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Yuhasz, William M.

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A Study of
Strongly Correlated Electron Behavior
in the
Filled Skutterudites

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in
Materials Science and Engineering

by

William M. Yuhasz

Committee in charge:
Professor M. Brian Maple, Chair
Professor Dimitri N. Basov
Professor John E. Crowell
Professor M. Lea Rudee
Professor Edward T. Yu

2006
The dissertation of William M. Yuhasz is approved, and it is acceptable in quality and form for publication on microfilm:

[Signatures]

Chair

University of California, San Diego

2006
To my wife and family,

for all their love and support.
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VITA

1997-2000 Research Assistant, Natural Sciences Department
University of Michigan, Dearborn
Advisor: Aruna Nadasen

2000 B.S. in Physics, University of Michigan, Dearborn

2000-2006 Research Assistant, Department of Physics
University of California, San Diego
Advisor: Brian Maple

2000-2001 Teaching Assistant, Department of Physics
University of California, San Diego

2001 M.S. in Materials Science and Engineering
University of California, San Diego

2006 Ph.D. in Materials Science and Engineering
University of California, San Diego

PUBLICATIONS


FIELDS OF STUDY

Major Field: Materials Science and Engineering
Studies in Superconductivity and Magnetism
M. Brian Maple, Bernd T. Matthias Professor of Physics,
University of California, San Diego
ABSTRACT OF THE DISSERTATION

A Study of
Strongly Correlated Electron Behavior
in the
Filled Skutterudites

by
William M. Yuhasz

Doctor of Philosophy in Materials Science and Engineering
University of California, San Diego, 2006
Professor M. Brian Maple, Chair

In the search for new and interesting strongly correlated electron phenomena, a detailed study has been underway of the rare earth-based filled skutterudite compounds. This work has been driven by the rich variety of strongly correlated electron phenomena exhibited by the filled skutterudites such as metal insulator transitions, heavy fermion behavior, quadrupole ordering, non-Fermi liquid behavior, and heavy fermion superconductivity. The filled skutterudite compounds have the chemical formula $MT_4X_{12}$ where $M =$ alkali metal, alkaline-earth, lanthanide, or actinide; $T =$ Fe, Ru, or Os; and $X =$ P, As, or Sb. To improve the general understanding of these systems and to look for other strongly correlated electron behavior, single crystals of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$, $\text{PrOs}_4\text{As}_{12}$, $\text{PrOs}_4\text{P}_{12}$, $\text{SmOs}_4\text{Sb}_{12}$, and $\text{NdOs}_4\text{Sb}_{12}$ were grown and characterized with X-ray diffraction, magnetization, electrical resistivity and specific heat measurements.
Measurements of the filled skutterudite compound Pr$_{0.87}$Fe$_4$Sb$_{12}$ reveal long range magnetic ordering below 4.1 K with indications of ferrimagnetic ordering. Features in the magnetization of the filled skutterudite PrOs$_4$As$_{12}$ are consistent with antiferromagnetic ordering below 2.3 K. The specific heat, electrical resistivity, and magnetization measurements on PrOs$_4$As$_{12}$ also show features consistent with at least 2 to 3 ordered phases. Strong crystalline electric field effects were observed in PrOs$_4$P$_{12}$ and SmOs$_4$Sb$_{12}$, with both systems exhibiting Schottky anomalies in specific heat measurements. Magnetic ordering was observed in SmOs$_4$Sb$_{12}$ below 2.6 K with a ferromagnetic component as indicated by hysteresis in the magnetization as a function of field at 2 K. Magnetic ordering was also observed in the filled skutterudite compound NdOs$_4$Sb$_{12}$ below 0.9 K. Analysis of the specific heat measurements on Pr$_{0.87}$Fe$_4$Sb$_{12}$, PrOs$_4$As$_{12}$, SmOs$_4$Sb$_{12}$, and NdOs$_4$Sb$_{12}$ reveal an enhanced electron effective mass, with SmOs$_4$Sb$_{12}$ showing the largest enhancement.
Introduction

The pursuit of new and interesting strongly correlated electron phenomena has led to a systematic investigation of the rare earth-based filled skutterudite compounds. This pursuit has been driven by the remarkable fact that one can observe metal insulator transitions [1], magnetic order [2], heavy fermion behavior [3], superconductivity [4, 5], quadrupolar ordering [9, 10], Kondo insulating behavior [11], non-Fermi liquid behavior [12], quantum critical points [13,14], and heavy fermion superconductivity all in the same family of compounds [3]. The filled skutterudite compounds have the general formula $MT_4X_{12}$ ($M =$ alkali metal, alkaline-earth, lanthanide, or actinide; $T =$ Fe, Ru, or Os; and $X =$ pnictogen such as P, As, or Sb) with the a LaFe$_4$P$_{12}$-type structure ($Im\bar{3}$ space group) [15]. There are two formula units in the filled skutterudite unit cell totaling 34 atoms. The filled LaFe$_4$P$_{12}$-type structure is formed by filling large voids found in the skutterudite compounds with the $M$ atoms listed above (shown in Fig. 1.1). The skutterudites have the CoAs$_3$-type structure (Fig. 1.1) and the general formula $TX_3$ ($T =$ Co, Rh, or Ir and $X =$ P, As, or Sb) with 8 formula units per unit cell for a total of 32 atoms. The mineral skutterudite (CoAs$_3$) was named after area of Skutterud Norway, where it was first found. In 1928, Oftedal determined the structure of CoAs$_3$ and since that time [16], compounds with the CoAs$_3$-type structure (Fig. 1.1) have been referred to as skutterudites.

The skutterudite structure is composed of 8 canted octahedra formed by
$TX_3$ groups. The $T$ atoms at the centers of the canted octahedra are arranged in a simple cubic structure. At the center of the 8 canted octahedra a large void is formed, which is enclosed by 12 pnictogen atoms. This void has a distorted icosahedral shape, which can be seen in Fig. 1.2. In the filled skutterudite compounds, the voids act as “cage” structures, effectively “trapping” the $M$ atoms in a bcc arrangement shown in Fig. 1.1. As the lattice constant is increased from $\text{MFe}_4\text{P}_{12}$ ($\sim 7.8 \, \text{Å}$) to $\text{MO}_4\text{Sb}_{12}$ ($\sim 9.3 \, \text{Å}$), the size of the cage increases [17]. As support for this, Braun and Jeitschko noted the large thermal displacement parameters for the $M$ atoms, the large $M-X$ bond lengths, and weak lanthanide contraction for the antimonides compared to the phosphide and arsenide filled skutterudites [17].

The large thermal displacement parameters exhibited by the $M$ atoms are due to the large size of the icosahedral cage, which prevents strong bonding with the $X$ atoms. This large structure and weak bonding allow the $M$ atom to effectively
Figure 1.2 Model of the pnictogen icosahedral cage in the filled skutterudite structure.

“rattle” in the icosahedral cage, while the $TX_3$ sublattice remains rigid.

The electronic properties of the filled skutterudites, as stated earlier, are of great interest. In the early 1990’s, research into the thermoelectric properties of antimonide skutterudites such as IrSb$_3$ and CoSb$_3$ found that they exhibited promising characteristics for thermoelectric applications [18, 19, 21, 22]. These findings spurred on further research into the thermoelectric properties of the filled skutterudite compounds [20, 23, 24]. The potential of a material for thermoelectric applications depends on its total thermal conductivity $\kappa$, electrical conductivity $\sigma$, and Seebeck coefficient $S$. These material properties have been combined into a dimensionless figure of merit $ZT = TS^2\sigma/\kappa$, where $Z$ is the figure of merit and $T$ is the absolute temperature. The value of $ZT$ determines the efficiency of the thermoelectric material, with current materials possessing values from 0.4 to 1.0. In order for a thermoelectric cooling device to compete economically with
a modern household refrigerator, a $ZT$ close to 3 at room temperature would be required [25].

Thermoelectric research into the filled skutterudites showed that the rattling of the $M$ filling atoms leads to a further reduction in the thermal conductivity as they scattered phonons. The thermoelectric behavior of the filled skutterudites follows the phonon glass and electron single crystal (PGEC) concept proposed by Slack [26]. The term PGEC implies that a well optimized thermoelectric material will have a phonon mean free path that is as short as possible and an electron mean free path that is as long as possible [26]. In the filled skutterudites, the rattling behavior of the $M$ atoms results in glass like thermal conductivity, while the rigid $TX_3$ sublattice allows for good electrical conductivity. Although the filled skutterudites displayed a reduced thermal conductivity, they did not display the optimal transport properties found in skutterudites such as $\text{CoSb}_3$ or $\text{IrSb}_3$ [18,19,21,22]. In order to optimize the properties of these materials, studies of partially filled structures were performed [23,24]. These studies found that the highest $ZT$ values ($\sim 0.9$ at 800 K) were obtained in the partially filled structure $\text{Ce}_y\text{Fe}_4\text{CoSb}_{12}$ ($y \sim 0.9$) [23,24,27].

Most recently, the correlated electron behavior of the filled skutterudites at low temperatures has garnered much attention. These types of behavior, as previously listed, range from magnetism ($\text{UFe}_4\text{P}_{12}$) to heavy fermion superconductivity ($\text{PrOs}_4\text{Sb}_{12}$) [3,28]. Lately, much of the interest in the low temperature properties of the filled skutterudites has been focused on $\text{PrFe}_4\text{P}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$. This attention is due to the heavy fermion superconductivity of $\text{PrOs}_4\text{Sb}_{12}$ [3], the field induced heavy fermion behavior of $\text{PrFe}_4\text{Sb}_{12}$ [9], as well as the antiferroquadrupolar ordering observed in both systems [8,10]. Along with the large amount of interest that has been devoted to these systems, the other filled skutterudites display many interesting types of behavior as well. The majority of the $\text{La}$-based filled skutterudites are superconducting, with the highest $T_C \sim 10.3$ K found in $\text{LaRu}_4\text{As}_{12}$ [4,5]. The only non-superconducting $\text{La}$-based filled skutteru-
dites are LaFe$_4$As$_{12}$ and LaFe$_4$Sb$_{12}$ [2,29,30]. The Ce-based filled skutterudites can be classified as semiconducting [11,28,29,31–34], with the exceptions of CeRu$_4$Sb$_{12}$ which features non-Fermi liquid behavior, and CeFe$_4$Sb$_{12}$, which displays moderate heavy fermion behavior [12,20,35]. The Pr-based compounds display a rich variety of interesting phenomena, which will be discussed further in Chapter 3. The Nd-based filled skutterudites are discussed in Chapter 5 and are found to display magnetic order. The Sm systems discussed in Chapter 4 all seem to feature magnetic order, though SmRu$_4$P$_{12}$ also exhibits a metal insulator transition and possibly quadrupolar or octopolar ordering [36,37]. The Eu-based filled skutterudites all show magnetic ordering with the highest transition temperatures currently found in the filled skutterudites [2,29,38,39]. The heavy lanthanides that have been formed from Gd to Ho display magnetic ordering, while no phase transitions have been reported for the filled skutterudite systems from Er to Yb, [40–46] although YbFe$_4$Sb$_{12}$ does display heavy fermion behavior [40]. Among the actinide-based filled skutterudites, UFe$_4$P$_{12}$ is ferromagnetic and measurements of ThFe$_4$P$_{12}$ show no indication of a phase transition down to 1.2 K [28,47]. The measurements listed above are an indication of the great deal of research that has gone into studying the properties of the filled skutterudite compounds. High temperature measurements have revealed potential thermoelectric applications for the filled skutterudites, while at low temperatures the filled skutterudites have proven to be useful systems for the study of correlated electron phenomena. There are still many areas of potential research in the filled skutterudites, especially since many of the arsenide and heavy rare earth filled skutterudites have yet to be synthesized.

This thesis presents the study of the magnetic and electronic properties of several filled skutterudite compounds at low temperatures. The first chapter of this work introduces the filled skutterudite compounds as well as some of their properties that will be studied. The experimental details of the measurements as well as the analysis procedure that followed are described in the second chapter. The remaining chapters detail the studies of PrFe$_4$Sb$_{12}$, PrOs$_4$As$_{12}$, PrOs$_4$P$_{12}$,
Chapter 3 is the first of these and focuses on the study of the three Pr-based filled skutterudites and reveals magnetic ordering in PrFe\textsubscript{4}Sb\textsubscript{12} near 4 K and in PrOs\textsubscript{4}As\textsubscript{12} below 2.3 K as well as the presence of strong crystalline electric field effects in PrOs\textsubscript{4}P\textsubscript{12}. In Chapter 4, measurements of SmOs\textsubscript{4}Sb\textsubscript{12} indicate unusually weak magnetic ordering below 2.6 K along with strong indications of heavy fermion behavior. In the final chapter, measurements of NdOs\textsubscript{4}Sb\textsubscript{12} find magnetic ordering below 1 K along with indications of heavy fermion behavior.

### 1.1 Properties of Rare Earth Compounds

#### 1.1.1 Crystalline Electric Field Effects

Filled skutterudites with magnetic $M$ atoms display crystalline electric field effects in a variety of measurements ranging from anisotropic magnetization to Schottky anomalies in specific heat measurements. The crystalline electric field (CEF) effects are due to the interaction between the magnetic $M$ ion and its surrounding crystalline environment. In free space, the magnetic ion is in a spherically symmetric environment with Hund’s rules describing the occupation of the electron energy levels. In a crystalline environment, the degeneracy of the energy levels is lifted due to the lowering of the site symmetry experienced by the magnetic ion. As an example, a case where the site symmetry is lowered from spherical to cubic is considered. Following a description by Hutchings for the basic point-charge ionic model [48], a potential

$$V(r, \theta, \phi) = \sum_j \frac{q_j}{(R_j - r)}$$

exists due to the $j$ surrounding ions, with charge $q_j$ a distance $R_j$ from the magnetic ion. For example, take a magnetic ion placed in a position of sixfold coordination due to ions each with charge $q$ placed at the corners of an octahedron equal dis-
tance \(d\) from the magnetic ion. At the center of an octahedron, the magnetic ion experiences a static potential \(V(x, y, z)\) due to point charges located at \((d,0,0)\), \((0,d,0)\), \((0,0,d)\), \((-d,0,0)\), \((0,-d,0)\), and \((0,0,-d)\) along the Cartesian axes. The potential \(V(x, y, z)\) can be written as the sum of \(V_x\), \(V_y\), and \(V_z\) with

\[
V_x = q \left[ \frac{1}{(r^2 + d^2 - 2dx)^{\frac{1}{2}}} + \frac{1}{(r^2 + d^2 - 2dx)^{\frac{1}{2}}} \right],
\]

where \(r^2 = x^2 + y^2 + z^2\), and in a similar manner \(V_y\) and \(V_z\) follow. The \(x\), \(y\), and \(z\) terms of the potential are summed and then, utilizing several expansions, the resulting equation is

\[
V(x, y, z) = 6q + \left( \frac{35q}{4d^5} \right) \left[ (x^4 + y^4 + z^4) - \frac{3}{5} r^4 \right] + \left( \frac{-21q}{2d^7} \right)
\]

\[
\times [(x^6 + y^6 + z^6) + \frac{15}{4} (x^2 y^4 + x^2 z^4 + y^2 x^4 + y^2 z^4 + z^2 x^4 + z^2 y^4) - \frac{15}{4} r^6].
\]

The initial term is ignored since it only affects the zero of energy, leaving only the 4th and 6th order terms.

The CEF Hamiltonian is given as the sum of the potentials experienced by the electrons in the unfilled shell of the magnetic ion, such that

\[
H_c = -|e| \sum_i V(x_i, y_i, z_i).
\]

The potential in Cartesian coordinates is then transformed using Stevens’ “operator equivalents” method [49]. The operator equivalents are determined by replacing \(x\), \(y\), \(z\), and \(r\) with \(J_x\), \(J_y\), \(J_z\), and \(J(J+1)\). To account for the non-commutation of \(J_x\), \(J_y\), and \(J_z\), the products of \(x\), \(y\), and \(z\) are substituted for an expression consisting of all possible combinations of \(J_x\), \(J_y\), and \(J_z\), divided by the number of combinations. The coefficients of the 4th and 6th order terms are replaced by multiplicative factors proportional to \((-|e|q/d^5)\langle r^4 \rangle\) and \((-|e|q/d^7)\langle r^6 \rangle\), where \(r\) is the expectation value of the radial wave function. The operator equivalents for
the 4th and 6th order terms for a system with cubic $O_h$ symmetry are

\begin{align}
O_4^0 &= 35J_z^4 - [30J(J + 1) - 25]J_z^2 - 6J(J + 1) + 3J^2(J + 1)^2 \\
O_4^4 &= \frac{1}{2}(J_+^4 + J_-^4) \\
O_6^0 &= 231J_z^6 - 105[3J(J + 1) - 7]J_z^4 + [105J^2(J + 1)^2 - 525J(J + 1) + 294]J_z^2 \\
&\quad - 5J^3(J + 1)^3 + 40J^2(J + 1)^2 - 60J(J + 1) \\
O_6^4 &= \frac{1}{4}[11J_z^2 - J(J + 1) - 38](J_+^4 + J_-^4) \\
&\quad + \frac{1}{4}(J_+^4 + J_-^4)[11J_z^2 - J(J + 1) - 38],
\end{align}

where $J_\pm = J_x \pm iJ_y$.

The CEF Hamiltonian for a system with cubic symmetry now has the form

\[ H_c = B_4^0(O_4^0 + O_4^4) + B_6^0(O_6^0 - O_6^4), \]

where $B_4^0$ and $B_6^0$ are the coefficients for the 4th and 6th order terms, associated with the multiplicative factors from above. Lea, Leask, and Wolf (LLW) set

\[ B_4^0 = \frac{W_{x_{LLW}}}{F(4)} \quad \text{and} \quad B_6^0 = \frac{W(1 - |x_{LLW}|)}{F(6)}, \]

where $F(4)$ and $F(6)$ are constants dependent on $J$ [51]. The values for $F(4)$ and $F(6)$ were determined previously by Stevens [49] and Elliott and Stevens [50]. Lea, Leask, and Wolf then tabulated the eigenfunctions and eigenvalues for the cubic CEF Hamiltonian as functions of $x_{LLW}$ (the ratio of the 4th to 6th order terms) and $W$ (an overall energy scale) for various $J$ operators [51]. In Bethe’s notation, the eigenvectors describing the sublevels created by the lifting of the $(2J + 1)$-fold ground state degeneracy are labelled as $\Gamma_i$, where $i = 1, 2, 3, 4, \text{and } 5$ for integral values of $J$ and $i = 6, 7, \text{and } 8$ for half-integral values of $J$ [52]. Taking the case of Sm$^{3+}$ as an example with $J = \frac{5}{2}$ in a cubic CEF, the eigenfunctions in terms of
\( J_z \) states are

\[
|\Gamma_7\rangle = \sqrt{1/6}|\pm 5/2\rangle - \sqrt{5/6}|\mp 3/2\rangle
\]
for \( x_{LLW} = \pm 1 \) and \( E = \mp 4 \),

\[
|\Gamma_8\rangle = \sqrt{5/6}|\pm 5/2\rangle + \sqrt{1/6}|\mp 3/2\rangle
\]
and

where \( E \) is the energy scale. The eigenfunctions are then scaled by \( W \), such that for a given \( x_{LLW} \) value, the sign of \( W \) determines the ground state. The zero of energy is assigned to the ground state and the difference from the ground state is given in units of Kelvin. Using the above eigenfunctions the relative positioning of the energy sublevels \( \Gamma_7 \) and \( \Gamma_8 \) can be described using \( x_{LLW} \) and \( W \). During the analysis the values of \( x_{LLW} \) and \( W \) are used as fitting parameters for fits to crystalline electric field effects observed in various measurements.

### 1.1.2 Local Moment Interactions

In the 1930’s, the observation of resistance minima in metals that could not be explained in terms of Matthiessen’s rule generated much interest. Further experimental research concluded that these minima were associated with dilute magnetic impurities, such as Co or Fe. One of the most used theoretical models for the interaction between conduction electrons and localized magnetic moments was developed initially by Anderson in 1961 [53]. This model consisted of the following Hamiltonian

\[
H = H_e + H_f + H_{\text{corr}} + H_{cf}
\]
The first term $H_e$ represents the energy $\varepsilon_c$ of the conduction electron and the second term $H_f$ is the energy $\varepsilon_f$ due to the unperturbed $f$ electron states. The term $H_{\text{corr}}$ is due to the repulsive energy $U$ between $f$ electrons. The final term $H_{cf}$ is a term due to the hybridization between the $f-$ and conduction electron states and contains a coupling constant $V$.

