is small. For malleable metals, it might be best to use a die and press to shape it into a compressed cylinder that fits into a BN cup; a diagram of this is shown in Fig. C.5.

For powders of several compounds, it is best to mix the powders thoroughly before placing into the crucible. Small metal rods like the steel dowel (used in the HPF) can be used to pack or stamp down the powder in the BN cup to get the powders compressed inside. After being packed down, if there is space at the top of the BN cup, it is filled with BN powder. This powder should also be packed down, using both the metal rod and the spatula. The BN powder should be flush with the BN cup as shown in Fig. C.6 for preparing MgB$_2$. 

Figure C.4 Wedge drivers and Anvils for the HPF. There are four wedge drivers, four wedges/anvils, and top and bottom anvil.
Figure C.5  Parts of the pyrophyllite cube that are ready to be assembled. Part of the bottom plug has been chipped off during the thermocouple drilling process, however it does not affect the pressure growth. If the chipped off piece is large, place it back during cube assembly. If not, no backfilling is necessary.

Figure C.6  Diagram of Mg, B, and BN powder packed into a BN cup.
Assembling the Cube

Figure C.7 shows a diagram of the assembled pyrophyllite cube. The graphite tube serves as the heater for the sample growth. The starting material in the BN cup sits in the middle of the cube and the thermocouple resides underneath the BN cup to measure the temperature nearest to it.

The WRe (tungsten-rhenium) thermocouples are purchased from Rhenium Alloys Inc. in pairs: one with 3% Re and the other with 25% Re and both with a diameter of 0.01”.

The bottom pyrophyllite plug needs to have a channel carved out for the thermocouple. A hole has already been drilled through the bottom plug (see below), so all that is needed is for the pyrophyllite above the hole to be carved out, shown in Figure C.8. Once this is done, the bottom plug is placed back into the cube.

About 2.5” of sheathing from the thermocouple wires need to be stripped, see Figure C.9. Then the alumina tubes should be cut long enough to span the distance between the inner edge of the carbon tube and the outer edge of pyrophyllite cube. This is done twice, one for each side.
Figure C.8 Image of bottom plug with the thermocouple hole carved out and alumina tubes cut to size.

This tube insulates the thermocouple wires thermally and electrically from the graphite tube (see Figure C.7). The alumina (Al$_2$O$_3$) tubes are purchased from Ozark Technical Ceramics and have one hole. The outer diameter is 0.58” and the inner diameter is 0.025”.

The thermocouple wire is fed through the small hole on the side of the cube through the hole in the graphite. Then it is pushed through the channel in the bottom pyrophyllite plug and finally through the other hole in the graphite and pyrophyllite on the other side. Put the alumina tubes on the exposed thermocouple wires, one for each wire (see Figure C.10).

Using the needle nose pliers, the last 2-3 mm of the end of the wires are bent back on itself, shown in Figure C.11.

The wires are hooked on each other and the hooks pinched closed so that the wires are mechanically well connected, see Figure C.12.

This connection point is pulled through the cube until it is in the middle of the cube, lying within the channel in the bottom plug, see Figure C.7. The alumina tubes need to be sitting within the pyrophyllite cube and peaking into the center hole, so that it is completely within the graphite, but barely within the central hole.

A visual check is done to make sure that the connection point of the two thermocouple wires is in the middle. With it positioned correctly, the thermocouple wires just outside the
Figure C.9  Thermocouple sheathing cut away leaving about 2.5” of exposed wire.

Figure C.10  Thermocouple wire fed through the cube. Alumina tubing is placed on both wires.
Figure C.11  Thermocouple wire bent using needle nose pliers.

Figure C.12  On the left, the thermocouple wires are shown with the bent ends. On the right, the ends are hooked together. These should be crimped with needle nose pliers to create a secure mechanical connection. Wiggle the wires together to see if the two wires are securely crimped together.
cube are bent towards the upper corners then bent again halfway to the lower corner and held there using scotch tape along the sides of the cube, see Figure C.13. This is done to prevent the thermocouple wires from snapping if ever they get snagged during the pressurization or heating process.

![Thermocouple wire taped to side of the pyrophyllite cube.](image)

Figure C.13  Thermocouple wire taped to side of the pyrophyllite cube.

This is done to the other side as well. Another piece of tape is used to hold a thin piece of copper on the bottom that covers the graphite tube. The tape should be just barely touching the copper, see Figure C.14.