The Kondo model can be described by the above Anderson Hamiltonian in the limit $U \gg |\varepsilon_f - E_F| \gg \Delta$, where $\Delta = \pi |V| N(E_F)$, $E_F$ is the Fermi energy, and $N(E_F)$ is the density of states at the Fermi energy. In the above limit, the large Coulomb repulsion allows for the exchange of spin between the conduction and $f-$ electrons without charge transfer. The resulting exchange Hamiltonian is $H_{\text{ex}} = -JS \cdot s(0)$, where $J$ is the coupling constant, $S$ is the spin of the localized magnetic moment, and $s(0)$ is the conduction electron spin. This Hamiltonian was used by J. Kondo in 1964 to account for the resistivity minima noted above due to dilute magnetic impurities [54]. Kondo used perturbation techniques to show that as temperature decreases the term in the electrical resistivity due to the exchange Hamiltonian increases as $-\ln(T)$ and eventually overtakes the lattice contribution leading to a minimum. Kondo’s use of the perturbation technique was limited to temperatures above a characteristic temperature $T_K$ (Kondo temperature). This work was later extended to temperatures below $T_K$ using a non-perturbative technique [55]. Using this technique, it was found that the effective coupling approaches infinity as the temperature is lowered below $T_K$ [56, 57]. The increased coupling leads to strong mixing between the $f-$ and conduction electrons below $T_K$. The strong interaction leads to the screening of the localized $f$ electrons by polarized conduction electrons and the formation of a spin singlet bound state (Kondo cloud). The binding energy of the spin singlet is related to $k_B T_K$, which can be expressed as

$$k_B T_K \sim E_F \exp(-1/(N(E_F)|J|)).$$

(1.14)

The screening of the $f$ electrons is primarily due to conduction electrons near $E_F$, which leads to an enhancement of the density of states at the Fermi level with the
formation of an Abrikosov-Suhl or Kondo resonance [58–60]. The electrons in the resonance region display an enhanced effective mass [61].

In the case of a periodic lattice of magnetic impurities (Kondo lattice), the results are similar to the single impurity case described above. The energy scales $k_B T_K$ and $k_B T_*$ for the single-impurity model and Kondo lattice respectively are often comparable [62]. At low temperatures, unlike the single impurity system the Kondo lattice develops coherence effects due to the lattice periodicity. Phase coherence between the Kondo clouds results in a band of mass enhanced electrons (heavy quasiparticles). As a result of this band of heavy quasiparticles, the Kondo lattice at low temperatures below the coherence temperature displays behavior consistent with Fermi liquid theory. In Landau Fermi liquid theory, electron-electron interactions are explained in terms of the free electron model applied to single particle excitations (quasiparticles). These quasiparticles can be thought of as free electrons renormalized with an effective electron mass $m^*$, which accounts for the strong electron-electron interactions. Systems that display very strong electron-electron interactions, feature effective masses above 100 $m_e$ and are known as heavy fermion systems. Within the Fermi liquid model the following temperature dependencies are found for the magnetic susceptibility $\chi = \chi_0$, the specific heat divided by temperature $C/T = \gamma_0$, and the electrical resistivity $\rho = \rho_0 + AT^2$.

Along with the Kondo effect, there is the intersite Ruderman and Kittel, Kasuya and Yosida (RKKY) interaction [63–65]. This indirect exchange interaction follows from the perturbative treatment of $H_{ex}$ described earlier. These interactions result from the spin polarization of the Kondo spin singlet combined with the periodicity of the Kondo lattice. The indirect exchange interaction between the local magnetic moments is mediated by the spin polarized conduction electrons of the Kondo clouds and has the form

$$H_{RKKY} \propto J^2 S_1 \cdot S_2 \left( \frac{\cos(k_F R)}{R^3} \right), \quad (1.15)$$

where $S_1$ and $S_2$ are magnetic moments separated by $R$ and $k_F$ is the Fermi wave vector. As a result of the damped oscillatory coupling, the lattice spacing of the
Figure 1.3 Schematic description of the RKKY interaction.

Magnetic moments can result in either ferromagnetic, antiferromagnetic, or more complex ordering as shown in Fig. 1.3. The characteristic energy for the RKKY interaction is $k_B T_{RKKY}$ derived from the $H_{RKKY}$ has the form

$$k_B T_{RKKY} \propto J^2 N(E_F).$$  \hspace{1cm} (1.16)
Figure 1.4 The Doniach diagram indicating competition between RKKY interaction and Kondo effect [66,67].

The “Doniach diagram” displayed in Fig. 1.4 displays $|J| N(E_F)$ as a function of temperature for the RKKY interaction and the Kondo effect [66,67]. The Doniach diagram illustrates the competition between the intersite RKKY interaction and the on-site Kondo interaction. Depending on the relative strengths of the interactions, magnetic or nonmagnetic behavior occurs at low temperatures. When $T_{RKKY} \gg T_K$ systems display stable $f$ moments with negligible screening, which results in magnetic ground states. In systems that display strong hybridization between $f-$ and conduction electrons, $T_K \gg T_{RKKY}$ and paramagnetic ground states are found. Systems that display heavy fermion behavior are typically found in the region where $T_{RKKY} \gtrsim T_K$. These systems display well localized moments that have been reduced due to the Kondo effect as well as complex magnetic structure [62]. When $T_K \gtrsim T_{RKKY}$, a nonmagnetic ground state occurs, with behavior consistent with Landau Fermi-liquid theory. In the case where $T_{RKKY} \approx T_K$, 

$$T_K \sim T_F e^{-1/N(E_F)|J|}$$

$$T_{RKKY} \sim J^2 N(E_F)$$

$$T_{\text{AFM}}$$
magnetic phase transitions become suppressed to zero temperature and unusual temperature dependencies in specific heat, magnetic susceptibility, and electrical resistivity measurements are observed [62]. This class of phenomena is known as non-Fermi liquid behavior and was first observed in $Y_{1-x}U_xPd_3$ [68,69]. The systems that exhibit non-Fermi liquid behavior have the following temperature dependencies for $T \ll T_0$

$$\frac{C(T)}{T} \propto -\frac{1}{T_0} \ln \left[ \frac{T}{T_0} \right] \text{ or } T^{-n} \text{ for } n < 1,$$

(1.17)

$$\chi(T) \propto \chi_0 \left[ 1 - \frac{1}{T_0} \right] \text{ or } T^{-n} \text{ for } n < 1,$$

(1.18)

$$\rho \propto T^n \text{ for } 1 \leq n \leq 1.5,$$

(1.19)

where $T_0$ is a scaling temperature, which has been identified as $T_K$ in some systems [70,71].

Bibliography


Experimental Techniques

2.1 Sample Preparation

2.1.1 Single Crystal Growth

In this section, the growth of the filled skutterudite phosphide and antimonide single crystals is discussed. The PrOs$_4$As$_{12}$ single crystals reported on in Section 3.2 were provided by our collaborator Zygmunt Henkie at the Polish Academy of Sciences and the details of their synthesis is not included.

The metallic flux-growth technique is a relatively inexpensive method of crystal growth, which allows the growth of compounds with high melting points at much lower temperatures [1, 2]. The first step in the growth process involves determining the correct growth parameters to use for a given compound. This primarily includes determining the correct metallic flux to use as well as the relative concentration of the constituent elements. A literature search was the first step in this process, since compounds with similar constituent elements can often be grown out of the same flux. For instance, Jeitschko and Braun were able to grow the phosphide filled skutterudites MT$_4$P$_{12}$ (where M = lanthanide and T = Fe, Ru, or Os) from a tin flux following a procedure used by Jolibois for the growth of NiP$_2$ and NiP$_3$ single crystals [3, 4]. The synthesis technique for PrOs$_4$P$_{12}$ in this work is based on the growth parameters previously determined by Jeitschko...
and Braun [3]. The synthesis method for the antimonide filled skutterudite single crystals follows from the work of Takeda and Ishikawa [5].

The source and purity of the elements are Cerac Pr and Sm ingots 99.9%, Research Chemicals Inc. Nd ingot 99.9%, Colonial Metals Os sponge (powder) 99.98%, Alfa Aesar Fe pieces (5 – 12 mm) 99.97%, Cerac Sb shot (1 – 3 mm) 99.999%, Alfa Aesar Puratronic red P lump 99.9999%, and Research Organic/Inorganic Chemical Corp. Sn bar 99.999%. Due to the size of the rare earth ingots, they were sawed into smaller pieces which were stored in oil, since the rare earth compounds readily oxidize in air. The rest of the elements were fairly stable in air and did not require special storage.

Single crystals of antimonide filled skutterudites were grown using a molten Sb flux, while PrOs₄P₁₂ was grown using a molten Sn flux with an excess of P. The relative concentrations of the elements were 1:4:20 (Pr,Nd,Sm:Fe,Os:Sb) for the various antimonides, while it was 1:4:20:50 (Pr:Os:P:Sn) for PrOs₄P₁₂. Prior to weighing out materials, it was necessary to prepare carbon coated quartz tubes for the growth process. The quartz tubes for the final growths ranged in size from 16 mm I.D. × 18 mm O.D. for PrOs₄P₁₂ to 21 mm I.D. × 24 mm O.D. for the antimonides. To increase the size of the antimonide single crystals, larger diameter carbon coated quartz tubes were used. The carbon coating (created by the pyrolysis of acetone) was necessary to prevent Sb and the rare earths from reacting with the quartz. The first step in carbon coating a quartz tube was to seal and flatten the end of the quartz tube (~ 10 – 24” long) with a hydrogen-oxygen torch. This process increased the thickness of the quartz where the sample would be resting, helping to prevent a rupture during the long growth (12 – 20 days). After the tube cooled it was then rinsed with acetone and cleaned inside with a Kimwipe. The cleaned tube was then filled with ~ 0.5” of acetone and one end was covered while the tube was shaken to coat the inside with acetone. Once coated, one or two large Kimpwpipes were then wadded up tightly and used to plug the open end of the quartz tube. The tube was then shaken again and flipped over so that the
acetone soaked into the Kimwipes and formed an airtight seal. The tube was then slowly heated with a hydrogen flame and a small amount of oxygen to increase the temperature to the point where the pyrolysis of acetone just began to occur. This process was visible as a faint orange glow on the inside wall of the quartz tube. The tube was rotated continuously to evenly coat the bottom three to four inches of the tube. A low heat was used initially to allow uniform coating to adhere to the quartz, since at higher temperatures larger chunks of carbon would form that did not seem to adhere as well to the quartz tube. Once an initial smooth coating had formed, the temperature of the torch was then raised by increasing the oxygen flow in order to increase the carbon coating thickness. The temperature was kept below the point at which the quartz would begin to soften. After achieving a thick coating, it was checked by holding the side of the tube up to a light. If light could be seen through the coating the thickness was increased further. Once the coating was complete and the tube has cooled, the Kimwipes were removed from the end of the tube. The tube was then filled half way with water and the open end was capped as the tube was vigorously shaken to loosen any excess carbon that had formed. The water was then drained and this process was repeated until the water drained out free of any significant amounts of carbon. The tube was then wiped with a Kimwipe, up to the carbon coating, to remove the majority of the water from the tube. Any remaining water was boiled away by heating the tube with a hydrogen flame. Once the tube had cooled, it was connected to a vacuum pump and pumped down to \(~30\) mTorr and then flushed with UHP Ar. The pump and flush was repeated three times; then, after the final pump down, the tube was heated in vacuum with a hydrogen flame again to drive off any remaining vapors from the carbon coating. The tube was again allowed to cool and removed from the vacuum pump. At this point, excess carbon coating was removed by simply burning it off in air with a hydrogen-oxygen flame. The tube was then pumped on again down to \(~30\) mTorr before being used.

The rare earth ingots first cleaned using acetone and Kimwipes in order
to remove the oil in which they were stored. After a thorough sanding to remove any oxide layer from the surfaces, the larger sanded pieces were cleaned again in acetone, cut into smaller pieces, and weighed. The weights of the rare earths were then used to calculate the weight of the other elements needed for a given growth. The cleaned rare earths were kept in vacuum, while the rest of the elements were weighed out to within $\sim 0.3$ mg of the calculated value.

For the antimonides, the Sb was split into two equal portions, one of which was placed into a carbon coated quartz tube. The rare earths were then removed from vacuum, cut into bits smaller than $\sim 3$ mm, and mixed with Os in order to make a more homogenous mixture. To prevent the loss of powder and to keep the walls of the carbon coated tube clean, the Os powder-rare earth mixture was then loaded into the end of a second quartz tube that had a slightly smaller O.D. than the I.D. of the carbon coated quartz tube. The smaller tube was held horizontal while the carbon coated tube was slowly slid onto it such that the end of the smaller tube, where the Os-rare earth mixture sat, was placed below the carbon coating. The two tubes were then held together as they were flipped vertically allowing the powder to fall into the carbon coated tube. This elaborate procedure was not required for the Fe since it was not in powder form, instead the Fe pieces ($5 - 12$ mm) were cut down to $1 - 3$ mm pieces and mixed with the rare earth. After the Os(Fe)-rare earth mixture was placed in the tubes, the remaining Sb was included. So, inside the tubes the final layering was Sb/Os-Nd(Sm)/Sb and Sb/Fe-Pr/Sb. The same steps as above were followed for PrOs$_4$P$_{12}$ with two exceptions. The first is that phosphorus chunks ($3 - 5$ mm) were included in the Os-rare earth mixture and the second is that Sb was replaced by Sn and excess P as the metal flux (Sn/Os-P-Pr/Sn). The Sn was cut down to $4$ mm to $6$ mm bits before being used since it was in the form of $\sim 7''$ long bars.

After all the elements were loaded into the carbon coated quartz tubes, quartz wool was wadded up and placed in the quartz tubes just above the carbon coating. The quartz wool would later act as a sieve to separate the crystals from
the flux. At this point the torch was used to slowly neck down the quartz tube to a thin capillary about one to one and a half inches above the quartz wool. Once a proper size capillary was formed, (∼ 2 mm diameter), the tube was connected to a mechanical vacuum pump. The tube was pumped down to ∼ 30 mTorr and flushed with 150 Torr UHP Ar three times. This was followed by briefly heating the tube with a hydrogen flame as it was being pumped on to drive out any remaining vapor. The tube was then left on the vacuum pump for 15 – 45 minutes as it cooled. Once the tube had cooled and a base pressure of ∼ 30 mTorr had been reached, it was backfilled with 150 Torr of UHP Ar. The capillary was then heated with the hydrogen-oxygen torch until the capillary sealed and the two ends separated.

Figure 2.1 (a) Furnace heating cycle for PrFe₄Sb₁₂, NdOs₄Sb₁₂, and SmOs₄Sb₁₂. (b) Furnace heating cycle for PrOs₄P₁₂.

The sealed tube was then placed in the back of a 1500 °C Lindberg box furnace near the thermocouple (which measures the furnace temperature). The sealed tubes were placed as close to being upright as possible, while remaining at least 0.5" from the heating elements. This often means that the tube had to rest at a slight angle, which did not seem to affect the growth significantly. The tube was placed in the back near the thermocouple since the temperature is more stable in the back and the sample temperature tracks the programmed furnace sequence.
better, due to its proximity to the thermocouple.

Figure 2.1(a) displays the furnace heating cycle for the the Sb-based filled skutterudite single crystal growth. The initial slow heating rate of 50 °C/hr was chosen to avoid the exothermic reaction between the rare earths and antimony. Once the melt reaches 1050 °C it dwells for 96 hrs to allow all the elements to dissolve into the flux and mix. This was followed by cooling at a rate of 2 °C/hr down to 700 °C. During the cooling process the filled skutterudite phase crystallizes out of the melt. The rate was chosen through trial and error to maximize the size of the crystals. After the furnace had reached 700 °C (∼ 70 °C above the melting point of Sb) the tubes were then removed from the furnace and placed upside down in a centrifuge. As the centrifuge spun the molten Sb flux would flow away from the crystals through the quartz wool and collect at the top of the quartz tube. After spinning off the flux, the tube was allowed to cool to room temperature. The cooled tube was then carefully cracked open to avoid damaging the crystals. The resulting crystals are cubic in shape with dimensions of 1 mm or less and tend to form large clusters. The antimonide filled skutterudites with Fe generally formed larger crystals than those with Os. Any remaining Sb flux was etched off with a 1:1 mixture of nitric acid:hydrochloric acid. The samples were left in the acid for no more than 15 minutes at a time, since prolonged exposure could damage the crystals. A concentrated hydrochloric acid etch that did not damage the crystals was often used for much longer etching times, though it was much less effective at removing the Sb flux.

The heating cycle for PrOs₄P₁₂ is shown in Fig. 2.1(b). The ramping rate is much slower for the phosphide growth than the antimonide growth to allow the large P chunks to dissolve into the Sn flux and prevent the formation of P-vapor, since red phosphorus sublimes at 417 °C. After ramping to 1130 °C, the furnace was left to dwell for 125 hrs to allow all the elements to mix and be incorporated into the melt. The furnace was ramped down at a slow rate of 2 °C/hr down to 600 °C. The tube was then removed from the furnace and flipped over and placed
in a centrifuge, such that the Sn would flow through the quartz wool and collect at the top of the quartz tube. After separating the Sn, the tube was allowed to cool and then carefully cracked open. The crystals that resulted were typically 1 – 2 mm in size and multifaceted. Unlike the antimonides, the phosphide crystals did not tend to form in large clusters. Any remaining Sn on the surface of the crystals was removed with concentrated HCl, which did not harm the crystals. Since tin inclusions could not be removed with etching, an additional tin contribution must be considered when measuring the properties of the phosphide filled skutterudite single crystals.

2.2

Characterization Techniques and Analysis

2.2.1 X-ray Diffraction

Room temperature X-ray powder diffraction was carried out in order to check for impurity phases and verify the unit cell parameters for the single crystals. These measurements required \( \sim 20 - 10 \) mg of finely crushed single crystals that had been etched to remove any flux. This fine powder was then mounted in a Rigaku D-MAX/B X-ray machine by sticking it to a glass slide using petrolatum (petroleum jelly). The jelly only contributed a broad background contribution to the intensity for \( 10 \leq 2\theta \leq 20 \) degrees. This did not affect the measurements since the majority of the powder diffraction peaks for the filled skutterudites occur above 30 degrees. X-ray diffraction patterns for the filled skutterudites were measured for \( 10 \leq 2\theta \leq 90 \) in 0.01 degree steps. When determining the lattice parameters, crushed Si was added to the sample. The well known Si peaks could then be used to correct for possible systematic errors in the X-ray machine.

The program CrystalMaker was used to construct virtual crystal structures based on the known lattice parameters and space group of a given compound [7]. This information was found in a Pearson’s handbook [6]. These virtual
crystals structures were then used in the program CrystalDiffract to calculate the X-ray diffraction pattern for that structure [8]. The calculated patterns were then used to verify the filled skutterudite phase and check for possible impurity phases such as Sn and Sb. The program XLAT was used to calculate the lattice parameters based on the X-ray diffraction patterns [9]. This program required the indices of the known skutterudite peaks along with their associated angles. To improve the accuracy of the lattice parameter determination the indices and angles of a Si standard measured along with the filled skutterudite phase were also entered into the program.

Single crystal X-ray refinement for PrFe$_4$Sb$_{12}$, PrOs$_4$P$_{12}$, SmOs$_4$Sb$_{12}$, and NdOs$_4$Sb$_{12}$ was performed at the University of Vienna by our collaborators Professor Peter Rogl and Dr. Gerald Giester. The single crystals were initially inspected with an AXS-Gadds texture goniometer prior to X-ray intensity data collection to assure the high quality of the specimens. The X-ray intensity data was collected on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated Mo K$_\alpha$ radiation ($\lambda = 0.071073$ nm). Orientation matrix and unit cell parameters were derived using the DENZO program [10]. No absorption corrections were necessary because of the regular crystal shape and small dimensions of the investigated crystals. The structure was refined with the aid of the SHELXS-97 program [11]. The single crystal X-ray refinement for PrOs$_4$As$_{12}$ was performed by Adam Pietraszko at the Polish Academy of Sciences and the experimental details are included in Section 3.2.1.

### 2.2.2 Magnetic Susceptibility

DC magnetization measurements were made from 1.7 to 300 K in fields up to 5.5 T in a commercial Quantum Design Magnetic Properties Measurement System (MPMS). The samples were mounted in a plastic drinking straw, which was then taped (3M 5413) on a long probe that was inserted into the MPMS system for measurement. Three methods for mounting the single crystals in the
straws were used. The first method was to pressure mount a single crystal between two straws inserted into a third straw which is mounted on the probe. There was essentially no background contribution using this method, though orienting the crystal was very difficult. A second method involved a Teflon disk on which a single crystal or several crystals could be glued (Duco Cement diluted with acetone 1 : 10) into specific orientations. This disk was then carefully inserted into the center of the straw. A small diamagnetic contribution from the glue and disk had to be considered in the measurements, although this contribution proved to be insignificant in most instances. The final method used was to make a mosaic of crystals on a piece of 3M 5413 tape which was then taped along the length of the straw. The tape was then punctured to allow any air bubbles that had formed to be evacuated once placed in the MPMS. There is no significant background contribution with this method.

Once the sample was mounted, the MPMS DC SQUID magnetometer would measure the magnetic moment \( m \) in units of emu. After accounting for any background contributions \( m \) was then converted to magnetization \( M \) (emu per unit volume, mole, or gram) usually by dividing by the sample mass and multiplying by the molecular weight \( MW \) to obtain units of emu per mole. The relation \( \chi_{dc} \approx M(\text{emu/mol})/H(\text{Oe}) \) was then used to determine the molar DC magnetic susceptibility with units of \( \text{cm}^3/\text{mol} \).

Measurements of the AC magnetic susceptibility \( \chi_{ac} \) were carried out above 1.7 K in a Quantum Design MPMS SQUID magnetometer in fields up to 1 T. Measurements were performed only in the vicinity of the phase transition for the systems with transitions above 1.7 K. Since an MPMS system was also used for these measurements, the samples were mounted in the same manner as above. The \( \chi_{ac} \) was determined by first applying an oscillating field \( dH = h\cos\omega t \) where \( h \) is the driving field amplitude and \( \omega \) is the frequency of the driving field. The oscillating moment \( dM \) that results from this driving field was measured by the MPMS SQUID magnetometer. The driving field divided by the resulting
moment $dM/dH$ is equal to $\chi_{ac}$. Since $\chi_{ac}$ is a direct measure of $dM/dH$, it is very sensitive to small changes in $M(H)$ and was very useful for determining the transition temperatures.

Magnetization measurements at low temperatures below (1.7 K) were performed by Nicholas P. Butch and Pei-Chun Ho using a $^3$He Faraday magnetometer. Measurements were performed in a gradient field of $\sim 0.05 - 0.1$ T/cm in applied fields up to 5.5 T for $0.4 \text{ K} \leq T \leq 10 \text{ K}$. Multiple single crystals were required for the measurements, due to their small size. The crystals were all oriented in the same manner in a mosaic on the bottom of a quartz bucket. The quartz bucket was connected to the end of a quartz fiber in the sample space in a gradient field ($\partial H/\partial z$). The magnitude of the magnetization $M$ was then determined by measuring the force $F$ experienced by the sample in the field gradient, through the relation $F = MV(\partial H/\partial z)$, where $V$ was the sample volume. The force on the sample was measured by a sensitive microbalance that was connected to the quartz fiber. Just as for the MPMS measurements, the sample holder background must be taken into account. Inaccurate determination of the sample position in the gradient field could result in measurement error.

The analysis of the $\chi_{dc}$ data involved Curie-Weiss fits at high and low temperatures as well as crystalline electric field (CEF) fits. High temperature Curie-Weiss fits were performed to determine the effective magnetic moment of the various systems studied. Low temperature Curie-Weiss fits were used to estimate the magnitude of the ground state moment as well as to estimate the the magnetic ordering temperature by the value of $\Theta_{CW}$. The Curie-Weiss fits have the form

$$\chi(T) = \frac{C}{T - \Theta_{CW}}$$

(2.1)

where $\Theta_{CW}$ is the Curie-Weiss temperature and $C$ is the Curie constant. The Curie constant is equal to $\mu_{\text{eff}}^2 N_A / (3k_B)$, where $\mu_{\text{eff}}$ is the effective magnetic moment. In general, a negative $\Theta_{CW}$ implies antiferromagnetic correlations while a positive value implies ferromagnetic correlations.
Crystalline electric field fits were also performed to the magnetic susceptibility data of several of the filled skutterudite compounds. The crystalline electric field splitting scheme was estimated from these fits and compared with fits to other measurements such as specific heat and electrical resistivity. The CEF fits to the molar magnetic susceptibility data have the form below which includes Curie- and Van Vleck-like terms

\[
\chi_{\text{CEF}}(T) = N_A g^2_J \mu_B^2 \left[ \sum_i \frac{|\langle i| J_z | i \rangle|^2}{k_B T} p_i - 2 \sum_{i,j(\neq i)} \frac{|\langle i| J_z | j \rangle|^2}{E_i - E_j} p_i \right],
\]

where \( N_A \) is Avogadro’s number, \( g_J \) is the Landé g-factor, \( \mu_B \) is the Bohr magneton, \( p_i = e^{-E_i/(k_B T)}/Z \) is the thermal population probability (\( Z \) is the partition function), and the \( E_i \)’s are the energies of the multiplets. In the notation developed by Lea, Leask, and Wolf (LLW) [12], for cubic \( O_h \) symmetry the \( E_i \)’s become linear functions of \( x_{\text{LLW}} \) and \( W \), where \( x_{\text{LLW}} \) is the ratio of the fourth- and sixth-order terms of the angular momentum operators and \( W \) is an overall energy scale. Although the filled skutterudites actually have \( T_h \) symmetry [13], cubic \( O_h \) symmetry simplifies the analysis and is a close approximation to \( T_h \).

The ground state of the filled skutterudites was also confirmed by the low-\( T \) values of \( \mu_{\text{eff}} \) and \( M_{\text{sat}} \) (the saturation magnetization). In general, high temperature behavior of \( \chi^{-1}(T) \) is due to the full rare earth moment; as the temperature is lowered, the higher CEF energy levels are depopulated and the ground state moment dominates (depending on the CEF Scheme). Since \( \chi(T) = \frac{C}{T - \Theta_{\text{CW}}} \), the lower moment due to the ground state results in a change of curvature in \( \chi^{-1}(T) \). In a similar manner, the low temperature magnetization is also primarily due to the ground state moment. In high fields, depending on the details of the CEF scheme, the low temperature \( M(H) \) may have a saturation magnetization equal to the ground state moment. Just as for the magnetic susceptibility this behavior depends on the relative proximity of the energy levels and their respective behaviors in field. In magnetic fields, the degenerate CEF energy levels will split due to the Zeeman effect, which also may result in CEF energy level crossing.
Therefore the low-\(T\) values for \(\mu_{\text{eff}}\) and \(M_{\text{sat}}\) are only estimates for the CEF ground state, which can then be compared to CEF fits to \(\chi(T)\), \(\rho(T)\), and \(C(T)\).

The low-\(T\) effective moment was estimated from a Curie-Weiss fit to the \(\chi_{\text{dc}}^{-1}(T)\) data. If the high field magnetization was linear, \(M_{\text{sat}}\) was estimated by performing a linear fit to the high field linear portion of the \(M(H)\) data and taking the \(M\)-intercept. In the systems where \(M(H)\) displayed high field curvature, \(M_{\text{sat}}\) was approximated as the value of the magnetization at the highest fields (5.5 T).

The calculated CEF \(\mu_{\text{eff}}\) was calculated from

\[
\chi_{\text{CEF}}(T) = N_A g_J^2 \mu_B^2 \left[ \sum_i \frac{|\langle i | J_z | i \rangle|^2}{k_B T} p_i \right],
\]

which a ground state contribution only. The CEF ground state moment is determined from \(\chi_{\text{CEF}}(T)\) by setting \(\chi_{\text{CEF}}(T) = C/T\) and solving for \(\mu_{\text{eff}}\). The CEF calculated value for \(M_{\text{sat}}\) was derived from the relation

\[
M_{\text{sat}} = M_z = -g_J \mu_B \langle \Gamma^i_{\text{g.s.}} | J_z | \Gamma^i_{\text{g.s.}} \rangle,
\]

where \(\Gamma^i_{\text{g.s.}}\) emphasized that \(M_z\) was calculated for each of the degenerate ground state energy levels. So for a triplet ground state \(M_z\) for \(\Gamma^1_{\text{g.s.}}, \Gamma^2_{\text{g.s.}},\) and \(\Gamma^3_{\text{g.s.}}\) were calculated. The CEF calculated value for \(M_{\text{sat}}\) was determined from the degenerate ground state level with the largest positive \(M_z\). This again assumes that at low temperatures in the highest fields as the Zeeman effect splits the degenerate ground state the lowest level dominates the contribution to the magnetization.

\[2.2.3 \text{ Specific Heat}\]

A semi-adiabatic \(^3\)He calorimeter was used to make specific heat \(C\) measurements from 0.6 K to 70 K using a standard heat pulse technique. The measurements using this system were made by Neil A. Frederick and Todd A. Sayles. Measurements were made on collections of single crystals (total mass ranging from 40 mg to 80 mg that were mounted on a sapphire platform using Apiezon N grease. The total heat capacity was measured, which includes the addenda (sapphire platform system), the grease, and the sample. The addenda represents a background
contribution that was previously measured. The heat capacity of the Apiezon N
grease was known from the literature and could be corrected for by measuring the
mass of the grease used. After accounting for the addenda and the Apiezon N
grease the sample heat capacity was left. The sample heat capacity was reported
in mJ/mol K by multiplying it by the molar mass of the filled skutterudite phase
and dividing by the sample mass.

Further specific heat measurements of PrOs$_4$As$_{12}$ (inset (b) to Fig 3.15)
were made by our collaborators at Lawrence Livermore National Lab (LLNL) by
Scott K. McCall and Mike W. McElfresh using a commercial Quantum Design
Physical Properties Measurement System (PPMS) with a $^3$He option.

The specific heat data for all the filled skutterudites were fit in terms
of electronic and lattice contributions well above their respective ordering tem-
peratures. The specific heat as a function of temperature $C(T)$ for the filled
skutterudites was fit to the form $C(T) = C_e(T) + C_{\text{lat}}(T)$ where the electronic
term $C_e(T) = \gamma T$ and lattice term $C_{\text{lat}} = \beta T^3$. These fits resulted in estimates for
the coefficient of the electronic contribution to the specific heat $\gamma$ which when
found to be enhanced (values $> 100$ mJ/mol K$^2$) was an indication of heavy
fermion behavior. The value of the Debye temperature was also estimated from
the coefficient of the lattice contribution to the specific heat through the relation
$\beta = (12/5)\pi^4 n k_B (1/\Theta_D)^3$, where, for the filled skutterudites, $n = 17N_A$ (17 ions
per formula unit).

Crystalline electric field effects arise in the form of Schottky anomalies in
specific heat measurements. A Schottky anomaly can be explained by considering
a system with two energy levels separated by $\Delta$, such that for $T \ll \Delta/k_B$ the upper
level is almost unoccupied and for $T \gg \Delta/k_B$ both levels are equally populated.
A maximum in the number of transitions between the two levels will only occur at
temperatures comparable to $\Delta/k_B$. The increased number of transitions results in
a rapid change in internal energy, which corresponds to an increased specific heat
contribution. This contribution takes the form of a hump in $C(T)$ that goes to zero
at high and low temperatures, with a maximum value at temperatures comparable to $\Delta/k_B$. In the case of more complicated systems, such as the filled skutterudites, the degeneracy of the energy levels must be included. While there are much more than two energy levels in the filled skutterudites, the relatively large contributions due to the ground state and first excited state are such that only these two levels need be considered in most cases. The specific heat measurements of the filled skutterudites that displayed clear Schottky anomalies were fit using the equation

$$\frac{C}{T} = \frac{C_e(T)}{T} + \frac{C_1(T)}{T} + AC_{\text{Sch}}(T)/T, \quad (2.5)$$

which includes an electronic, lattice, and Schottky contribution. The Schottky contribution has the form

$$C_{\text{Sch}}(T) = N_A k_B (\delta/T)^{-2}(g_a/g_b)[1 + (g_a/g_b)exp(-\delta/T)]^{-2}exp(-\delta/T) \quad (2.6)$$

where $g_a(g_b)$ is the degeneracy of the ground state (first excited state) [14], $\delta$ is the energy level splitting, and $A$ is a scaling factor.

The filled skutterudites PrOs$_4$As$_{12}$ and NdOs$_4$Sb$_{12}$ were fit below their magnetic phase transitions in the ordered state. In the case of PrOs$_4$As$_{12}$ an extra term due to a nuclear Schottky anomaly was included. A nuclear Schottky anomaly is a Schottky anomaly due to the energy levels of the nucleus and since the nuclear moments are much smaller than the electronic they occur in the much lower temperature range ($10^{-2}$ K). The contribution from the high temperature tail of the nuclear Schottky goes as $T^{-2}$ [14], and can be observed as an upturn in the $C(T)/T$ data below 1 K for PrOs$_4$As$_{12}$. A spin wave (magnon) contribution to the specific heat for magnetically isotropic metals, with the form $C(T) \propto T^n$ ($n = 3$ for antiferromagnetism and $n = 1.5$ for ferromagnetism) were considered for both PrOs$_4$As$_{12}$ and NdOs$_4$Sb$_{12}$ [15]. For NdOs$_4$Sb$_{12}$ a spin wave contribution in an anisotropic metal was also considered, with the form $C(T) \propto T^{3/2}e^{-\Delta/T}$, where $\Delta$ represents the minimum energy required to excite a spin wave [16].
2.2.4 Electrical Resistivity

Single crystals for the electrical resistivity ($\rho$) measurements ranged in size and shape. Most of the antimonide filled skutterudite single crystals were either rectangular bar shaped or cubic, while the PrOs$_4$As$_{12}$ and PrOs$_4$P$_{12}$ single crystals were multifaceted. In most instances, much of the error in the $\rho(T)$ data was due to the unusual shape of the single crystals, since the electrical resistivity is dependent on the sample dimensions. Once the crystals were obtained, a surface for mounting the leads was chosen. This surface was then sanded to allow a better bond with the silver epoxy (used to attach leads) and to reduce the contact resistance. The surface was then prepared for sputtering Au contact pads, which also help reduce the contact resistance. This involved creating a mask over the sanded surface such that four parallel strips were exposed that spanned the sanded surface. One method used for making the mask was to take one component of the EPO-TEK H20E silver epoxy and paint the mask onto the crystal (since only one component is used the epoxy can be removed easily). The mask was then allowed to dry in a furnace at 200 °C for 10 min. A layer of Au was then sputtered onto the surface for $\sim$ 15 min. After sputtering, the mask was removed by briefly sonicating (1 – 5 min) the crystal in ethanol. If sonicated too long the Au pads or even the crystal could be damaged. Once the mask was removed Au wires($\sim$ 0.5” long) with diameters of either 0.002” or 0.001”, depending on the crystal size, were glued to the crystal with EPO-TEK H20E silver epoxy. The epoxy was allowed to cure in a small box furnace for $\sim$ 8 min at 200 °C.

Electrical resistivity $\rho$ measurements at UCSD were made from 1.9 K to 300 K in fields up to 9 T using a Quantum Design PPMS. Further measurements down to $\sim$ 0.05 K in fields up to 8 T were made in a $^3$He-$^4$He dilution refrigerator by Pei-Chun Ho, Nick P. Butch, and Tatsuya Yanagisawa at UCSD. Measurements were made using a standard four wire AC technique with currents ranging from 1 – 10 mA in the PPMS and 0.1 – 0.3 mA in the dilution refrigerator.

Further measurements in high fields for PrFe$_4$Sb$_{12}$, SmOs$_4$Sb$_{12}$, and NdOs$_4$Sb$_{12}$
were made at the National High Magnetic Field Laboratory at Los Alamos National Laboratory by Pei-Chun Ho in collaboration with Jon B. Betts and Alex H. Lacerda. These measurements were made in magnetic fields up to 18 T down to \(\sim 0.05\) K using a \(^3\)He-\(^4\)He dilution refrigerator.

Electrical resistivity measurements as a function of applied pressure were made for PrFe\(_4\)Sb\(_{12}\), PrOs\(_4\)As\(_{12}\), and NdOs\(_4\)Sb\(_{12}\) by Jason R. Jeffries at UCSD using a standard four wire AC technique. These measurements were made at pressures up to 28 kbar using a beryllium-copper piston-cylinder clamp for \(1.2\) K \(<\ T \leq 300\) K in a \(^4\)He cryostat \([17]\), with an applied current of \(1 - 10\) mA, using an AC resistance bridge. Pressure was determined inductively based on the pressure-dependent superconducting transition of Pb.

To confirm the type of magnetic ordering as well as to check for Fermi liquid or non-Fermi liquid behavior, the electrical resistivity was fit at low temperatures. At higher temperatures, CEF fits were performed to aid in determining the CEF energy level splitting scheme. The high and low temperature fits to the electrical resistivity measurements were dependent on the assumption that Matthiessen’s rule is valid. Matthiessen’s rule states that the electrical resistivity due to various scattering mechanisms are additive such that \(\rho = \rho_{\text{imp}} + \rho_{\text{lat}} + \rho_{\text{mag}} + \ldots\). This, for instance, allows impurity, lattice, and magnetic contributions to be treated separately.

The low temperature electrical resistivity consists of several contributions. There is the impurity resistivity \(\rho_{\text{imp}}\) due to electrons scattering from static crystalline defects and nonmagnetic impurities. This type of scattering does not vary with temperature and in some systems the residual resistivity \(\rho_0\) (the value of \(\rho(T)\) extrapolated to zero temperature \(\rho(0\ \text{K})\)) is a good estimate of the impurity contribution. Since \(\rho_0\) can be an estimate of the impurity contribution, the ratio of the room temperature resistivity to the extrapolated zero temperature value \(\rho(300\ \text{K})/\rho(0\ \text{K})\) is used to compare the relative quality of the crystals of similar composition. The lattice contribution \(\rho_{\text{lat}}\) due to electron-phonon scattering has
been found to vary as $T^5$ for $T << \Theta_D$. In metals, electron-electron scattering is predicted by Fermi liquid theory to go as $T^2$ and is normally a very weak contribution in most metals. However, in the case of systems that display an enhanced electron effective mass, this contribution can become significant, especially for temperatures below 1 K [18]. A class of materials has also been found that exhibit features that deviate from Fermi liquid theory and are said to exhibit non-Fermi liquid behavior. This behavior is recognized by characteristic features in the low-$T$ temperature dependence of various measurements such as specific heat, magnetic susceptibility, and electrical resistivity. In the case of low temperature power-law fits to the electrical resistivity of these compounds, a characteristic $T^n$ behavior has been observed where $n$ ranges from 1 to 1.5 [18–20]. Current theories attribute this behavior to disorder or proximity to a quantum critical point (a second order phase transition that has been suppressed to $T = 0$ K, via a tuning parameter such as field, pressure, and composition) [21–25]. Another scattering mechanism is electron-magnon scattering, which varies as $T^2$ for an isotropic ferromagnet and as $T^5$ for an antiferromagnet [26,27]. In the case of a system with magnetic anisotropy a preferential alignment of the spins develops along an easy axis. In order to rotate the spins and excite a magnon, in the presence of this preferred magnetic orientation, an energy $\Delta$ is required. This energy then appears as a gap in the magnon spectrum, such that the electrical resistivity below the magnetic ordering temperature varies approximately as $T^2 e^{\Delta/(k_B T)}$ [16,26]. It is important to note that there are always exceptions to the above forms; for instance, at low temperatures $\rho_{\text{lat}}$ for Gd varies as $\sim T^{3.5}$ instead of the expected $T^5$ behavior [28]. So, care must be taken when interpreting an observed power-law dependence.

Given the above contributions to the electrical resistivity and assuming Matthiessen’s rule to be valid, power-law fits of the form $\rho(T) = \rho_0 + BT^n$ (with residual resistivity $\rho_0$, power-law coefficient $B$, and exponent $n$) were made to the electrical resistivity data of the filled skutterudites. The fits were performed at low temperatures (usually below 2 K) such that the lattice contribution was negligible
and did not need to be subtracted. As a result of these fits, estimates for the residual resistivity for the various samples were found along with insight into the low temperature behavior of the filled skutterudites.

Anisotropic magnetic order arises in the filled skutterudites due to the structure and tetrahedral symmetry of these compounds. As a result of this anisotropy the $\rho(T)$ data for the compounds PrOs$_4$As$_{12}$ and NdOs$_4$Sb$_{12}$, below their respective ordering temperatures, could be fit with the following form due to electron-magnon scattering [29]

$$\rho(T) = \rho_0 + b \frac{T}{\Delta} \left(1 + 2 \frac{T}{\Delta}\right) e^{-\Delta/T}, \quad (2.7)$$

where $\Delta$ is the magnon energy gap.