The copper is used as a barrier between the graphite tube and the tungsten carbide anvils in order to prevent any reaction occurring between them. The BN cup with the sample is gently dropped into the tube, then the BN cap on top. Then the top pyrophyllite plug is placed over the BN cap. Once again, a small amount of tape is used to affix a thin (0.1 mm in thickness) square of copper to the top. The finished cube is shown in Figure C.15

**Preparation of the High Pressure Furnace**

Using the vacuum cleaner, the inside of the pressure chamber is thoroughly cleaned. Two strips of Mylar with thickness 0.002” are cut, with each one the same dimensions as the inner wall of the chamber. The Mylar strips are then spray-coated on each side with Teflon (shown in Fig. C.16). This is done under the fume hood.
Figure C.14  Bottom view of the cube. (a) Copper piece on the bottom is affixed with tape that also covers the thermocouple wire again. (b) The two pieces of tape should completely surround the thermocouple wire at the corner.

Figure C.15  The assembled pyrophyllite cube
These strips are placed along the inner wall of the pressure chamber, see Figure C.17. They should sit in the channel along the inner wall as shown in Fig. C.17. The ends of one strip should be on the opposite side of the ends of the other strip. This is to prevent any crumpling of ends during pressurization.

A G10 layer (with a thickness of 0.018") is placed on the bottom of the pressure chamber, with the holes lined up. The G10 has a cutout in the middle so that the outer bottom wedges are electrically insulated from the bottom pressure plate while the middle bottom anvil is not. An diagram of the G10 disc is shown in Figure C.18.

As will be explained later, during the heating schedule, the current exits out of the bottom anvil. The wires of the prepared cube are threaded through holes in the G10 (Figure C.19) and the bottom plate to the outside of the chamber (Figure C.20).

The thermocouple wires are attached to the temperature controller to check that the thermocouples within the cube are okay. Then molybdenum sulfide powder (MoS$_2$) suspended in an acetone solution is painted onto the faces of the bottom wedges. The MoS$_2$ acts as a lubricant at high pressure. The bottom wedges are placed so that the thermocouple wires are free to move. Then the bottom anvil is placed and the cube seated on top, see Figure C.21.
Figure C.17  Mylar placed in pressure chamber with the ends of each sheet on opposite sides. The inset diagram shows a more clear picture of how the sheets should be arranged.

Figure C.18  Diagram of the G10 disc.
Inside the pressure chamber, the Mylar sheet has been placed along the wall and the G10 bottom layer has been laid down. A thermocouple wire is being fed through the hole in the G10 and the bottom of the chamber.

Thermocouple fed to the outside of the pressure chamber.
Figure C.21 The bottom wedge drivers with a coating of molybdenum sulfide powder, bottom anvil, (a) dowel, (b) G10 mini spacers, and prepared cube are assembled. (c) space is made between the wedges so that the thermocouples can freely move.
The side anvils are carefully placed, two at a time. Then using a mallet and a level, the side anvils are tapped to ensure they are all parallel, see Figure C.22.

![Figure C.22 Side anvils placed in pressure chamber. A level and mallet are used to make sure that the side anvils are all parallel.](image)

Then the top wedges are also coated with MoS\(_2\) then placed on top of the side anvils slowly and in pairs. This is done using the long screws to hold the wedges, see Figure C.23.

Finally, the top anvil is carefully dropped in. At this point G10 spacers can be placed between the wedges to ensure there is space for the thermocouple wires, see Figure C.24.

A G10 disc is placed on top; this one also has a square cut out so that the top wedges are electrically insulated while the top anvil is not, see Figure C.25.

Then the top pressure plate is placed very gently and carefully, see Figure C.26.

Being careful with the thermocouple wires, the chamber is rolled into the center of the press and the two guiding pins are placed. At this point, the thermocouple wires are reattached to the thermocouple connector, see Figure C.27.
Figure C.23  Long screw to slowly drop in the top wedge drivers.

Figure C.24  After the top anvil is placed, G10 thermocouple spacers can be placed (white arrow).
Figure C.25  Top G10 placed.

Figure C.26  Top pressure plate placed over everything.
Applying the Load

A linear actuator lift generates the high pressure needed to apply a load to the pressure chamber. It has a finite length it can traverse, therefore, in order to reach the highest pressures, a smaller pump is used for the initial raising of the pressure chamber. The small pump should be set to "Up" to increase pressure on the bottom part of the press. Using the hand held pump operator (remote), the pressure chamber is lifted until the top pressure plate is flush with the top of the press. Once this is done, the top middle valve on the valve panel (Figure C.28) is almost completely closed. It is opened just enough so that one small increase of pressure with the remote causes the gauge to spike to 4000 psi and then back to zero in about one full second. This is done until 200 psi of pressure is achieved (check the control panel for this reading). Then the valve is completely closed and the control panel is set to Auto and Increase and Hold (Inc Hold). The maximum pressure is typically set to 6500 psi.