Crystalline electric field fits were also performed to the electrical resistivity data in the paramagnetic state. In order to perform the CEF fits, the lattice contribution to the $\rho(T)$ data was first subtracted, since the CEF fits were performed in a temperature range where $\rho_{\text{lat}}$ becomes significant. The details of the lattice subtraction are discussed individually for each system in the latter chapters. Once $\rho_{\text{lat}}$ was subtracted, CEF fits, which considered magnetic exchange scattering between the disordered local moments and the conduction electrons, were performed [30,31] and in the case of NdOs$_4$Sb$_{12}$ an extra aspherical Coulomb scattering contribution, due to the direct Coulomb interaction between the conduction electrons and the 4$f$ electron charge distribution, was also considered [32]. The form of the CEF fit follows from a paper by Fisk and Johnston [33], which utilized the notation of Andersen et al. [31]. The contribution to the electrical resistivity due to the exchange interaction is written as $\rho = \rho_{\text{ex}}[\text{Tr}(PQ_{\text{ex}})]$ and the aspherical Coulomb scattering contribution is $\rho = \rho_{\Lambda}[\text{Tr}(PQ_{\Lambda})]$. The constants $\rho_{\text{ex}}$ and $\rho_{\Lambda}$ signify the strengths of the 4$f$-conduction electron exchange and direct Coulomb interactions, respectively. The trace of each term is over the $2J + 1$ CEF states $|i\rangle$ with energies $E_i$. The matrices $P_{ij}, Q_{ij}^{ex}$, and $Q_{ij}^{A}$ are given by the
following forms

\[ P_{ij} = \frac{e^{-E_i/k_B T}}{\sum_k e^{-E_k/k_B T}} \frac{(E_i - E_j)/k_B T}{1 - e^{-(E_i - E_j)/k_B T}}, \]  
\( (2.8) \)

\[ Q_{ij}^{\text{ex}} = \frac{1}{2} \left| \langle i | J_z | j \rangle \right|^2 + \frac{1}{2} \left| \langle i | J_+ | j \rangle \right|^2 + \frac{1}{2} \left| \langle i | J_- | j \rangle \right|^2, \]  
\( (2.9) \)

\[ Q_{ij}^{\text{A}} = \sum_{m=-2}^{+2} \left| \langle i | y_{2m}^j | j \rangle \right|^2, \]  
\( (2.10) \)

where the \( y_{2m}^j \)'s represent operator equivalents of the spherical harmonics for \( L = 2 \) (i.e., quadrupolar terms). These terms can be found in ref. [37]. The two contributions are then combined for the total CEF contribution with the form

\[ \rho_{\text{CEF}} = \rho_{\text{ex}} [x \text{Tr}(PQ^M) + (1 - x)\text{Tr}(PQ^A)], \]  
\( (2.11) \)

where ratio of the magnetic exchange term to the aspherical Coulomb scattering term \( \rho_{\text{ex}}/\rho_{\text{A}} \) is \( x \). The \( Q_{ij} \) matrices were also normalized for convenience [33], such that

\[ \sum_{i,j} Q_{ij}^{\text{ex}} = \sum_{i,j} Q_{ij}^{\text{A}} = (2J + 1)J(J + 1). \]  
\( (2.12) \)

Equation 2.11 above along with the associated \( Q_{ij} \) matrices were entered into a computer program in a functional form that could be solved by inputting various \( T \) and \( E_i \) matrix elements of \( P_{ij} \) as well as \( J \) for Pr, Nd, or Sm depending on which filled skutterudite system is being fit. In some instances linear functions of \( x_{\text{LLW}} \) and \( W \) (calculated from the cubic LLW Hamiltonian) were used to replace \( E_i \). Fits were then made to the \( \rho(T) \) data with \( r, x_{\text{LLW}}, \) and \( W \) as variables. In some instances \( \rho_{\text{imp}} \) and a functional form of \( \rho_{\text{lat}} \) were included to improve the quality of the fit. The functional form of \( \rho_{\text{lat}} \) was derived by fitting a polynomial to the \( \rho(T) \) data for the estimated lattice contribution, such as the \( \rho(T) \) data for \( \text{LaOs}_4\text{Sb}_{12} \) below 100 K. CEF fits to the electrical resistivity were performed for all of the filled skutterudite systems except for \( \text{PrOs}_4\text{As}_{12} \) and of these only \( \text{NdOs}_4\text{Sb}_{12} \) required aspherical Coulomb scattering to accurately fit the measured \( \rho(T) \) data. So, in most instances the \( \rho_{\text{CEF}} \) term is referred to as \( \rho_{\text{ex}} \).
Bibliography


Praseodymium-based filled skutterudites

The filled skutterudite compounds, with the formula $MT_4X_{12}$ ($M =$ alkali metal, alkaline-earth, lanthanide, or actinide; $T =$ Fe, Ru, or Os; and $X =$ P, As, or Sb), display a wide variety of strongly correlated electron phenomena [1–3]. Of particular interest are the Pr-based filled skutterudites. The physical properties of these compounds are dominated by the ground state and low lying excited state of the Pr$^{3+}$ ion in the crystalline electric field (CEF), and the hybridization of the Pr 4$f$-states with the ligand-states of the surrounding Sb ions that compose the atomic cage within which each Pr$^{3+}$ ion resides. A variety of correlated electron phenomena have been observed in the Pr-based filled skutterudites: conventional (BCS) and unconventional superconductivity, magnetic order, quadrupolar order, metal-insulator transitions, Kondo phenomena, and heavy fermion behavior.

One of the most interesting of these systems is the compound PrOs$_4$Sb$_{12}$, which is the first Pr-based heavy fermion superconductor. In PrOs$_4$Sb$_{12}$ superconductivity occurs below 1.85 K with an enhanced electron effective mass $m^* = 50m_e$ [4, 5]. A nonmagnetic $\Gamma_1$ singlet ground state has been confirmed by inelastic neutron scattering [6]. In high fields (4.4 T $\leq B \leq$ 15 T) as superconductivity is suppressed and at temperatures below 1.3 K an antiferroquadrupolar (AFQ) phase arises [7–12]. A nonmagnetic ground state along with the presence of magnetic field induced AFQ ordering and an enhanced electron effective mass suggest a novel superconducting pairing mechanism mediated by quadrupole fluctuations [1].
The unconventional nature of the superconductivity in PrOs$_4$Sb$_{12}$ is shown by the breaking of time reversal symmetry in the superconducting state along with the presence of multiple superconducting phases as well as indications of multiband superconductivity [7,9,13–15].

The filled skutterudite PrFe$_4$P$_{12}$ also exhibits AFQ ordering; however, in PrFe$_4$P$_{12}$ the AFQ phase occurs in zero-field below 6.5 K [16,17,20]. In the AFQ phase, an applied field induces a weak antiferromagnetic (AFM) moment on the Pr-ion sites [17], and in high magnetic fields, (≥ 5.5 T) where the AFQ phase is suppressed, heavy fermion behavior develops (γ ~ 1.4 J/mol K$^2$ at 6 T) [18–20]. Along with AFQ ordering, PrFe$_4$P$_{12}$ has also been found to exhibit a structural change from Im¯3 to Pmmm at temperatures close to $T_{AFQ}$. Additionally, for $T \leq 1$ K, a high field ordered state has been observed for 8 T ≤ $H$ ≤ 12 T along the [111] direction [21,22]. Further high pressure studies of PrFe$_4$P$_{12}$ have resulted in the discovery of a metal-insulator (MI) transition above 2.4 GPa [23].

As in PrFe$_4$P$_{12}$ under pressure, the Pr-based filled skutterudite PrRu$_4$P$_{12}$ exhibits a MI transition at 62 K [68]. In PrRu$_4$P$_{12}$ the MI transition has been ascribed to the formation of a charge-density-wave (CDW) due to hybridization between 4$f$ and conduction electron states [24,25]. This transition has also been associated with a structural change from Im3 to Pm3 [26–28]. High pressure measurements of PrRu$_4$P$_{12}$ reveal possible pressure induced superconductivity below 1.8 K at pressures ≥ 12 GPa [29]. Superconductivity has also been observed in other Pr-based filled skutterudite compounds, such as PrRu$_4$Sb$_{12}$ and PrRu$_4$As$_{12}$, which are superconducting at ~ 1 K and 2.4 K, respectively [30,31]. Weak magnetic order has been observed in polycrystalline PrFe$_4$Sb$_{12}$ below ~ 5 K along with possible heavy fermion behavior [32,33].
3.1

\textbf{PrFe}_4\textbf{Sb}_{12}

Among the Pr-based filled skutterudite compounds, \textit{PrFe}_4\textit{Sb}_{12} is one of the few that display magnetic ordering. Magnetic susceptibility measurements of polycrystalline \textit{PrFe}_4\textit{Sb}_{12} were initially performed by Danebrock \textit{et al.}, along with measurements of polycrystalline \textit{SmFe}_4\textit{Sb}_{12}, \textit{EuFe}_4\textit{Sb}_{12}, and \textit{NdFe}_4\textit{Sb}_{12}, all of which were found to display effective paramagnetic moments larger than the free ion values of their rare earth constituents [32]. They found that the enhanced effective moments in these compounds were due to the magnetic moment carried by the Fe-Sb sublattice [32]. This was later confirmed by Bauer \textit{et al.} through neutron-diffraction experiments which revealed ferromagnetic ordering in polycrystalline \textit{NdFe}_4\textit{Sb}_{12} with collinear moments on both the Nd and Fe sites [34]. It was also shown that the magnitude of the effective moment \( \mu_{\text{eff}} \) associated with this Fe-Sb sublattice contribution was on the order of 2.8 \( \mu_B \) [32, 33]. Besides magnetic susceptibility measurements, magnetization measurements by Danebrock \textit{et al.} of polycrystalline \textit{PrFe}_4\textit{Sb}_{12} at a temperature of 2 K found a weak nonsaturating magnetic moment in an applied magnetic field of 5.5 T, equal to half of the Pr\(^{3+}\) free-ion value, along with a small coercivity and remanence [32].

Structural refinement of X-ray diffraction data by Bauer \textit{et al.} found partial occupancy of the rare earth site in such that the corrected formula is \textit{Pr}_{0.73}\textit{Fe}_4\textit{Sb}_{12} [34]. Specific heat measurements of the same polycrystalline \textit{Pr}_{0.73}\textit{Fe}_4\textit{Sb}_{12} in field found a large electronic contribution to the specific heat at low temperatures, along with possible field-induced non-Fermi liquid behavior for 3 T \( \leq H \leq 9 \) T. A further indication of field-induced non-Fermi liquid behavior came from power-law fits to electrical resistivity measurements in field [34]. These measurements showed a power-law exponent of 2 (consistent with Fermi liquid behavior) at 0 T, which deviated from Fermi liquid behavior by 3 T with a power-law exponent of only 1. A study of the crystalline electric field effects in \textit{Pr}_{0.73}\textit{Fe}_4\textit{Sb}_{12}, based
on magnetization, resistivity, and specific heat data, indicated that the nine-fold degenerate Pr$^{3+}$J = 4 multiplet has a magnetic Γ$_5$ ground state.

In order to improve upon previous polycrystalline measurements of PrFe$_4$Sb$_{12}$, single crystals of Pr$_{0.87}$Fe$_4$Sb$_{12}$ were synthesized. These crystals were characterized through specific heat, magnetization, and electrical resistivity measurements in an attempt to clarify the nature of the magnetic ordering in PrFe$_4$Sb$_{12}$. A thorough study of the magnetic properties of Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystals was performed through measurements of the AC and DC magnetic susceptibility, along with scaling and Arrott analysis, which indicated magnetic ordering below ∼ 4.1 K. These results were supported by zero field specific heat measurements and electrical resistivity measurements in field that revealed features around 4 K.

### 3.1.1 Experimental Details

Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystals were grown by a self-flux method in excess molten Sb using elemental Pr (3N), Fe (3N) and Sb (6N) combined in the atomic ratio 1 : 4 : 20 and prepared as described in Section 2.1.1. The resulting crystals were cubic in shape, and primarily grew in clusters, with dimensions less than 1 mm.

X-ray diffractometry was used to determine crystal quality. Powder X-ray diffraction was carried out using a Rigaku D/MAX B on several ground single crystals in order to check for impurity phases. X-ray structural refinement was performed at the University of Vienna as described in Section 2.2.1.

Measurements of specific heat $C_p(T)$ over temperatures $T$ ranging from 0.6 K to 82 K were performed using a $^3$He refrigerator-based semi-adiabatic calorimeter. In order to obtain enough mass for the measurement, a number of single crystals with a total mass of 49.9 mg were measured together.

Electrical resistivity $\rho(H,T)$ measurements were performed in a Quantum Design Physical Properties Measurement System (PPMS), for 2 K $\leq T \leq$ 300 K and applied magnetic fields $H$ up to 9 T. For $T \leq$ 2.6 K, $\rho(H,T)$ was measured
in $^3$He-$^4$He dilution refrigerators at UCSD ($H \leq 8$ T) and at the National High Magnetic Field Laboratory at Los Alamos National Laboratory ($8$ T $\leq H \leq 18$ T). The electrical resistivity measurements used constant currents of 100 and 300 $\mu$A, with magnetic fields applied perpendicular to the current flow. Electrical resistivity under applied pressure $P$ was measured in a quasi-hydrostatic Be-Cu cell over the range $1$ atm $\leq P \leq 22.9$ kbar. These measurements were performed in a $^4$He cryostat for $1.2$ K $\leq T \leq 300$ K with an applied current of $1-10$ mA, using an AC resistance bridge. An inductive measurement of the superconducting transition of a Pb manometer was used to determine the pressure.

Magnetization $M(H, T)$ measurements were made with a Quantum Design SQUID magnetometer in the temperature range $1.7$ K to $300$ K in $H$ up to $5.5$ T. AC magnetic susceptibility measurements $\chi_{ac}$ as a function of temperature $T$ were used to screen crystals for a sharp magnetic transition. Measurement of $M(H, T)$ in a constant $H$ was subsequently performed, with $H$ parallel to [001].

3.1.2 Single-Crystal Structural Refinement

Single phase Pr$_{0.87}$Fe$_4$Sb$_{12}$ was indicated by X-ray powder diffraction patterns with no indication of impurity peaks. The structure of the single crystals was refined using the program SHELXS-97 [36]. The results from this structural refinement are listed in Table 3.1. The crystals had a LaFe$_4$P$_{12}$-type BCC structure [37], a lattice parameter $a = 9.140$ Å (unit cell volume of 763.6 Å$^3$) and a Pr site occupancy of 0.87. Among the filled skutterudite compounds, a partial vacancy of the rare earth site is common and may vary between samples with the same nominal composition. Earlier measurements of polycrystalline PrFe$_4$Sb$_{12}$ by Bauer et al. found a Pr occupancy of 0.73, a lattice parameter $a = 9.1369$ Å, and a 3% Sb impurity content [33,34]. In general, sample properties should depend on rare earth occupancy, however, comparable effects may also arise from differences in microstructure and phase homogeneity, which are also sample dependent. The following discussion is simplified by weighting data from various samples equally.
and site occupancy is analyzed only when it can be readily accounted for.

Table 3.1 Structural data for Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystals (LaFe$_4$P$_{12}$-type, space group Im$\overline{3}$; No. 204) taken at $T = 296$ K, with scattering angles of $2^\circ < 2\theta < 80^\circ$.

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3.1.3 Magnetization

Figure 3.1 displays the inverse DC magnetic susceptibility $\chi_{dc}^{-1}(T)$ for a Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystal with an applied field $H = 0.05$ T along the [001] direction, for $2$ K $\leq T \leq 300$ K. A Curie-Weiss fit to the $\chi_{dc}^{-1}(T)$ data from 70 K to 240 K is also displayed in Fig. 3.1, which reveals an effective moment $\mu_{\text{eff}} = 4.34 \mu_B$/f.u. (f.u. = formula unit) and a Curie-Weiss temperature $\Theta_{\text{CW}} = 4.19$ K. Inset (a) of Fig. 3.1 displays the low-$T$ $\chi_{dc}(T)$ data at $H = 0.05$ T along the [001], which reveals an enhancement around 5 K, close to $\Theta_{\text{CW}}$. Significant magnetic anisotropy was not detected in magnetization measurements in a constant magnetic field on the same single crystal rotated from [001] through [111].

The low temperature $\chi_{dc}^{-1}(T)$ data taken at $H = 0.05$ T along the [001] is displayed in Fig. 3.5 (b). The line in Fig. 3.5(b) is a Curie-Weiss fit to the data for $20$ K $< T < 45$ K, which indicates $\mu_{\text{eff}} = 4.22 \mu_B$/f.u. and $\Theta_{\text{CW}} = 4.02$ K. The
Figure 3.1 Inverse DC magnetic susceptibility $\chi_{dc}^{-1}$ as a function of temperature from 2 K to 300 K measured at $H = 0.05$ T, indicating Curie-Weiss $T$-dependence. Inset (a) displays the low-$T$ DC magnetic susceptibility $\chi_{dc}(T)$ at $H = 0.05$ T. Inset (b) shows the AC magnetic susceptibility $\chi_{ac}(T)$ data for Pr$_{0.87}$Fe$_4$Sb$_{12}$ measured in an oscillating magnetic field with an amplitude of 0.5 Oe and frequency of 100 Hz, indicating the onset of magnetic ordering between 4 K and 5 K.

A slight change in $\mu_{\text{eff}}$ between the high temperature and low temperature Curie-Weiss fits may be related to crystalline electric field (CEF) effects as discussed in Section 2.2.2.

The Pr$^{3+}$ free-ion moment of 3.58 $\mu_B$ is much less than the $\mu_{\text{eff}}$ determined from the high and low temperature Curie-Weiss fits. The calculated effective moment is comparable to values determined by Danebrock et al. [32], and Bauer and coworkers [33, 34], for polycrystalline PrFe$_4$Sb$_{12}$, which was attributed to an additional Fe-Sb sublattice contribution to $\mu_{\text{eff}}$.

Figure 3.1 inset (b) is a plot of the $\chi_{ac}(T)$ data for the same Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystal measured above. Much like the results found for polycrystalline
Figure 3.2 Magnetization $M$ as a function of field $H$ isotherms for several temperatures above and below the magnetic ordering transition. Below 4.2 K, the $M(H)$ curves overlap for applied fields greater than $H_{\text{merge}} \approx 0.5$ T. The inset shows a $T = 2$ K hysteresis loop, which demonstrates the small coercivity and remanence of Pr$_{0.87}$Fe$_4$Sb$_{12}$.

Pr$_{0.87}$Fe$_4$Sb$_{12}$ [33], the midpoint on the paramagnetic side of the peak in $\chi_{\text{ac}}(T)$ is $\sim 4.6$ K, while the peak occurs at $\sim 4.2$ K. Spin glass behavior was not detected since the position and shape of the peak in the $\chi_{\text{ac}}(T)$ data did not change with frequency.

Displayed in Figure 3.2 are the results of isothermal $M(H)$ measurements, made in the region around the magnetic transition temperature $T_c$. It can be seen that in high fields ($\sim 5$ T) at temperatures below the magnetic transition temperature the $M(H)$ isotherms still exhibit significant curvature and do not saturate. However, the magnetization isotherms for $T < T_c$ merge onto the same magnetization curve by $H_{\text{merge}} \approx 0.5$ T. Based on the 2 K $M(H)$ isotherm displayed in the inset to Figure 3.2, $M(H)$ of Pr$_{0.87}$Fe$_4$Sb$_{12}$ is characterized by a small coercive
Figure 3.3 (a) A conventional Arrott plot for PrFe$_4$Sb$_{12}$ using the critical exponents from the molecular field approximation ($\beta = 1/2$ and $\gamma = 1$). (b) The modified Arrott plot for Pr$_{0.87}$Fe$_4$Sb$_{12}$.

field close to 1 mT, a remanent magnetization less than 0.2 $\mu_B$/f.u. and a magnetization close to half the Pr$^{3+}$ free-ion saturation moment $M_{\text{sat}} = gJ = 3.2 \mu_B$ by 5.5 T.

To further characterize the features in the magnetization of Pr$_{0.87}$Fe$_4$Sb$_{12}$,
Arrott plots of $M^2$ vs $H/M$ were constructed as shown in Fig. 3.3(a). It can be seen in Fig. 3.3(a) that the $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ magnetization isotherms possess substantial curvature in all $H$. Such curvature implies that the magnetic ordering does not follow typical mean-field behavior. To account for this, a modified Arrott plot based on the Arrott-Noakes equation of state was used where $|M|/|t|^{\beta}$ is plotted as function of $|H/M|^{1/\gamma}$ (Fig. 3.3(b)) [38]. In a modified Arrott plot, linear and parallel magnetization isotherms are recovered about the magnetic transition temperature $T_c$ when the critical exponents $\beta$ and $\gamma$ are chosen correctly. These critical exponents can be related to a third critical exponent $\delta$ through the Widom scaling relation $\delta - 1 = \gamma/\beta$ [39]. The above critical exponents are defined for the reduced magnetization $m$, field $h$ and temperature $t = (T - T_c)/T_c$ by $m \sim t^\beta$ ($T < T_c$), $m \sim h^{1/\delta}$ ($T = T_c$), and $\partial m/\partial h = \chi \sim t^{-\gamma}$ ($T > T_c$). An initial
estimate of $T_c \approx 4.1$ K and $\delta = 2.55$ was determined by plotting $\partial \ln H / \partial \ln M$ vs $H$ and noting that $\partial \ln H / \partial \ln M = \delta$ for $T = T_c$. An initial estimate of $\gamma = 1$ was determined from the slopes of the $M(H)$ isotherms for $T > T_c$ as $H$ approaches 0 T, and from the Widom relation $\beta = 0.645$. The initial estimates for $\delta$, $\beta$ and $T_c$ were refined by plotting scaled $H^* = H/|t|^\beta$ as a function of scaled $M^* = |M|/|t|^\gamma$ (Fig. 3.4). When $\delta$, $\beta$ and $T_c$ are chosen correctly the scaled magnetization isotherms within the critical $T$ range from 3.5 K to 4.5 K collapse onto two curves, corresponding to $T > T_c$ and $T < T_c$. During this analysis only $M(H)$ data from 0.02 T to 2 T was used, since the analysis is only applicable over intermediate field range due to the presence of magnetic domains at low fields and effects of terms of higher order in $M$ at higher $H$. As seen in Fig. 3.4, values of $\beta = 0.57$, $\delta = 2.55$ (from Widom relation $\gamma = 0.884$) and $T_c = 4.15$ K collapse the $M(H)$ isotherms onto two curves for $T > T_c$ and $T < T_c$. In the Modified Arrott plot (Fig. 3.3(b)), it is clear that the critical exponents from the scaling analysis result in $M$ isotherms that are linear and parallel over the $M(H)$ range that was used in the scaling analysis. Linear fits to the isotherms in the modified Arrott plot are used to determine the spontaneous magnetization $M_s$ (positive intercepts to $M^{1/\beta}$) and the initial susceptibility $\chi_0$ (positive intercepts to $|H/M|^{1/\gamma}$). A plot of $M_s^{1/\beta}$ vs $T$ is displayed in Fig. 3.5(a) along with a linear fit, which indicates a magnetic ordering temperature $T_c = 4.08$ K and gives an estimate of $M_{sat} = 0.60 \mu_B$/f.u. from the $T = 0$ K intercept—which for a simple ferromagnet, corresponds to the spontaneous moment $M_0$ of the ordered state. The scaled Arrott analysis is consistent with the Curie-Weiss analysis, which can be seen by the proximity of the $|H/M|^{1/\gamma}$ intercepts (raised to the $\gamma$ power) to the extrapolated Curie-Weiss fit (inset of Fig. 3.5(b)).

### 3.1.4 Specific Heat

In Figure 3.6 the specific heat of Pr$_{0.87}$Fe$_4$Sb$_{12}$ is displayed from 0.6 K to 25 K. The only feature is a hump at low-temperatures that can be associated with
Figure 3.5 (a) $M^{1/\beta}$ intercepts from the scaled Arrott plot (Fig. 3.3(b)). The dashed line is a linear extrapolation to $T = 0$ K yields the value $M_0 = 0.60 \mu_B/\text{f.u.}$ (b) Inverse DC magnetic susceptibility $\chi_d^{-1}$ at low $T$ (open circles) and the initial susceptibility $\chi_0^{-1}$ (Open squares) determined from the intercepts to $(H/M)^{1/\beta}$. The solid line is a low-$T$ Curie-Weiss fit to $\chi_d^{-1}(T)$ from 20 K to 40 K. The inset more clearly shows $\chi_0^{-1}(T)$ in comparison with the low-$T$ Curie-Weiss fit. 

the onset of magnetic order as defined by $\chi_{ac}(T)$ and $M(H)$ measurements described earlier. The hump in $C(T)/T$ is much broader and not as well defined as a typical ferromagnetic transition and is too wide to be due to a distribution of critical temperatures. In general the behavior of the $C(T)/T$ data for the Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystals is consistent with the results obtained by Bauer et al for polycrystals [33]. An enhanced electronic contribution to the specific heat is indicated by the magnitude of $C(T)/T$ data at low temperatures and may be a possible indication of heavy fermion behavior. Determination of the electronic contribution to the specific heat is complicated by the persistence of the broad hump to the lowest measured temperature and the difficulty in determining a crystalline electric field
(CEF) energy level scheme, which is discussed in more detail in Section 3.1.6. It should also be noted that previous studies by Bauer et al. of polycrystalline Pr$_{0.73}$Fe$_4$Sb$_{12}$ revealed a contribution to the specific heat from a Pr nuclear Schottky anomaly at $T < 1$ K [33], adding further complications to any attempt at determining the electronic contribution to the specific heat. The resonance level model of Schotte and Schotte has been used to estimate the electronic specific heat in other Pr-based filled skutterudites [40], but it is an approximate single-ion model and was not applied in this case. Disregarding the CEF contribution and taking the nuclear and magnetic contributions to be negligible by 10 K, a fit was performed to the $C(T)$ data that included electronic ($C_e(T) = \gamma T$) and lattice terms ($C_l(T) = \beta T^3$). In Fig. 3.7(a) a fit of $C/T = \gamma + \beta T^2$ was performed in the range $14$ K $\leq T \leq 22$ K and resulted in an electronic specific heat coefficient $\gamma = 483$ mJ/mol K$^2$ and a Debye temperature $\Theta_D = 246$ K. An estimate
of the magnetic contribution to the entropy \( S_{\text{mag}} \) was determined by subtracting \( C_e(T)/T \) and \( C_l(T)/T \) from \( C(T)/T \), extrapolating to zero temperature, and then integrating over \( T \) (Fig. 3.7(b)). The resulting magnetic entropy reaches a value of only 80% of \( R \ln 2 \) by 12 K. The magnetic entropy is much less than \( R \ln 3 \), which would be expected for a magnetic \( \Gamma_5 \) triplet ground state (see Section 3.1.6). The reduced entropy may be due to hybridization of the localized 4\( f \) and conduction electron states, which may result in a transfer of entropy from the localized 4\( f \) states to the conduction electron states.

### 3.1.5 Electrical Resistivity

Displayed in Figure 3.8 is the electrical resistivity \( \rho(T) \) data for a representative \( \text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12} \) single crystal at \( H = 0 \) T and pressure \( P = 1 \) atm. In general the electrical resistivity of \( \text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12} \) is metallic, from \( \sim 18 \) K up there
is a gradual decrease in the slope of the $\rho(T)$ data until $\sim 200$ K, at which point $\rho$ becomes linear in $T$ up to 300 K. In the $\rho(T)$ data below 18 K a shoulder-like feature is observed centered around 10 K. This feature may be due to a reduction in spin-flip scattering as a result of weak magnetic correlations that persist well above $T_c$. It may be that these weak magnetic correlations are related to the broad transition in $C(T)/T$, which extends up to 10 K. Inset (a) of Fig. 3.8 features the $\rho(T)$ data of Pr$_{0.87}$Fe$_4$Sb$_{12}$ at various applied pressures. The only significant change observed with increasing pressure is a slight positive shift in $\rho$ below 30 K.

Figure 3.8 The zero-field $\rho(T)$ data for Pr$_{0.87}$Fe$_4$Sb$_{12}$ at a pressure $P = 1$ atm. Pr$_{0.87}$Fe$_4$Sb$_{12}$ exhibits little $H$- or $P$-dependence over most of this temperature range. Inset (a) displays the low-$T$ $\rho(T, P)$ data. Inset (b) shows the $\rho(T, H)$ data at low-$T$, featuring a change from positive to negative magnetoresistance around the magnetic ordering temperature.
Figure 3.9 Power-law fits to the low-temperature $\rho(T)$ data for (a) $0 \leq H \leq 8$ T and (b) $10 \leq H \leq 18$ T. Parameters for the power-law fits are displayed in Fig. 3.10.

The electrical resistivity is also weakly dependent on the applied magnetic field, with a decrease in $\rho(T)$ of only $\sim 15 \mu\Omega$ cm between 20 K and 300 K at $H = 9$ T and little change in the curvature of $\rho(T)$ (not shown). Though the effect of $H$ on $\rho$ is small, the magnetic ordering can be observed in the $\rho(T, H)$ data as
a change from positive to negative magnetoresistance as \( T \) increases through \( T_c \) (Inset (b) of Fig. 3.8). Below \( T \leq 2.6 \) K the \( \rho(T) \) data were fit with a power law of the form: \( \rho(T) = \rho_0 + B T^n \) with residual resistivity \( \rho_0 = \rho(0 \) K), a power law coefficient \( B \), and exponent \( n \) (Fig. 3.9). The dependence of \( \rho_0 \) and the exponent

Figure 3.10 Power law exponent \( n \) and residual resistivity \( \rho_0 \) as a function of applied field \( H \). Derived from power-law fits to the low-\( T \) \( \rho(T) \) data for Pr\(_{0.87}\)Fe\(_4\)Sb\(_{12}\) (Fig. 3.9).

\( n \) on \( H \) is shown in Fig. 3.10. It can be seen that \( n \) decreases for \( 2 \) T \( \leq H \leq 10 \) T and then reaches a value of \( \sim 2 \) in highest fields. While, in low applied field, \( 0 \) T \( \leq H \leq 10 \) T, \( \rho_0 \) increases with \( H \), but for \( H > 10 \) T, \( \rho_0 \approx 127 \) \( \mu \)\( \Omega \) cm. Fits to the data of the form \( \rho(T) = \rho_0 + B T^n \exp(-\Delta/k_B T) \), where \( \Delta \) is a spin wave energy gap, resulted in worse fits than those of the bare power law, and yielded exponents \( n \) that still had significant \( H \)-dependence. In polycrystalline Pr\(_{0.73}\)Fe\(_4\)Sb\(_{12}\) this behavior was interpreted as the absence of long-range magnetic order at intermediate fields [33,34].
3.1.6 Crystalline Electric Field Effects

Crystalline electric field (CEF) analysis was performed on the magnetic susceptibility and electrical resistivity data to determine the CEF energy level splitting scheme for the Pr\(^{3+}\) ion in Pr\(_{0.87}\)Fe\(_4\)Sb\(_{12}\). The CEF analysis was simplified, as stated in Section 2.2, by assuming cubic \(O\_h\) symmetry for PrFe\(_4\)Sb\(_{12}\). In a cubic CEF, the nine-fold degenerate Pr\(^{3+}\) \(J = 4\) multiplet splits into a \(\Gamma_1\) singlet, \(\Gamma_3\) doublet, \(\Gamma_4\) triplet, and \(\Gamma_5\) triplet. The CEF fits were performed assuming a \(\Gamma_5\) ground state since a cubic CEF splits the Pr\(^{3+}\) multiplet such that \(\Gamma_5\) is the only allowed magnetic ground state. The LLW notation discussed in Section 1.1.1 is used to describe the CEF fits.

As previously noted, there is an Fe\(_4\)Sb\(_{12}\) sublattice contribution to the calculated \(\mu_{\text{eff}}\) [32, 33], this sublattice contribution must be subtracted from the magnetic susceptibility data in order to analyze it. The Fe\(_4\)Sb\(_{12}\) sublattice contribution to the effective moment was determined with the assumption that the Pr\(^{3+}\) moment \(\mu_{\text{Pr}}\) and the Fe\(_4\)Sb\(_{12}\) sublattice moment \(\mu_{\text{Fe}4\text{Sb}_{12}}\) are additive and follow the same Curie-Weiss law. In general both species do not necessarily have the same \(\Theta_{\text{CW}}\). However, in Pr\(_{0.87}\)Fe\(_4\)Sb\(_{12}\) their magnitudes can not be much larger than 4 K since there would have been ordering at temperatures higher than \(T_c\). Since the Curie-Weiss law is applicable over a wide temperature range (Fig. 3.1) and both magnetic species order below \(T_c\), it is reasonable to relate the high-temperature paramagnetic moments by

\[
\mu_{\text{meas}}^{\text{eff}} = \sqrt{f_{\text{Pr}} (\mu_{\text{Pr}}^{\text{eff}})^2 + (\mu_{\text{Fe}4\text{Sb}_{12}}^{\text{eff}})^2}
\] (3.1)

with \(\mu_{\text{meas}}^{\text{eff}} = 4.34 \mu_\text{B}\), filling fraction \(f_{\text{Pr}} \approx 0.87\) determined via X-ray refinement, and assuming that \(\mu_{\text{Pr}}^{\text{eff}}\) is equal to the Pr\(^{3+}\) free ion moment (\(\mu_{\text{eff}} = 3.58 \mu_\text{B}\)). Equation 3.1 yields \(\mu_{\text{Fe}4\text{Sb}_{12}}^{\text{eff}} = 2.77 \mu_\text{B}\), comparable to a value found by Bauer et al. [33]. A Curie-Weiss law susceptibility with \(\mu_{\text{Fe}4\text{Sb}_{12}}^{\text{eff}} = 2.77 \mu_\text{B}\) was subtracted from the \(\chi(T)\) data and resulted in a susceptibility curve that represents the Pr\(^{3+}\) contribution only. After scaling to correct for partial Pr\(^{3+}\) filling, the corrected...
magnetic susceptibility $\chi_{Pr}$ was fit to $\chi_{Pr}^{-1} = \chi_{CEF}^{-1} - \lambda$, which includes a molecular field parameter $\lambda$ to account for the presence of magnetic order in $Pr_{0.87}Fe_4Sb_{12}$ and the CEF term $\chi_{CEF}^{-1}$ follows from Section 2.2.2.

Fits to the $\rho(T)$ data for $PrFe_4Sb_{12}$ included lattice $\rho_{lat}$, an impurity $\rho_{imp}$ ($\sim 115\mu\Omega$ cm), and $s$-$f$ exchange scattering $\rho_{ex}$ contributions. The lattice contribution was estimated from the isostructural nonmagnetic compound $LaFe_4Sb_{12}$, although data from that compound could not be used above 100 K where $\rho(T)$ of $LaFe_4Sb_{12}$ exhibits significant negative curvature, a common feature of La-based compounds [42,43]. Alternative candidates for the lattice contribution are $YFe_4Sb_{12}$ and $LuFe_4Sb_{12}$, which may have less pronounced curvature in $\rho(T)$, but have yet to be synthesized, to our knowledge. An initial estimate of $\rho_{imp}$ was determined from the low temperature $\rho(T)$ data (Fig. 3.9). The final contribution is due to $s$-$f$ exchange scattering $\rho_{ex}$ from the $Pr^{3+} 4f$ energy levels in a cubic CEF. This was calculated for splitting of the Hund’s rule $J = 4$ multiplet of $Pr^{3+}$ in a cubic CEF as described in Section 2.2.4. An aspherical Coulomb scattering contribution to the fit of the $\rho(T)$ data was not included since it did not improve the quality of the CEF fits. The final form of the fit to the $\rho(T)$ data up to 100 K was $\rho(T) = \rho_{lat}(T) + \rho_{imp}(T) + \rho_{ex}(T)$.

The $\chi_{Pr}^{-1}(T)$ and $\rho(T)$ data were fit with various energy level schemes, all of which assumed a $\Gamma_5$ ground state. All of the resulting fits were indistinguishable and a unique energy level scheme was not found, though the splittings between the various energy levels for each scheme were comparable. The $\chi_{Pr}^{-1}(T)$ and $\rho(T)$ data for $10\,K \leq T \leq 100\,K$ were fit reasonably well with the following $x_{LLW}$ and $W$ values in the three regions of the $x_{LLW} - W$ plane with a $\Gamma_5$ ground state: $(x_{LLW},W) = (-0.93,-5.0), (0.69,3.8)$, and $(1.0,4.3)$. The energy level splittings from the various best fits ranged from 70 K to 130 K between the ground state and the first excited state, 130 K to 180 K between the ground state and second excited state, and 180 K to 270 K between the ground state and the third excited state. Since the various CEF fits are all similar in shape, one representative set,
\( (x_{LLW}, W) = (-0.93, -5.0) \), was chosen for display in Fig. 3.11(a). These \( x_{LLW} \) and

\[ (x_{LLW}, W) = (-0.93, -5.0) \]

\( W \) parameters correspond to the following energy level scheme: \( \Gamma_5 \) ground state, \( \Gamma_3 \) at 110 K, \( \Gamma_4 \) at 177 K, and \( \Gamma_1 \) at 272 K. In the \( \chi_{Pr}^{-1}(T) \) data it can be seen that

![Figure 3.11](image-url)

Figure 3.11 (a) A representative CEF fit to the \( \chi_{dc}(T) \) data from 10 K to 100 K, after subtraction of the Fe\(_4\)Sb\(_{12}\) contribution and correction for partial filling. (b) A representative CEF fit to the \( \rho(T) \) data from 10 K to 100 K, which includes lattice, impurity, and magnetic contributions.
there are almost no features to fit except for a slight curvature that occurs around 20 – 30 K. This curvature is fit quite well with the CEF energy splittings described above along with a molecular field parameter $\lambda \approx 7.65 \text{ mol/cm}^3$. Like the $\chi_{\text{Pr}}^{-1}(T)$ data, the $\rho(T)$ data do not possess any significant features in the range from 10 K to 100 K as seen in Figure 3.11(b). The $\rho(T)$ data were fit reasonably well with the CEF energy splittings described above along with a lattice term equal to 1.57 times that due to LaFe$_4$Sb$_{12}$ and an impurity term of 115 $\mu\Omega$ cm. The CEF energy level splittings determined above for single crystals of Pr$_{0.87}$Fe$_4$Sb$_{12}$ are comparable to those calculated for polycrystalline Pr$_{0.73}$Fe$_4$Sb$_{12}$ by Bauer et al. [33].

In fitting the $\chi_{\text{Pr}}^{-1}(T)$ and $\rho(T)$ data, difficulties arose in determining a unique CEF fit to the data for several reasons. The first reason being that the lattice contribution to the $\rho(T)$ data is not known accurately above 100 K, which limited the range of fits to the $\rho(T)$ data. A second reason is that there are few features in the $\chi_{\text{Pr}}^{-1}(T)$ and $\rho(T)$ data from 10 K to 100 K, that can be used to distinguish between the quality of various fits. In fact, the data are so featureless that a fit that does not include a term due to CEF splitting is barely distinguishable from one that does. The lack of a Schottky anomaly in the $C(T)$ data also made it difficult to settle on a unique CEF scheme.

### 3.1.7 Weak Magnetic Ordering

Based on the above results it seems clear that Pr$_{0.87}$Fe$_4$Sb$_{12}$ exhibits magnetic ordering below 4.1 K. These results are supported further by neutron-diffraction experiments, which find the onset of magnetic ordering is $\sim 4$ K [44]. These measurements indicate a complex magnetic structure with both Pr and Fe ions carrying moments. The data, though inconclusive, seem to imply a ferromagnetic (FM) alignment of the Pr ions along with three possible Fe spin configurations. Two of the possible configurations involve antiferromagnetic (AFM) configurations of the Fe moments, while the third involves a FM Fe configuration coupled ferrimagnetically (antiparallel) to the FM Pr sublattice.
A better understanding of Pr$_{0.87}$Fe$_4$Sb$_{12}$ can be obtained by relating the characteristic features observed in the various measurements. One such feature is the nonsaturating $M(H)$ isotherms in the magnetization measurements, which prevents an accurate determination of $M_{\text{sat}}$. Attempts to account for the curvature of the $M(H)$ data with Brillouin functions were unable to account for the high field curvature of the data. The high field curvature of $M(H)$ also did not allow for the subtraction of a linear paramagnetic contribution below $T_c$. This behavior is consistent with the neutron-diffraction data, which suggests ordering at both Pr and Fe sites. Though there is significant curvature in the $M(H)$ data, an estimate of $M_{\text{sat}} = 0.60 \ \mu_B/\text{f.u.}$ was derived earlier from the modified Arrott analysis (Fig. 3.5(a)). This value of $M_{\text{sat}}$ is also consistent with the magnitude of the magnetization found at $H_{\text{merge}} \approx 0.5 \ \text{T}$ shown in Fig. 3.2, where the $M(H)$ isotherms collapse below $T_c$. However, $M_{\text{sat}}$ is far from the limiting value of the magnetization, since a magnetization of $\sim 2.6 \ \mu_B/\text{f.u.}$ has been measured at $H = 15 \ \text{T}$ by Bauer et al. [33].

Another unusual feature of the magnetization of Pr$_{0.87}$Fe$_4$Sb$_{12}$ is that, unlike the filled skutterudite NdOs$_4$Sb$_{12}$ discussed in Chapter 5, the ordered moment cannot be explained fully by CEF splitting. In the case of Pr$_{0.87}$Fe$_4$Sb$_{12}$ the CEF analysis in Section 3.1.6 indicates a $\Gamma_5$ ground state. However, the $\Gamma_5$ ground state should contribute 2 $\mu_B/\text{f.u.}$ while measurements by Bauer et al. indicate $M(15 \ \text{T}) \approx 2.6 \ \mu_B/\text{f.u.}$ [33]. This implies an extra contribution to the magnetization besides that of Pr, consistent with an ordered moment arising from the Fe$_4$Sb$_{12}$ sublattice.

The weak ordered moment of Pr$_{0.87}$Fe$_4$Sb$_{12}$ is an indication of itinerant magnetism, which is characterized by persistent spin fluctuations above the magnetic ordering temperature $T_c$. The nonsaturating high-field moment, the broad magnetic transition in the $C(T)$ data, and the downturn in the $\rho(T)$ data at $\sim 10 \ \text{K}$ are features in Pr$_{0.87}$Fe$_4$Sb$_{12}$ that may be associated with itinerant magnetism.

The small value of the estimated $M_{\text{sat}}$ of Pr$_{0.87}$Fe$_4$Sb$_{12}$ has further implica-
tions. A comparison of $M_{\text{sat}}$ with the paramagnetic effective moment of $4.3 \, \mu_B$/f.u. yields a ratio $\mu_{\text{eff}}/M_{\text{sat}}$ of $\sim 7$, an indication of weak ferromagnetism in conventional FM systems [47, 48]. Small ordered moments are often the hallmark of itinerant magnetism, which is characterized by persistent spin fluctuations above the ordering temperature $T_c$. This notion is compatible with the drop in $\rho(T)$ at $\sim 10$ K, the broad magnetic $C_p(T)$ peak, and the unsaturated high-field moment observed in $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$. When considering the large Pr-Sb interatomic distance in $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ (Table 3.1) combined with the tendency toward local moment behavior of Pr $f$-electrons, an itinerant $\text{Fe}_4\text{Sb}_{12}$ sublattice moment is not unexpected. In fact work by Leithe-Jasper et al. has shown that $\text{NaFe}_4\text{Sb}_{12}$ and $\text{KFe}_4\text{Sb}_{12}$ are both weak itinerant ferromagnets [49, 50], while recent measurements by Viennois et al. reveal the presence of strong spin fluctuations in $\text{LaFe}_4\text{Sb}_{12}$ [51].