Heating Schedule

The heating schedule is controlled by the Eurotherm on the control panel. Before anything is started, the water chiller MUST be turned on. It is a closed cycle water chiller set to
21 °C. The computer program can then be started to monitor the pertinent values. Using the Eurotherm, an initial temperature of 150 °C is manually set. This is necessary because the thermocouple reading at these lower temperatures is unstable during slow temperature ramps, so they typically trigger a temperature fault. By initially ramping the heat to 150 °C, the fault region is avoided.

The heating schedule is the most common time a growth fails. This is typically due to an electrical break or short in the thermocouple contact.

**Unloading the Pressure**

Once the heating schedule is done and the temperature reading is back to room temperature, the water chiller can be turned off. The "Heater" is turned off. Set both the Auto Pressure and Manual Pressure dials to “off” and wait a few seconds. Set the Mode to “Manual.” Then set the Manual Pressure to “Decrease.”

Going down in pressure should take about 6 to 10 hours depending on the Motor Speed, which is typically set to 25%.
Even after this, the chamber will still be above its railings. Make sure the pressure reading on the control panel says 0 psi. Then open the top middle valve on the valve panel. Set the small pump to “down,” then then use the remote to lower the chamber. Stop when the wheels on the chamber do not spin freely. Lowering with the small press even further than this will cause a leak in the pressure relief valve, see Figure C.29.

![Pressure relief valve indicated by the white arrow.](image)

Remove the guiding pins and while being careful with the thermocouple wires, roll the pressure chamber out. Use the wrench to pry open the top gently. Flip it and put it to the side. Use the long screws to pull out the top wedge drivers. Break off the thermocouple wires from the cube (see Figure C.30) and set the cube aside. Then the rest can be taken out with your hands. Throw away the mylar sheet and vacuum up the pyrophyllite remnants.

For the next growth, the wedge drivers, the wedge/anvils, and the top and bottom anvils will need to be cleaned. A new straight edge razor is used each time to carefully and thoroughly scrape off the molybdenum sulfide and the pyrophyllite, see Fig. C.31. This should be done carefully so that the faces of these components are not scratched in any way, as that could introduce increased friction on the surface.

**Opening the Cube**

In order to open the cube, first wrap it in a sheet of paper to prevent pieces of it flying everywhere. With a chisel oriented parallel to the graphite tube, use a hammer to make one or
Figure C.30  Pressure chamber and pyrophyllite after a pressure growth.

Figure C.31  Dirty (background) and clean (foreground) wedge drivers.
two solid strikes and crack open the cube, see Figure C.32. The sample is then removed from its housing.

![Sample is here]

Figure C.32 Pyrophyllite cube opened after a pressure growth.

C.3 Components of a Prepared Cube

The following are descriptions of the components used to prepare a cube for pressure growth.

Pyrophyllite

The pyrophyllite cube is used as a self-gasketing pressure medium for the HPF. In its original state when it is delivered, it is a dark grey color. The pyrophyllite needs to be baked appropriately to convert it to the desired hardness. Over-baking the pyrophyllite causes it to harden beyond our capability to machine it with tungsten carbide tools. Furthermore, under load, the pyrophyllite will crack and break apart instead of extruding between the anvils as pressure is increased. An example of the extruded pyrophyllite is shown in Fig. C.30. A cube that cracks under pressure (instead of extruding) causes a sharp drop in pressure causing a fault to occur in the pressure monitor thereby ending the experiment. Typically, baking for too long at 1000 °C or at too high of a temperature 1300 °C will make the pyrophyllite too hard.
If the pyrophyllite is not heated enough, then it is too malleable, thus extruding too much between the anvils and high pressure is not achieved. Figure C.33 shows the color difference before and after baking. The temperature should increased slowly to prevent the pyrophyllite from cracking and possibly exploding.

![Figure C.33 Color difference of pyrophyllite cube (1) before and (2) after baking.](image)

Pyrophyllite expands (linearly) by 2\% after baking to 1000 °C. It also changes color from dark grey to a range of greyish pink and light pink. Cube to cube color variation is typical. There are batch to batch variations in pyrophyllite, therefore the heating schedule for the pyrophyllite will need to be tested with each new batch. Typically, after being heated, a pyrophyllite cube should be broken in half, see Figure C.34. It should be a uniform light pink color throughout. If there is still some grey color in the pyrophyllite, it was not heated for long enough. If the cube is difficult to machine afterwards, then it has been heated too long or at too high a temperature. From the difficulty or ease of machining the pyrophyllite after heating, one should eventually be able to discern whether the heating was done properly. If unsure, a cube from a batch that has been heated should be cracked open to look for any gray regions.