All the features that are observed in the $M(H,T)$ of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ are consistent with a possible ferrimagnetic arrangement of Pr and Fe magnetic sublattices. This view is supported by both neutron scattering and bulk magnetization data, which indicate the presence of Pr and Fe ordered moments. A calculation using Eq. (3.1) adds support to existence of ferrimagnetic ordering in $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$. In this case, $\mu_{\text{meas}}^{\text{meas}} = 4.22 \, \mu_B$ from the low-$T$ Curie-Weiss law fit (Fig. 3.5), Pr filling fraction $f^{\text{Pr}} \approx 0.87$, and assuming that $\mu_{\text{eff}}^{\text{Pr}}$ is due to the Pr$^{3+}$ cubic CEF-split $\Gamma_5$ ground state ($\mu_{\text{eff}} = 2.83 \, \mu_B$), $\mu_{\text{eff}}^{\text{Fe}_4\text{Sb}_{12}} = 3.29 \, \mu_B$. The paramagnetic moment is related to the spin by $(\mu_{\text{eff}}^{\text{Fe}_4\text{Sb}_{12}})^2 = g^2 J(J + 1)$, with $g = 2$ for Fe, yielding an effective spin of 1.22 for the $\text{Fe}_4\text{Sb}_{12}$ sublattice. The Fe saturated moment $\mu_{\text{sat}}^{\text{Fe}_4\text{Sb}_{12}} = gJ = 2.44 \, \mu_B$, while for the Pr$^{3+}$ $\Gamma_5$ ground state, $\mu_{\text{sat}}^{\text{Pr}} = 2 \, \mu_B$ and correction for partial filling results in $\mu_{\text{sat}}^{\text{Pr}} = 1.74 \, \mu_B$. An antiparallel arrangement of the Pr and Fe sublattices yields a moment of 0.7 $\mu_B$, while a parallel arrangement has a moment of 4.18 $\mu_B$. In the ferrimagnetic state, $M$ would increase from 0.7 to 4.18 $\mu_B$ with increasing applied field, as one of the magnetic sublattices aligns with $H$. In the case of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ this simple picture is complicated by the itinerant nature of the Fe moment, which is most likely responsible for the absence
of saturation in the magnetization at high fields. A possible moment realignment of a ferrimagnetic structure may result in the field-dependence of the power-law exponents determined from fits to the low temperature resistivity of Pr$_{0.87}$Fe$_4$Sb$_{12}$ (Fig. 3.10(b)) for applied fields between 0.5 and 10 T. In an applied field the magnetic moments of Pr and Fe would reorient, causing the magnon excitation spectrum of Pr$_{0.87}$Fe$_4$Sb$_{12}$ to change, which may influence the electron-magnon scattering at low temperatures.

In other rare earth systems such as Yb$_{0.8}$Y$_{0.2}$InCu$_4$ [53] and SmFe$_4$P$_{12}$ [54], the features observed in the magnetization of Pr$_{0.87}$Fe$_4$Sb$_{12}$ have been attributed to Kondo screening. However, in Pr$_{0.87}$Fe$_4$Sb$_{12}$, $\chi^{-1}_{dc}(T)$ follows a Curie-Weiss law down to 20 K, below which there are no indications of moment screening through $T_c$, and the $\rho(T)$ does not display the characteristic Kondo-lattice shoulder.

Another difficulty in understanding Pr$_{0.87}$Fe$_4$Sb$_{12}$ is that the critical exponents derived from the modified Arrott analysis ($\beta = 0.57$, $\gamma = 0.884$, $\delta = 2.55$) are difficult to interpret. For instance, the best-fit value for $\gamma$ is less than 1, unlike most theories and experiments which find values greater than 1, independent of the ordered state. [39,55–60] Attempts to force $\gamma \geq 1$ result in $H/|t|^{\delta \beta}$ vs $|M|/|t|^\beta$ plots of significantly lower quality. It is interesting to note that despite differences in both rare earth and transition metal constituents, the magnetic behavior of Pr$_{0.87}$Fe$_4$Sb$_{12}$ is similar to that of SmOs$_4$Sb$_{12}$ in Chapter 4. The compound SmOs$_4$Sb$_{12}$ has similar critical exponents ($\beta = 0.73$, $\gamma = 0.60$, and $\delta = 1.82$) and SmOs$_4$Sb$_{12}$ also exhibits a nonsaturating magnetization in high $H$. Unfortunately, the magnetic structure of SmOs$_4$Sb$_{12}$ has not been determined. It should be pointed out that this behavior is not observed in all filled skutterudites that exhibit magnetic ordering. In Chapter 5 it is found that the magnetic ordering of the filled skutterudite compound NdOs$_4$Sb$_{12}$ is described by critical exponents consistent with mean-field ferromagnetism.

Further experiments are necessary in order to determine the complex nature of the magnetic ordering in PrFe$_4$Sb$_{12}$, which may be composed of both local
and itinerant moments. One of the most useful experiments would be inelastic neutron scattering, since it would determine the correct CEF energy splitting scheme as well as the critical exponents $\eta$ and $\nu$. A precise CEF scheme for $\text{PrFe}_4\text{Sb}_{12}$ would allow for the calculation of the Schottky contribution to the specific heat, this contribution could then be used to more accurately determine the electronic contribution to the specific heat. An accurate determination of the electronic contribution to the specific heat would verify if $\text{PrFe}_4\text{Sb}_{12}$ is a heavy-fermion system. The values of $\nu$ and $\eta$ [correlation length $\xi \sim t^{-\nu}$ and correlation function $G(q) \sim q^{-2+\eta}$ for the wave vector $q$] could be used through the hyperscaling relations to verify the critical exponents determined for $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ from the modified Arrott analysis.

3.1.8 Summary

Modified Arrott plot analysis and neutron-diffraction experiments have confirmed long range magnetic ordering in $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ single crystals. A consistent picture forms in which a complex magnetic structure, possibly ferrimagnetic, results from ordering on both the Pr and Fe sites. Numerous features seem to indicate the presence of itinerant magnetism, such as the lack of saturation in the $M(H)$ isotherms, the low value of $M_{\text{sat}}$, the broad peak in $C(T)/T$, and the shoulder in $\rho(T)$ at 10 K. The critical exponents ($\beta = 0.57$, $\gamma = 0.884$, and $\delta = 2.55$) derived from the modified Arrott plot for $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ are not consistent with classical or quantum critical models. However, the critical exponents are similar to those found for SmOs$_4$Sb$_{12}$ in Chapter 4. Specific heat measurements of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ indicate an enhanced electron effective mass at low temperatures. Over most of the temperature range the electrical resistivity of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ is fairly insensitive to applied pressure and magnetic field. Attempts to fit the magnetic susceptibility and electrical resistivity of $\text{Pr}_{0.87}\text{Fe}_4\text{Sb}_{12}$ with a unique CEF splitting scheme for a Pr$^{3+}$ ion in a cubic crystal field were unsuccessful. These CEF fits were hampered by the lack of features in the magnetic susceptibility and
electrical resistivity data. Further study of PrFe$_4$Sb$_{12}$ is warranted, since it could lead to an improved understanding of magnetic critical behavior in systems that exhibit both localized and itinerant characteristics.
Unlike the Pr-based filled skutterudite phosphides and antimonides, the arsenides have not been investigated in much detail. The only Pr-based arsenic filled skutterudite to be characterized is PrRu$_4$As$_{12}$, which was found to exhibit superconductivity below 2.4 K [31]. The two remaining systems that have yet to be studied provide an opportunity to discover other examples of strongly correlated electron behavior displayed by the Pr-based filled skutterudites. In this section of Chapter 3 an investigation of the physical properties of PrOs$_4$As$_{12}$ single crystals is presented. These measurements reveal that PrOs$_4$As$_{12}$ is a Kondo lattice compound with an enhanced electronic specific heat coefficient $\gamma \approx 50-200$ mJ/mol K$^2$ for temperatures $10$ K $\leq T \leq 18$ K, and $\sim 1$ J/mol K$^2$ for $T \leq 1.6$ K. Multiple ordered phases are observed below 2.3 K and 3.2 T, at least one of which appears to be AFM in nature.

3.2.1 Experimental Details

Single crystals of PrOs$_4$As$_{12}$ were grown from elements with purities $\geq 99.9\%$ by a molten metal flux method at high temperatures and pressures, the details of which will be reported elsewhere [62]. After removing the majority of the flux by distillation, PrOs$_4$As$_{12}$ single crystals of an isometric form with dimensions up to $\sim 0.7$ mm were collected and cleaned further in acid to remove any Pr impurity phases from the surfaces. X-ray powder diffraction measurements were performed with a Rigaku D/Max B X-ray machine on a powder prepared by grinding several single crystals along with a high purity Si(8N) standard. The crystal structure of PrOs$_4$As$_{12}$ was determined by X-ray diffraction (XRD) on a crystal with a regular octahedral shape and dimensions of $0.12 \times 0.12 \times 0.12$ mm. A total of 5158 reflections (583 unique, $R_{int} = 0.1249$) were recorded and the structure was resolved by the full matrix least squares method using the SHELX-97 program.
with a final discrepancy factor R1 = 0.0462 (for I > 2σ(I), wR2 = 0.1124) [63,64].

Magnetization $M$ measurements for temperatures $0.4 \leq T \leq 10$ K and magnetic fields $-5.5 \leq H \leq 5.5$ T were made in a $^3$He Faraday magnetometer. A mosaic of 27 crystals, with a total mass of 27 mg, was measured with the [111] axis of the crystals nominally aligned parallel to $H$. Measurements of $M(T,H)$ were also performed using a Quantum Design Magnetic Properties Measurement System (MPMS) in $H$ up to 5.5 T for $1.7 \leq T \leq 300$ K. Electrical resistivity $\rho(H,T)$ measurements were made using a four probe ac technique in fields up to 9 T for $2 \leq T \leq 300$ K in a Quantum Design PPMS using a constant current of $1 - 10$ mA and in $H$ up to 8 T for $0.06 \leq T \leq 2.6$ K using a $^3$He-$^4$He dilution refrigerator and a constant current of 300 $\mu$A, with $H$ perpendicular to the electrical current and parallel to the [100] axis. Measurements of $\rho(T)$ at various pressures $P$ up to $\sim 23$ kbar were made down to 1 K in a $^4$He cryostat using a BeCu piston-cylinder clamp. Specific heat $C(T)$ measurements on PrOs$_4$As$_{12}$ were performed for $0.6 \leq T \leq 35$ K at the University of California San Diego (UCSD) in a semi-adiabatic $^3$He calorimeter on a collection of single crystals with a total mass of 49 mg. Additional $C(T)$ measurements for $0.4 \leq T \leq 20$ K were performed at Lawrence Livermore National Laboratory (LLNL) in a Quantum Design $^3$He PPMS.

3.2.2 Single-Crystal Structural Refinement

Analysis of the X-ray powder diffraction pattern indicates single phase PrOs$_4$As$_{12}$ with no major impurity peaks. A unit cell parameter $a = 8.5319(11)$ Å was determined, in excellent agreement with an earlier measurement of $a = 8.5311(3)$ Å [65]. Single crystal structural refinement by Adam Pietraszko at the Polish Academy of Sciences, shows that the unit cell of PrOs$_4$As$_{12}$ has the LaFe$_4$P$_{12}$-type structure (Im$ar{3}$ space group) with two formula units per unit cell, and $a = 8.520(1)$ Å. Other crystal structure parameters are summarized in Table 3.2.2. The displacement parameter $U_{eq}$ represents the average displacement of an atom vibrating
around its lattice position and equals its mean-square displacement along the Cartesian axes. The displacement parameters determined for PrOs₄As₁₂ show behavior which is typical of the lanthanide filled skutterudites [66,67]. Table 3.2.2 also indicates that the Pr site in PrOs₄As₁₂ can be assumed to be fully occupied since there is a ~ 2% uncertainty in the occupancy factors.

Table 3.2 Atomic coordinates, displacement parameters, and occupancy factors for PrOs₄As₁₂. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$ ($\AA^2 \times 10^3$)</th>
<th>Occupancy factor</th>
</tr>
</thead>
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</tr>
<tr>
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<td>0.1487(1)</td>
<td>7(1)</td>
<td>0.98(2)</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>16(1)</td>
<td>0.99(2)</td>
</tr>
</tbody>
</table>

### 3.2.3 Magnetization

The DC magnetic susceptibility $\chi_{dc}(T)$, measured in $H = 0.05$ T along the [111] direction, for 0.4 K ≤ $T$ ≤ 10 K, is shown in Fig. 3.12(a). The clear peak in the $\chi_{dc}(T)$ data suggests an AFM transition at $T = 2.3$ K. Figure 3.12(b) displays $\chi_{dc}^{-1}$ vs $T$ in $H = 0.1$ T between 2 K and 300 K. Above 50 K, the data are well-described by a Curie-Weiss law with an effective moment $\mu_{eff} = 3.81 \mu_B$/f.u. and a Curie-Weiss temperature $\Theta_{CW} = -25.8$ K. Below 20 K, $\chi_{dc}^{-1}(T)$ can be described by a different Curie-Weiss law, with $\mu_{eff} = 2.77 \mu_B$/f.u. and $\Theta_{CW} = 0.44$ K [Fig. 3.12(b) inset]; this behavior is consistent with crystalline electric field (CEF) effects (Section 2.2.2), which will be discussed later. The value of $\mu_{eff}$ derived from the high temperature (above 50 K) Curie-Weiss fit is larger than the the Pr$^{3+}$ free-ion value of $\mu_{eff} = 3.58 \mu_B$/f.u. A similar $\mu_{eff} = 3.84 \mu_B$/f.u. was also found for PrRu₄P₁₂ [68]. In contrast, PrOs₄Sb₁₂ displays an effective moment of 2.97 $\mu_B$/f.u. [5], while both PrOs₄P₁₂ and PrFe₄P₁₂ display effective moments close to the Pr$^{3+}$ free-ion value [68,69]. The larger-than-expected moment may be due
to an unaccounted-for constant Pauli paramagnetic contribution. When a constant contribution $\chi_0$ of $\sim 5.5 \times 10^{-4}$ cm$^3$/mol is assumed, which is consistent with a value of $5.16 \times 10^{-4}$ cm$^3$/mol found for LaFe$_4$P$_{12}$ [70], the effective moment estimated from a Curie-Weiss law fit approaches the Pr$^{3+}$ free-ion value with $\Theta_{CW} = -12.5$ K. The values of $\mu_{\text{eff}}$ and $\Theta_{CW}$ for the low temperature (below 20 K) Curie-Weiss law fit remain unchanged when the $\chi_{\text{dc}}(T)$ data are corrected for this value of $\chi_0$.

Figure 3.12 (a) Magnetic susceptibility $\chi_{\text{dc}}$ vs $T$, indicating a magnetic transition at 2.3 K. (b) Inverse magnetic susceptibility $\chi_{\text{dc}}^{-1}$ vs $T$. The line represents a Curie-Weiss law fit to the data above 50 K. The inset shows the low-$T$ behavior of $\chi_{\text{dc}}^{-1}(T)$ along with a low-$T$ Curie-Weiss law fit.
Figure 3.13 Magnetization $M$ vs $H$ isotherms at several values of $T$. Features in $M(H)$ at constant $T$, with $H_1$ and $H_2$ defined by a kink in $M(H)$, are illustrated for $T = 0.425$ K. The inset shows $M(H)$ at higher temperatures.

Low-$T$ magnetization data taken with $H$ parallel to [111] are shown in Fig. 3.13 and 3.14. An inflection point at low $H$ is evident, along with two kinks in $M(H)$ (denoted $H_1$ and $H_2$) that are suppressed toward lower field with increasing $T$. The inset of Fig. 3.13 shows the evolution of $M(H)$ from higher temperatures down to the ordering temperature. No magnetic hysteresis was observed. Features corresponding to $H_1$ and $H_2$ are found in $M(T)$ in constant $H$ and displayed in Fig. 3.14. With increasing $H$, a peak in $M(T)$ [labeled as $T_1$ in Fig. 3.14] shifts towards $T = 0$ K, while a kink in $M(T)$ at higher $T$ (denoted $T_2$) becomes apparent, splits off from $T_1$, and eventually also moves towards $T = 0$ K.
Figure 3.14 Magnetization $M$ vs $T$ for several values of $H$. Features in $M(T)$ at constant $H$, with $T_2$ defined by a small peak, and $T_1$ defined by the prominent peak, are illustrated for $H = 1.5$ T.

3.2.4 Specific Heat

Specific heat $C(T)$ measurements on PrOs$_4$As$_{12}$ in zero field (Fig. 3.15) display two clear features: a slight shoulder at $T_2 \approx 2.3$ K, on the high temperature side of a well defined peak at $T_1 \approx 2.2$ K. Zero-field measurements made at LLNL show similar behavior [Fig. 3.15 inset (b)], except that in the LLNL experiment, the peak at $T_1$ was further resolved into two distinct features separated by $\sim 0.02$ K. This additional feature may indicate an additional transition or it may be due to a variation in composition among the measured crystals. At the lowest temperatures, there is a slight upturn in $C(T)$ associated with a nuclear Schottky anomaly. The low-$T$ specific heat can be described by four contributions, $C(T) = C_n(T) + C_e(T) + C_l(T) + C_m(T)$, which are the nuclear Schottky, electronic, lattice, and magnetic terms, respectively. At higher temperatures, $C_m(T)$ and $C_n(T) \approx$
Figure 3.15 Specific heat $C$ divided by $T$ vs $T$ (UCSD data). Inset (a) shows the transitions at $T_1$ and $T_2$ in more detail (UCSD data). Inset (b) shows the apparent resolution of the transition at $T_1$ into two transitions at $T_1$ and $T_1'$ (LLNL data).

0, and the specific heat is dominated by the electronic and lattice terms. In Fig. 3.16(a), a fit of $C/T = \gamma + \beta T^2$ in the range $10 \text{ K} \leq T \leq 18 \text{ K}$ reveals an enhanced $\gamma \approx 200 \text{ mJ/mol K}^2$ and, from $\beta$, a Debye temperature $\Theta_D \approx 260 \text{ K}$.

To analyze the specific heat in the ordered state, the three terms of the specific heat after subtraction of the lattice contribution (using $\Theta_D \approx 260 \text{ K}$), $\Delta C(T) = C_n(T) + C_e(T) + C_m(T)$, were assumed to have the following forms: $C_n(T) = A/T^2$, $C_e(T) = \gamma T$, and $C_m(T) = BT^n$. Using these equations, fits of $\Delta C T^2 = A + \gamma T^3 + BT^{n+2}$ were performed for $T < 0.6T_1$. The best fit results in a nuclear Schottky coefficient $A = 128 \text{ mJ K/mol}$ and an exponent in the power-law term of $n = 3.2 \pm 0.1$, close to the expected value of $n = 3$ for AFM spin waves. The electronic specific heat coefficient $\gamma$ is strongly enhanced, with a value near $1 \text{ J/mol K}^2$. A temperature dependent $\gamma$ is not uncommon and has been observed in numerous
Figure 3.16 (a) Zero field $C/T$ vs $T^2$, with a linear best fit yielding the enhanced $\gamma$ and value of $\Theta_D$ given in the figure. (b) Magnetic entropy $S_m$ determined from the specific heat after the zero field lattice and electronic contributions to the specific heat were subtracted.

compounds that exhibit heavy fermion behavior [75]. The value of 260 K for $\Theta_D$ is consistent with other filled skutterudite arsenides with typical values ranging from 230 K (LaRu$_4$As$_{12}$) to 340 K (PrRu$_4$As$_{12}$) [31,76]. The magnetic entropy $S_m(T)$ was calculated from the specific heat by integrating $C_m(T)/T$ with temperature [Fig. 3.16(b)], resulting in an entropy release of 90% $R \ln 3$ that levels off by 8 K, a value consistent with a triply degenerate ground state. The reduction of the entropy from a full $R \ln 3$ is presumably due to hybridization of the localized $4f$ and itinerant electron states, as is observed for PrOs$_4$Sb$_{12}$, where entropy is apparently transferred from the localized $4f$ states to the conduction electron states.
3.2.5 Electrical Resistivity

The electrical resistivity $\rho(T)$ was measured in the range $0.06 \text{ K} \leq T \leq 300 \text{ K}$ (Fig. 3.17). Kondo lattice behavior is evident, as $\rho(T)$ decreases with decreasing $T$ down to $T_{\text{min}} \approx 16.5 \text{ K}$ and then increases until $\sim 5.5 \text{ K}$, where the resistivity drops due to the onset of the ordered state. Measurements in high magnetic fields can be analyzed in terms of a single ion Kondo model for an impurity effective spin of 1, yielding an estimate of $T_K$ on the order of 1 K [71]. A small $T_K$ with respect to the ordering temperature ($\sim 2.3 \text{ K}$) prohibits the observation of $T^2$ dependence of $\rho(T)$. Measurements of $\rho(T)$ under $P$ up to $\sim 23 \text{ kbar}$ between 1 K and 300 K revealed no significant $P$ dependence.

![Figure 3.17 Electrical resistivity $\rho$ vs $T$ from 2 K to 300 K. The inset shows $\rho(T)$ from 0.06 K to 25 K.](image)

The electrical resistivity for $1.9 \text{ K} \leq T \leq 300 \text{ K}$ in $H$ up to 8 T is displayed in Fig. 3.18. The sharp transition at the ordering temperature is suppressed with field, going from a steep drop to a broad downturn. The minimum in the zero-
Figure 3.18 Electrical resistivity $\rho$ vs $T$ from 2 K to 300 K at various fields $H$. Inset (a) emphasizes $\rho(T)$ from 2 K to 25 K. Inset (b) displays $\rho(H)$ at various temperatures around $T_2$.

Field $\rho(T)$ data $T_{\text{min}}$ is not observed in fields greater than 4 T. Overall the electrical resistivity in an applied field does not feature much field dependence above 40 K. At temperatures below 40 K a negative magnetoresistance is observed with increasing field (insets (a) and (b) of Fig. 3.18) and at the lowest temperatures below 1.75 K, $\rho$ increases with $H$, reaching a maximum at 1.5 T, then decreases with increasing $H$ (inset (a) of Fig. 3.18 and Fig. 3.19(a) and (b)). Eventually the $\rho(H)$ curves at various constant $T$ merge in the highest fields (Fig. 3.19). At $H = 1$ T, two features in the $d\rho/dT$ vs $T$ curves are associated with the two phase transitions at $T_2$ and $T_1$ (inset to Fig. 3.19(a)). The $\rho(H)$ isotherms are shown in inset (b) to Fig. 3.18 and Fig. 3.19(b), displaying the development of a peak at $T < 2.3$ K, indicative of a field-induced transition at $H_1$. The peak shifts to higher fields with decreasing temperature, up to 1.5 T below 0.5 K. A change in slope, apparently due to a field-induced transition to the paramagnetic state at $H_2$ (Fig. 3.19(b)).
Figure 3.19 (a) Low-temperature electrical resistivity $\rho$ vs $T$ for $0 \leq H \leq 8$ T. The inset indicates $T_2$ and $T_1$ as determined from features in $d\rho/dT$ vs $T$ at 1 T. (b) Isotherms of $\rho$ vs $H$. The inset shows an expanded view of the 0.1 K $\rho(H)$ isotherm with two linear fits indicating a break in slope at 2.56 T.

inset), is observed in $H > H_1$.

At the lowest temperatures, electrical transport in PrOs$_4$As$_{12}$ is not dominated by quasiparticle scattering ($\rho \sim T^2$) or simple AFM magnon scattering ($\rho \sim T^5$), but the $\rho(T)$ data are well described by the formula for an antiferromagnet with an energy gap $\Delta$ in the magnon spectrum as [77]

$$\rho(T) = \rho_0 + b \frac{T}{\Delta} \left(1 + 2 \frac{T}{\Delta}\right) e^{-\Delta/T}. \quad (3.2)$$

The $\rho(T)$ data are fit well by Eq. 3.2 for $H < 2$ T (Fig. 3.20(a)), and a plot of the energy gap $\Delta$ vs $H$ is shown in Fig. 3.21(a). Notably, the value of $\Delta$ drops sharply near 1.5 T in the vicinity of the transition at $H_1$.

To check for possible non-Fermi liquid behavior associated with a field-tuned phase transition ($H \geq 3$ T), the $\rho(T)$ data in $H \leq 8$ T were fit with
a power-law $\rho(T) = \rho_0 + B T^n$ (Fig. 3.20(b)). The residual resistivity $\rho_0$ has a pronounced maximum at $H = 1.5$ T, corresponding to $H_1$ (Fig. 3.21(c)). The power-law exponent $n$ decreases from $\sim 2.9$ to $\sim 2.3$ as $H$ increases from 0 T to 2 T, reaches a minimum between 2 T and 3 T, then gradually increases to $\sim 2.8$ when $H$ reaches 8 T (Fig. 3.21(b)). In no range of $H$ does PrOs$_4$As$_{12}$ display the $T^{3/2}$ non-Fermi-liquid behavior predicted to occur near a three-dimensional AFM quantum critical point [78].
3.2.6 Crystalline Electric Field Effects

As mentioned earlier, features in the $\chi_{dc}(T)$ data for PrOs$_4$As$_{12}$ reflect CEF effects (Section 2.2.2). Just as for Pr$_{0.87}$Fe$_4$Sb$_{12}$, in a CEF with $O_h$ symmetry, the ninefold degenerate Pr$^{3+} J = 4$ multiplet is split into a $\Gamma_1$ singlet, a $\Gamma_3$ doublet, and $\Gamma_4$ and $\Gamma_5$ triplets. The low-$T$ calculated effective moment of 2.77$\mu_B$/f.u. is indicative of a $\Gamma_5$ ground state, which has a theoretical effective moment of 2.83$\mu_B$/f.u. In addition, $M = 1.68\mu_B$/f.u. at 2 K and 5.5 T, a value much less than the full 3.2$\mu_B$/f.u. saturated moment expected for a Pr$^{3+}$ free ion, but more consistent with the 2.0$\mu_B$/f.u. expected for a $\Gamma_5$ ground state. Reasonable CEF fits to the $\chi_{dc}(T) - \chi_0$ data (not shown) can be made using a CEF splitting as low as $\sim 15$ K between a $\Gamma_5$ ground state and a $\Gamma_1$ first excited state. If there were...
a large Schottky contribution due to this CEF splitting in the temperature range of the high temperature fit to $C(T)$, the values of $\gamma$ and $\Theta_D$ determined from the fit would be altered. Based on the CEF fits to the $\chi_{dc}(T) - \chi_0$ data, the worst case scenario (which would lead to the largest possible change in $\gamma$) occurs for a splitting of 23 K. The resulting Schottky contribution to the specific heat would result in a reduced $\gamma$ (50 mJ/mol K$^2$) and a slightly lower $\Theta_D$ (246 K). Since the CEF contribution to $C(T)$ is not significant below 1.6 K for energy level splittings greater than 15 K, the large value of $\gamma$ ($\sim$ 1 J/mol K$^2$) determined from the low temperature fit to $C(T)$ is not affected by potential CEF effects. The various acceptable CEF splitting schemes do not significantly alter the magnetic entropy release of 90% $R \ln 3$ by 8 K, which remains in support of a triplet ground state.

### 3.2.7 Discussion

A schematic representation of the $(H - T)$ phase diagram for PrOs$_4$As$_{12}$ (Fig. 3.23), is shown in Fig. 3.22(a). The vertical line labeled “b” in the schematic phase diagram represents an $M(H)$ measurement at $T = 0.425$ K shown in Fig. 3.22(b). The points $H_1$ and $H_2$ along line b are features in the $M(H)$ data, which are defined using the derivative $dM/dH$ shown in Fig. 3.22(d) as a function of $H$. The horizontal line labeled “c” represents an $M(T)$ measurement at $H = 1.5$ T (Fig. 3.22(c)). The features at $T_1$ and $T_2$ along c are defined from the $M(T)$ data shown in Fig. 3.22(c). Similar features in the other $M(H,T)$ measurements were used to generate the full $H - T$ phase diagram for PrOs$_4$As$_{12}$ shown in Fig. 3.23. The error bars are rough estimates of the transition widths, based upon the widths of features in the derivatives of $M(H)$ (Fig. 3.22(d)) and $M(T)$ (not shown). It may be inferred from the features in the UCSD $C(T)$ data that there are two phase transitions. Thus, PrOs$_4$As$_{12}$ appears to have an AFM ground state, a second ordered state at intermediate $T$ and $H$, and is paramagnetic at high $T$ and $H$.

The AFM nature of the ground state is supported by several observations.
Figure 3.22 (a) Schematic representation of the PrOs$_4$As$_{12}$ magnetic field - temperature ($H - T$) phase diagram. The vertical and horizontal lines represent isothermal $M(H)$ and constant field $M(T)$ measurements as depicted in (b) and (c). (b) Magnetization $M$ vs $H$ at 0.425 K, with features at $H_1$ and $H_2$ used to define the phase diagram. (c) Magnetization $M$ vs $T$ at 1.5 T, along with two clear features at $T_1$ and $T_2$, used to contrast the phase diagram. (d) The derivative $dM/dH$ as a function of $H$ indicates two features used to define $H_1$ and $H_2$ in Fig. 3.22(b). The dotted lines represent estimated transition widths for $H_1$ and $H_2$.

The peak in $\chi_{dc}(T)$ is a traditional indication of the onset of AFM, which is also suggested by the lack of hysteresis in $M(H)$, and is compatible with a CEF-split $\Gamma_5$ magnetic triplet ground state. Furthermore, the suppression of the ground state order with $H$ is consistent with AFM order. The nature of the second ordered phase is difficult to establish from the results of this study, but in light of the low-$T$ behavior of other Pr-based filled skutterudites such as PrFe$_4$P$_{12}$ [17], magnetic or quadrupolar ordering seem likely possibilities. Recent neutron diffraction experiments on PrOs$_4$As$_{12}$ confirm that the low-field ordered phase is antiferromagnetic [71].
3.2.8 Summary

To summarize, magnetization and specific heat measurements on PrOs$_4$As$_{12}$ indicate the existence of at least two distinct phase transitions at temperatures below 2.3 K and in fields below 3 T. The magnetic behavior of the low temperature phase is consistent with AFM order. The electrical resistivity displays a sharp decrease due to the onset of ordering and has features consistent with Kondo lattice behavior. The $\rho(T)$ data in fields displays a negative magnetoresistance below 40 K down to the ordering temperature. At 0.1 K the $\rho(H)$ isotherm features a peak at 1.5 T and a change in slope at higher fields which may be associated with the observed phase transitions. Fits to the low-$T$ $\rho(T)$ data, below 2 T, can be fit by a formula for an antiferromagnet with an energy gap in the magnon spectrum. In the paramagnetic state, specific heat measurements indicate an electronic spe-
cific heat coefficient with $\gamma \approx 50-200 \text{ mJ/mol } K^2$. In the antiferromagnetic state, analysis of $C(T)$ data yields a very large $\gamma \sim 1 \text{ J/mol } K^2$ at low $T$ ($T \leq 1.6 \text{ K}$).
Many of the features observed in various measurements on the filled skutterudite compounds have been interpreted in terms of crystalline electric field (CEF) effects [5, 20, 72–74]. These features range from Schottky anomalies in the specific heat [5] to deviations of the magnetic susceptibility from Curie-Weiss behavior at temperatures comparable to the CEF splittings between the Pr\(^{3+}\) energy levels [69]. In developing an understanding of the various types of phenomena exhibited by the Pr-based filled skutterudite compounds, it is important to determine the Pr\(^{3+}\) energy level scheme and how it depends on structure and composition. For instance, the filled skutterudite compound PrOs\(_4\)Sb\(_{12}\), which represents the first Pr-based heavy fermion superconductor, exhibits several features that reflect CEF effects [5, 72, 73]. A complete picture of the CEF splitting in PrOs\(_4\)Sb\(_{12}\) may shed light on how the heavy fermion behavior and the unconventional superconductivity occurs in this system. This idea can be extended to include a comparison of the properties of the various Pr-based filled skutterudites and their associated CEF effects, which may lead to a more general understanding of how strongly correlated electron behavior develops in these compounds. With this in mind, the filled skutterudite compound PrOs\(_4\)P\(_{12}\) was considered for study. Previous measurements of polycrystalline PrOs\(_4\)P\(_{12}\) showed no indication of a phase transition down to 1.7 K [68, 79]. In this section of Chapter 3 new measurements are presented of PrOs\(_4\)P\(_{12}\) in single crystal form that were performed to determine the CEF energy level scheme and to check for magnetic or quadrupolar ordering below 1.7 K.

### 3.3.1 Experimental Details

Single crystals of PrOs\(_4\)P\(_{12}\) were synthesized as described in Section 2.1.1 using a molten Sn flux growth technique from a mixture of elemental Pr (3N), Os
(3N8), P (5N), and Sn (5N) in a ratio of 1: 4: 20 : 50. The resulting crystals typically had overall dimensions of less than 1 mm. X-ray powder diffraction using a Rigaku D/MAX B X-ray machine was performed on a powder composed of ground single crystals. Further X-ray structural refinement was performed on two single crystals with similar dimensions in a manner described in Section 2.2.1.

Magnetization measurements were performed using a Quantum Design Magnetic Properties Measurement System (MPMS) in magnetic fields $H$ up to 5.5 T for $1.7 \text{ K} \leq T \leq 300 \text{ K}$. Electrical resistivity $\rho(H,T)$ measurements were made using a four probe ac technique for $2 \text{ K} \leq T \leq 300 \text{ K}$ in fields up to 8 T in a Quantum Design Physical Properties Measurement System (PPMS) with a constant current of 1 mA and for $0.1 \text{ K} \leq T \leq 2.6 \text{ K}$ in fields up to 8 T using a $^3\text{He} - ^4\text{He}$ dilution refrigerator with a constant current of 300 $\mu$A. Specific heat $C(T)$ measurements on PrOs$_4$P$_{12}$ were performed for $0.5 \text{ K} \leq T \leq 90 \text{ K}$ on a collection of single crystals with a total mass of 80 mg.
3.3.2 Single-Crystal Structural Refinement

The X-ray powder diffraction pattern indicates that PrOs$_4$P$_{12}$ is single phase with no major impurity peaks and a cubic unit cell parameter $a = 8.0751(5)$ Å, in good agreement with a previous measurement where $a = 8.0710(10)$ Å [37]. The single crystal structural refinement confirmed that PrOs$_4$P$_{12}$ possesses a LaFe$_4$P$_{12}$-type structure (Im3 space group) with two formula units per unit cell, and $a = 8.080(1)$ Å. The crystal structure parameters, from the structural refinement of PrOs$_4$P$_{12}$, are collected in Table 3.3.

Table 3.3 Single crystal structural data for PrOs$_4$P$_{12}$ (LaFe$_4$P$_{12}$-type, space group Im3; No. 204) taken at $T = 296$ K, with scattering angles of $2\theta < 2\theta < 80\degree$.

<table>
<thead>
<tr>
<th>PrOs$<em>4$P$</em>{12}$</th>
<th>Crystal size</th>
<th>Lattice parameter [Å]</th>
<th>Density [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$60 \times 74 \times 83\mu$m$^3$</td>
<td>$a = 8.080(1)$</td>
<td>$\rho = 8.017$</td>
</tr>
<tr>
<td>Reflection in refinements</td>
<td>Number of variables = 12</td>
<td>Goodness of fit = 1.068</td>
<td>$R^2_F = \sum</td>
</tr>
<tr>
<td>$286 \leq 4\sigma(F_o)$ of 322</td>
<td></td>
<td></td>
<td>$= 0.0156$</td>
</tr>
<tr>
<td>Pr in 2a (0, 0, 0);</td>
<td>Thermal displacements [Å$^2$]</td>
<td>Interatomic distances [Å]</td>
<td></td>
</tr>
<tr>
<td>Occupancy = 1.02(2)</td>
<td>Pr: $U_{11} = U_{22} = U_{33} = 0.0079(1)$</td>
<td>Pr - 12 P 3.1091</td>
<td></td>
</tr>
<tr>
<td>Os in 8c (1/4, 1/4, 1/4);</td>
<td>Thermal displacements [Å$^2$]</td>
<td>Interatomic distances [Å]</td>
<td></td>
</tr>
<tr>
<td>Occupancy = 1.00(1)</td>
<td>Os: $U_{11} = U_{22} = U_{33} = 0.0004(1)$</td>
<td>Os - 6 P 2.3617</td>
<td></td>
</tr>
<tr>
<td>P in 24g (0, y, z);</td>
<td>Thermal displacements [Å$^2$]</td>
<td>Interatomic distances [Å]</td>
<td></td>
</tr>
<tr>
<td>y: 0.14304(6)</td>
<td>P: $U_{11} = 0.0017(2)$</td>
<td>P - 1 P 2.3073</td>
<td></td>
</tr>
<tr>
<td>z: 0.35722(6)</td>
<td>$U_{22} = 0.0023(2)$</td>
<td>- 1 P 2.3115</td>
<td></td>
</tr>
<tr>
<td>Occupancy = 1.00(1)</td>
<td>$U_{33} = 0.0028(2)$</td>
<td>- 2 Os 2.3617</td>
<td></td>
</tr>
</tbody>
</table>

3.3.3 Magnetic Susceptibility

The dc magnetic susceptibility $\chi_{dc}$ and inverse dc magnetic susceptibility $\chi_{dc}^{-1}$ vs $T$ are displayed from 2 K to 300 K in Fig. 3.24. A Curie-Weiss fit to the $\chi_{dc}^{-1}(T)$ data from 100 K to 250 K reveals an effective moment $\mu_{eff} = 3.57\mu_B$/f.u. and a Curie-Weiss temperature $\Theta_{CW} = -18$ K. The value of $\mu_{eff}$ obtained from
the Curie-Weiss fit is close to the Pr\(^{3+}\) free ion value of \(\mu_{\text{eff}} = 3.58\mu_\text{B}/\text{f.u.}\) as well as the measured value of 3.63\(\mu_\text{B}/\text{f.u.}\) for polycrystalline PrOs\(_4\)P\(_{12}\) \[68\]. At low temperatures, \(\chi^{-1}_{\text{dc}}(T)\) deviates from a Curie-Weiss law, while \(\chi_{\text{dc}}(T)\) develops a broad peak centered at 12 K. This peak is much more pronounced than the feature observed in the \(\chi(T)\) data for polycrystalline PrOs\(_4\)P\(_{12}\) and is a strong indication of CEF effects \[68\], which will be discussed in more detail in the following Section 3.3.5.

### 3.3.4 Electrical Resistivity and Specific Heat

Displayed in Fig. 3.25 are electrical resistivity \(\rho(T)\) data of PrOs\(_4\)P\(_{12}\) from 0.1 K to 300 K at \(H = 0\) T and 8 T. In zero field, \(\rho(T)\) displays a linear decrease below 75 K, followed by a rapid downturn that approaches a constant value of 0.65 \(\mu\Omega\cdot\text{cm}\) below 5.5 K. Except for a small positive magnetoresistance
Figure 3.25 Electrical resistivity $\rho$ vs temperature for PrOs$_4$P$_{12}$ at $H = 0$ T and 8 T. The inset displays the low temperature behavior from 0 K to 50 K.

below 30 K, the behavior of $\rho(T)$ does not change in applied fields up to 8 T. Specific heat divided by temperature $C/T$ vs $T$ data for PrOs$_4$P$_{12}$ from 0.6 K to $\sim$ 80 K are shown in Fig. 3.26. The only clear feature is a Schottky-like shoulder centered around 13 K [inset to Fig. 3.26], which gives further evidence for CEF effects in PrOs$_4$P$_{12}$.

3.3.5 Crystalline Electric Field Effects

The $T$-dependencies of $\chi_{dc}$, $\rho$, and $C/T$ of PrOs$_4$P$_{12}$ reveal features that indicate the presence of strong CEF effects. These features, as discussed in Section 2.2, can be fit by expressions that depend on the CEF splitting scheme and provide more information about the ground and excited states and their splittings of the Pr$^{3+}$ ions in PrOs$_4$P$_{12}$. The Pr$^{3+}$ ninefold degenerate $J = 4$ Hund’s rule ground state multiplet splits in a cubic CEF into a $\Gamma_1$ singlet, $\Gamma_3$ doublet, and
Figure 3.26 Specific heat $C$ divided by $T$ vs $T$ for PrOs$_4$P$_{12}$. The inset reveals the low temperature behavior of $C(T)/T$, which features a Schottky anomaly centered around 13 K.

Γ$_4$ and Γ$_5$ triplets. The CEF fits were made using the variables $x_{LLW}$ and $W$ as discussed in Section 2.2, where $x_{LLW}$ is the ratio of the fourth- and sixth-order terms of the angular momentum operators and $W$ is an overall energy scale [45]. The lack of magnetic order in PrOs$_4$P$_{12}$ down to 0.1 K, as well as magnetization $M$ versus $H$ measurements (not shown) that indicate a magnetization of only 0.4μ$_B$/f.u. by 5.5 T, imply a nonmagnetic ground state for PrOs$_4$P$_{12}$. In the case of a nonmagnetic Γ$_3$ doublet ground state, an applied magnetic field should result in a low temperature Schottky anomaly in $C(T)$. Since previous specific heat measurements of polycrystalline PrOs$_4$P$_{12}$ do not show any indication of a Schottky anomaly from 1.8 K to 10 K in fields up to 5 T [79], only CEF fits assuming a nonmagnetic Γ$_1$ singlet ground state will be presented.

Figure 3.27 shows CEF fits to $\chi_{dc}(T)$ and $\chi_{dc}^{-1}(T)$ from 2 K to 300 K. The best fits were found for $x_{LLW} = 0.47$ and $W = 4.86$, which result in an energy level
Figure 3.27 Fits of $\chi_{dc}(T)$ (open circles) and $\chi^{-1}_{dc}(T)$ (open squares) by a CEF model with a Pr$^{3+}$ $\Gamma_1$ ground state for PrOs$_4$P$_{12}$. The Pr$^{3+}$ energy level scheme is depicted in the figure.

splitting of 30 K between a $\Gamma_1$ singlet ground state and a $\Gamma_5$ triplet first excited state. The low temperature behavior of $\chi_{dc}(T)$ is not accurately reproduced by the CEF fit, similar to the case of PrOs$_4$Sb$_{12}$ which was determined to possess a nonmagnetic $\Gamma_1$ singlet ground state [6]. To confirm this CEF scheme, the zero field electrical resistivity data (Fig. 3.28(a)) were fit with the following equation

$$\rho(T) = \rho_{imp}(T) + \rho_{lat}(T) + \rho_{ex}(T),$$

(3.3)

where $\rho_{imp}$ is the residual resistivity due to scattering of electrons by impurities and defects, $\rho_{lat}$ is the lattice contribution associated with scattering of electrons by phonons, and $\rho_{ex}$ is the term due to s-f exchange scattering of electrons from the Pr$^{3+}$ 4f energy levels in a cubic CEF [46]. The electrical resistivity of LaOs$_4$P$_{12}$ scaled by 0.26 was used to represent the temperature dependence of the lattice contribution and $\rho_{imp}$ was found to be 0.57 $\mu\Omega$ cm. The exchange scattering
contribution $\rho_{\text{ex}}$ was best described with a CEF splitting of $\sim 48$ K between a $\Gamma_1$ singlet ground state and $\Gamma_5$ triplet first excited state. The final fit to the $\rho(T)$ data that includes each of the above terms is displayed in Fig. 3.28(a).