When pyrophyllite is ordered, they come as a long square rod. The Ames Laboratory machine shop cuts these rods into cubes of 0.96” sides. Any remaining material are made into pyrophyllite cylinders to be used as the top and bottom plugs. For heated sample growths the cylinders are machined to 0.280” in diameter and 0.325” in length. For pressure calibration runs with Bi, cylinders are machined to 0.318” in diameter and 0.480” in length so that both
plugs fit snugly within the pyrophyllite without the graphite tube. A visual check is done to make sure the edges of the cube are perpendicular. Lopsided cubes cannot be used in the HPF.

With the unheated pyrophyllite cubes, using the back tip of a scalpel and a ruler, make “X” marks on one side of all the cubes. This will be considered the top of the cube and marks where the main hole will be drilled.

Assuming the “X” mark is the top, the side of the cube is marked for the thermocouple hole. Using the aluminum pieces marked “Bottom” and “Side,” scratches are made into the the bottom center of the cube (see Figures C.35(b) and (c)), using the “Side” piece twice, once on either side. Once the markings are made, it looks like the cube in Figure C.35(d).

The drill press with the 5/16” drill bit, is used to drill a hole at the center of the “X” mark all the way through the cube. This is a preliminary hole for the cube. Because the pyrophyllite expands after annealing, this hole is smaller than the final hole. However, since the pyrophyllite is more difficult to machine after annealing, this initial hole is drilled beforehand. Using the 3.5 mm drill bit, a hole is drilled through the side (at the cross mark) all the way through the cube. Since the size of the hole for the thermocouple is not as crucial as the main hole, the 3.5 mm drill bit is used both before and after heating of the cube. This creates a hole big enough for the electrical/thermal insulator (Al₂O₃ tubes) to sit in.
Figure C.35 Unheated pyrophyllite cubes being prepared for drilling. (a) Metal ruler and scalpel used to mark “X”s on the pyrophyllite cubes. (b) Aluminum piece used to mark the bottom line for the thermocouple hole. (c) Aluminum piece used to mark the center of the hole. This should be used twice, once on either side. (d) Finished pyrophyllite cube with positions for drilling marked.
After the pyrophyllite cubes have been baked, a larger bigger drill bit (Size P 0.3230) is used to make the final hole. This should be done in a smooth single motion and can not be done too slow or too fast. The drilling causes the pyrophyllite to heat up and makes the pyrophyllite nearly impossible to machine.

**Graphite Furnace**

A graphite tube is used as the heating element for the HPF. In order to heat the sample space, a large current is run through the top anvil, through the graphite tube, then out through the bottom anvil. Typically, a current of \(\sim 200\) mA is needed to sustain a temperature of roughly \(1450^\circ\text{C}\). The carbon tubes need to be machined with outer diameter (OD) 0.321”, inner diameter (ID) 0.292” and length 0.98”. This should fit snugly into the baked and machined pyrophyllite cube.

**Boron Nitride (BN) Cup and Cap**

The HPF crucible is made out of BN. Other materials can be used as a crucible, but for the typical samples that we grow, BN has worked the best is and the also easiest to be machined. The BN cups and caps are machined to the following dimensions:

- BN Cup: OD 0.282”, ID 0.215”, Length 0.281”, and Inner Depth 0.247”
- BN Cap: OD 0.282” and Thickness 0.034”

Alternatively, MgO can be used, however, it is more brittle and thus more difficult to machine. The components of the cube can be seen in Figure C.5.
APPENDIX D. PUBLICATIONS AND SUMMARY OF EXPERIMENTS

Publications


Summary of Experimental Activity

Over the course of my studies, I have used the high pressure furnace for materials growth 84 times, assembled the modified Bridgman anvil cell 90 times, and taught a post-doctoral scientist how to prepare the modified Bridgman anvil cell as well as how to operate the high pressure furnace. Appendix E shows a list of all the high pressure materials growths and the modified Bridgman anvil cell packings that I have done.
## APPENDIX E. LISTS OF HIGH PRESSURE MATERIALS GROWTHS AND MODIFIED BRIDGMAN ANVIL CELL PREPARATIONS

### High Pressure Materials Growths

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<th>Sample</th>
<th>Batch #</th>
<th>Sample</th>
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High Pressure Materials Growths

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## High Pressure Cell Preparations

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\(^1\)Photos of most of these prepared pressure cells are shown in the album in Appendix B

\(^2\)1:1 FC70 : FC770

\(^3\)Clear Stycast
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$^4$1:1 n-pentane : iso-pentane  
$^5$1:5 n-pentane : iso-pentane
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