Further verification of the magnitude of CEF splitting for PrOs$_4$P$_{12}$ was
found through fits to a Schottky-like anomaly in the $C(T)/T$ data. In Fig. 3.28(b), the Schottky-like anomaly centered around 13 K was fit from 2 K to 15 K by the equation

$$C/T = C_e(T)/T + C_1(T)/T + AC_{\text{Sch}}(T)/T,$$

which includes an electronic, lattice, and 2-level Schottky contribution with the forms:

$$C_e(T) = \gamma T,$$

$$C_1(T) = \beta T^3, \text{ and}$$

$$C_{\text{Sch}}(T) = N_A k_B (\delta/T)^{-2}(g_a/g_b)[1 + (g_a/g_b)\exp(-\delta/T)]^{-2}\exp(-\delta/T),$$

where $g_a$ ($g_b$) is the degeneracy of the ground state (first excited state), $\delta$ is the energy level splitting, and $A$ is a scaling factor. The best fit results in an electronic specific heat coefficient $\gamma \approx 27 \text{ mJ/mol K}^2$, a Debye temperature $\Theta_D \sim 340 \text{ K}$, and a Schottky contribution scaled by $A = 0.7$, with an energy splitting of 44 K between a singlet ground state and a triplet first excited state. The value of the electronic specific heat coefficient is close to that found for LaOs$_4$P$_{12}$ (21.6 mJ/mol K$^2$) and is less than the value of 56.5 mJ/mol K$^2$ found for polycrystalline PrOs$_4$P$_{12}$ [79].

The Debye temperature is slightly different from a previous measurement for polycrystalline PrOs$_4$P$_{12}$ which yielded $\Theta_D = 285 \text{ K}$ [79]. One possible source for the discrepancy between the values of $\gamma$ and $\Theta_D$ for polycrystalline and single crystal PrOs$_4$P$_{12}$ are tin inclusions in the single crystals, which would result in an overestimate of the PrOs$_4$P$_{12}$ mass, although no indication of a tin superconducting transition at 3.72 K was observed. The scaling of the Schottky anomaly required to achieve an accurate fit could be a result of significant hybridization of the localized 4f and itinerant electron states. This transfer of entropy from the localized $f$-electrons to the conduction electrons has been observed previously in the heavy fermion superconductor PrOs$_4$Sb$_{12}$ [5].
3.3.6 Summary

Measurements of PrOs$_4$P$_{12}$ single crystals do not show any indication of a phase transition to temperatures as low as 0.01 K. Features found in the temperature dependence of the magnetic susceptibility, electrical resistivity, and specific heat can be interpreted in terms of crystalline electric field effects. CEF fits to these various features indicate a $\Gamma_1$ ground state separated by $\sim 40$ K from a $\Gamma_5$ first excited state. Linear fits to the high temperature specific heat data yield an electronic specific heat coefficient comparable to that of LaOs$_4$P$_{12}$.

A portion of the text and data of Chapter 3 Section 3.1 is a reprint of the material as it appears in “Ordered magnetic state in PrFe$_4$Sb$_{12}$ single crystals,” N. P. Butch, W. M. Yuhasz, P.-C. Ho, J. R. Jeffries, N. A. Frederick, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, F. M. Woodward, J. W. Lynn, P. Rogl, and G. Giester, Phys. Rev. B 71, 214417 (2005). The dissertation author was second author in this article and contributed to the single crystal growth, magnetization and electrical resistivity measurements, the specific heat discussion, and crystalline electric field analysis. A portion of the text and data of Chapter 3 Section 3.2 is a reprint of the material as it appears in “Multiple ordered phases in the filled skutterudite compound PrOs$_4$As$_{12}$,” W. M. Yuhasz, N. P. Butch, T. A. Sayles, P.-C. Ho, J. R. Jeffries, T. Yanagisawa, N. A. Frederick, M. B. Maple, Z. Henkie, A. Pietraszko, S. K. McCall, M. W. McElfresh, and M. J. Fluss, Physical Review B 73, 144409 (2006). The dissertation author was the primary investigator and author of this article. Chapter 3 Section 3.3 is a reprint of the material as it appears in “Characterization of single crystals of the filled skutterudite PrOs$_4$P$_{12}$,” W. M. Yuhasz, N. A. Frederick, T. A. Sayles, P.-C. Ho, T. Yanagisawa, M. B. Maple, P. Rogl, and G. Giester, submitted to Physica B. The dissertation author was the primary investigator and author of this article.
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Much like the Pr-based filled skutterudites, the Sm-based systems also display a wide variety of interesting correlated electron behavior, though only a few systems have been studied at low temperatures. These include all three Sm-based phosphide filled skutterudites and SmFe$_4$Sb$_{12}$; of these systems, only SmFe$_4$P$_{12}$ and SmRu$_4$P$_{12}$ have been studied in single crystal form [1–10]. These studies have revealed that SmFe$_4$P$_{12}$ is ferromagnetic below 1.6 K, SmRu$_4$P$_{12}$ has a metal-insulator transition at 16 K, SmOs$_4$P$_{12}$ is an antiferromagnet below 4.6 K, and SmFe$_4$Sb$_{12}$ is ferromagnetic below 45 K. Experiments on SmFe$_4$P$_{12}$ have also uncovered heavy fermion and Kondo-lattice behavior, with a Kondo temperature of about 30 K and an electronic specific heat coefficient of $\sim 370$ mJ/mol K$^2$ [1,4].

By 7 T, the magnetization of SmFe$_4$P$_{12}$ at 1.8 K does not saturate and only reaches a value of 0.15 $\mu_B$/f.u. which is much less than the Sm$^{3+}$ free ion value of $M_{\text{sat}} = g_J J \mu_B = 0.71 \mu_B$/f.u. This behavior was attributed to screening of the magnetic moment due to the Kondo effect. Like SmFe$_4$P$_{12}$, the compound SmFe$_4$Sb$_{12}$ has also been found to be ferromagnetic; however, unlike the magnetization of SmFe$_4$P$_{12}$, SmFe$_4$Sb$_{12}$ is characterized by a saturation magnetization at 5 K of $M_{\text{sat}} = 0.7 \mu_B$/f.u. in agreement with the Sm$^{3+}$ free ion value. After taking into account the contribution from the FeSb$_3$ polyanions, the effective magnetic moment of SmFe$_4$Sb$_{12}$ was found using Van Vleck’s formula to be $\mu_{\text{eff}} = 1.66 \pm 0.2 \mu_B$/f.u. consistent with the calculated value of $\mu_{\text{eff}} = 1.66 \mu_B$/f.u. [10].
4.1 

SmOs$_4$Sb$_{12}$  

The variety of interesting phenomena displayed in the Sm-based phosphide filled skutterudites as well as the behavior of PrOs$_4$Sb$_{12}$ discussed in the introduction to Chapter 3 are motivation for the study of SmOs$_4$Sb$_{12}$ in Chapter 4. In this chapter X-ray diffraction, specific heat, magnetization, and electrical resistivity measurements are reported for the filled skutterudite compound SmOs$_4$Sb$_{12}$. These measurements revealed the presence of crystalline electric field effects, heavy fermion behavior, and magnetic order. Analysis of the magnetization using scaling theory and modified Arrott plots shows signs of a ferromagnetic component to the magnetic order.

4.1.1 Experimental Details  

SmOs$_4$Sb$_{12}$ single crystals were grown in a molten Sb flux as described in Section 2.1.1 using high purity Sm(3N), Os (3.5N), and Sb (6N). The resulting crystals were cubic and tended to form large interconnected clusters, with most of them much less than 1 mm in dimension. A small batch of ultra-high purity single crystals were also produced using Sm (AMES 4N), Os (Alfa Aesar 5N), and Sb (CERAC 5N). However, these single crystals were only used as a subsequent check for impurities.

The quality of the single crystals was determined by X-ray powder diffraction measurements, which were performed with a Rigaku D/MAX B X-ray machine on a powder prepared by grinding several single crystals. Single crystal structural analysis was performed on two single crystals with similar dimensions as described in Section 2.2.1.

Specific heat $C(T)$ measurements were made between 0.6 K and 70 K in a semi-adiabatic $^3$He calorimeter using a standard heat pulse technique. Many single crystals were combined for a total mass of 49.34 mg and were attached to the
thermometer (Cernox)/heater sapphire platform with about 7.44 mg of Apiezon N grease. The electrical resistivity $\rho(T)$ of several samples with dimensions of $\sim 1 \times 0.5 \times 0.5$ mm was measured using a four probe technique from 1.1 K to 300 K. Magnetoresistance $\rho(H,T)$ measurements were made using a four probe ac technique in fields up to 9 T in the 2 K to 300 K temperature range in a Quantum Design Physical Properties Measurement System and in magnetic fields up to 18 T down to $\sim 0.05$ K using $^3$He-$^4$He dilution refrigerators at UCSD ($0 - 8$ T) and the National High Magnetic Field Laboratory at Los Alamos National Laboratory ($8 - 18$ T). All of the resistivity measurements were made with a constant current of $100 - 300$ $\mu$A, perpendicular to the applied magnetic field. Magnetization measurements were made with Quantum Design SQUID magnetometers in the temperature range 1.7 K to 300 K in magnetic fields up to 5 T. Measurements of the DC and AC magnetic susceptibility $\chi_{dc}(T)$ and $\chi_{ac}(T)$, respectively, and the isothermal magnetization $M(H)$ were made on a 5.37 mg single crystal with dimensions $\sim 0.6 \times 1.16 \times 1.18$ mm mounted such that the field was applied along the long axis of the crystal.

4.1.2 Single-Crystal Structural Refinement

Analysis of the X-ray powder diffraction pattern indicated single phase SmOs$_4$Sb$_{12}$ with a minor impurity peak of OsSb$_2$ ($\lesssim 5\%$). Table 4.1 lists the results of a structural refinement performed on X-ray diffraction data taken from two SmOs$_4$Sb$_{12}$ single crystals. The structural refinement indicated that SmOs$_4$Sb$_{12}$ has a LaFe$_4$P$_{12}$-type structure [11], with a lattice parameter $a = 9.3085$ Å and a unit cell volume of 806.6 Å$^3$. The Sm site was found to be fully occupied and Sm was found to have large isotropic thermal displacement parameters $U_{ii}$ relative to those of Os and Sb. The values of $U_{ii}$ for Sm are consistent with the “rattling” behavior of the filled skutterudite compounds [12].
Table 4.1 Structural data for SmOs$_4$Sb$_{12}$ single crystals (LaFe$_4$P$_{12}$-type, space group Im3; No. 204) taken at $T = 296$ K, with scattering angles of $2^\circ < 2\theta < 80^\circ$.

<table>
<thead>
<tr>
<th>Crystal size</th>
<th>Lattice parameter [Å]</th>
<th>Density [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$84 \times 84 \times 56\mu$m$^3$</td>
<td>$a = 9.3085(2)$</td>
<td>$\rho = 9.767$</td>
</tr>
</tbody>
</table>

| Reflection in refinements | Number of variables = 11 | $R_F^2 = \frac{\sum |F_0^2 - F_c^2|}{\sum F_0^2}$ |
|---------------------------|--------------------------|---------------------------------------------|
| 447 $\leq 4\sigma(F_0)$ of 482 | Goodness of fit = 1.284 | = 0.0207                                  |

<table>
<thead>
<tr>
<th>Sm in 2a (0, 0, 0);</th>
<th>Thermal displacements [Å$^2$]</th>
<th>Interatomic distances [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occupancy = 1.00(2)</td>
<td>Sm: $U_{11} = U_{22} = U_{33}$</td>
<td>Sm - 12 Sb 3.4824</td>
</tr>
<tr>
<td></td>
<td>= 0.0552(6)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Os in 8c (1/4, 1/4, 1/4);</th>
<th>Thermal displacements [Å$^2$]</th>
<th>Interatomic distances [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occupancy = 1.00(1)</td>
<td>Os: $U_{11} = U_{22} = U_{33}$</td>
<td>Os - 6 Sb 2.6241</td>
</tr>
<tr>
<td></td>
<td>= 0.0019(1)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sb in 24g (0, y, z);</th>
<th>Thermal displacements [Å$^2$]</th>
<th>Interatomic distances [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>y: 0.15589(3)</td>
<td>Sb: $U_{11} = 0.0019(1)$</td>
<td>Sb - 1 Sb 2.9022</td>
</tr>
<tr>
<td>z: 0.34009(3)</td>
<td>$U_{22} = 0.0037(1)$</td>
<td>- 1 Sb 2.9771</td>
</tr>
<tr>
<td>Occupancy = 1.00(1)</td>
<td>$U_{33} = 0.0063(1)$</td>
<td>- 2 Os 2.6241</td>
</tr>
</tbody>
</table>

### 4.1.3 Specific Heat

Displayed in Fig. 4.1(a) is a plot of the specific heat divided by temperature $C/T$ vs $T$ of SmOs$_4$Sb$_{12}$ between 0.6 K and 25 K. Two features are readily apparent in the data represented by the open circles in Fig. 4.1(a). The first feature, a hump which peaks at $\sim 2$ K, can be associated with the onset of ferromagnetic order when corroborated by $\chi_{ac}(T)$ and $M(H)$ measurements, described later in Section 4.1.5. The ferromagnetic ordering temperature (Curie temperature) was approximated by taking the maximum negative slope of $C/T$, which occurs at 2.6 K. This feature is not as well defined as that expected for a typical ferromagnetic transition and may be due to the presence of an impurity phase. However, this hump is similar to a broad feature in the specific heat of PrFe$_4$Sb$_{12}$ that is associated with the occurrence of magnetic order [13].

The second feature observed in the specific heat data is a Schottky-like anomaly centered at $\sim 10$ K. The data between 3.5 K and 20 K were fitted by
an equation containing electronic, lattice, and Schottky terms. These results are also displayed in Fig. 4.1(a). The Debye temperature $\Theta_D \approx 294$ K, inferred from the fit, is typical for a filled skutterudite compound, while the resultant electronic specific heat coefficient $\gamma \approx 880$ mJ/mol K$^2$ is extremely large. It is important to note that this value of $\gamma$ is fairly insensitive to the Debye temperature $\Theta_D$ and the splitting $\Delta E$ of the crystal field levels, changing by less than 5% for various reasonable values of $\Theta_D$ and $\Delta E$. The effective mass $m^*$ can be estimated from $\gamma$ using the relation

$$\gamma = \frac{\pi^2 (Z/\Omega) k_F^2 m^*}{\hbar^2 k_F^2},$$

(4.1)

where $Z$ is the number of charge carriers per unit cell, $\Omega$ is the unit cell volume, and $k_F = (3\pi^2 Z/\Omega)^{1/3}$ is the Fermi wave vector using a spherical Fermi surface.
approximation. We assume that \( Z = 2 \), since there are two formula units per unit cell and in each formula unit, \( \text{Sm}^{3+} \) contributes 3 electrons and each of the \((\text{OsSb}_3)^{-1}\) polyanions contribute one hole. Eq. 4.1 yields \( m^* \approx 170 m_e \), where \( m_e \) is the free electron mass, revealing that \( \text{SmOs}_4\text{Sb}_{12} \) is a heavy fermion compound.

The magnetic contribution to the entropy, \( S_{\text{mag}} \), shown in Fig. 4.1(b) was determined by subtracting the electronic and lattice contributions from \( C/T \), extrapolating to zero temperature, and then integrating over \( T \). At the \( \sim 2.6 \) K magnetic transition, the magnetic entropy was found to be \( \sim 94 \) mJ/mol K (1.6% of \( R \ln 2 \)) and it only reaches a value of \( \sim 4.2 \) J/mol K by 25 K, where the Schottky contribution is in its high temperature tail and significantly reduced.

4.1.4 Electrical Resistivity

![Figure 4.2 Electrical resistivity \( \rho \) vs temperature \( T \) for \( \text{SmOs}_4\text{Sb}_{12} \) samples A and B. The low temperature behavior is shown in the inset.](image)

Electrical resistivity measurements were performed on several single crys-
Figure 4.3 Electrical resistivity $\rho(T)$ at various fields for SmOs$_4$Sb$_{12}$ (Sample A). $\rho(T, H)$ for $2 \text{ K} \leq T \leq 300 \text{ K}$ and $0 \text{ T} \leq H \leq 9 \text{ T}$. Inset (a) $\rho(T, H)$ for $0.02 \text{ K} \leq T \leq 2.5 \text{ K}$ and $0 \text{ T} \leq H \leq 18 \text{ T}$. Inset (b) $d\rho/dT$ vs $T$ at fields up to $9 \text{ T}$ showing a peak at $\sim 7.5 \text{ K}$ for all fields.

tals of SmOs$_4$Sb$_{12}$. Figure 4.2 displays the room temperature normalized electrical resistivity $\rho/\rho(294 \text{ K})$ vs $T$ for two representative samples. Samples A and B both exhibit metallic behavior with residual resistivity ratio (RRR) values of 12.7 and 19.1, respectively, and room temperature resistivity $\rho(294 \text{ K})$ values of 313 $\mu\Omega \text{ cm}$ and 379 $\mu\Omega \text{ cm}$, respectively. At low temperatures, there is a broad hump in $\rho(T)$ between 6 K and 40 K for sample A and a kink in $\rho(T)$ at $\sim 12.5 \text{ K}$ for sample B. These features occur well above $T_{\text{mag}} \approx 2.6 \text{ K}$ determined from $C(T)$, as well as from $\chi_{\text{ac}}(T)$ and $M(H, T)$ data presented later. The sample dependence of the electrical resistivity along with the high room temperature resistivity values indicate the presence of atomic disorder.

The temperature and magnetic field dependencies of the electrical resistivity for SmOs$_4$Sb$_{12}$ are shown in Figs. 4.3 and 4.4. Figure 4.3 displays the
Figure 4.4 Electrical resistivity $\rho(H)$ at various temperatures for SmOs$_4$Sb$_{12}$ (Sample A) along with $\rho(H)$ at 1.5 K for LaOs$_4$Sb$_{12}$. (a) $\rho(H,T)$ for $0 \leq T \leq 9$ T and $0.02 \leq T \leq 40$ K. (b) $\rho(H,T)$ for $0 \leq H \leq 18$ T and $0.02 \leq T \leq 2.75$ K. The $\rho(H)$ data for LaOs$_4$Sb$_{12}$ (solid circles) at 1.5 K (shifted upwards by adding 20 $\mu\Omega$ cm) for comparison with the low-$T$ $\rho(H)$ data of SmOs$_4$Sb$_{12}$.

electrical resistivity of SmOs$_4$Sb$_{12}$ from 2 K to 300 K in fields up to 9 T. Inset a to Fig. 4.3 features the low temperature behavior of the $\rho(T,H)$ data for 0.02 K
\( \leq T \leq 2.5 \text{ K} \) in fields up to 18 T. In general, the resistivity increases with increasing field at all temperatures. The shoulder in \( \rho(T) \), which is observed at \( \sim 30 \text{ K} \), becomes more prominent as the magnetic field increases. The behavior of the low temperature \( \rho(H) \) data above 4 T for SmOs\(_4\)Sb\(_{12}\) is very similar to that of LaOs\(_4\)Sb\(_{12}\); however, below 4 T, the \( \rho(H) \) data exhibit a rapid increase with \( H \), whose origin is not understood.

The heavy fermion behavior inferred from the specific heat measurements is also reflected in the electrical resistivity. The electrical resistivity of a typical \( f \)-electron heavy fermion compound has a relatively weak temperature dependence at high temperatures and then decreases rapidly with decreasing temperature below a characteristic “coherence temperature”, until, at the lowest temperatures, the resistivity varies as \( T^2 \). The \( T^2 \) dependence is indicative of Fermi-liquid behavior and is strong enough to be readily observable in most heavy fermion compounds. In
order to ascertain whether the resistivity of SmOs$_4$Sb$_{12}$ follows this $T^2$ dependence at low temperatures, power law fits of the form $\rho = \rho_0 + BT^n$ (where $\rho_0$ is the residual resistivity and $B = \rho_0/(T_0^n)$ with $T_0$ equal to a characteristic temperature) were made to the $\rho(T)$ data in the temperature range from $\sim 0.05$ K to $\sim 10$ K up to 8 T and from $\sim 0.02$ K to 2.6 K from 10 T to 18 T (Fig. 4.5(c)). The fits show that the exponent $n$ is approximately 2 up to 4 T, consistent with Fermi-liquid behavior, and then decreases with increasing field, possibly indicating a crossover to field-induced non-Fermi-liquid behavior. The value of $T_0$ determined from the power law fits varies between $\sim 7$ K and 8 K, and may be associated with the peak observed in the derivative of the resistivity $d\rho/dT$ vs $T$, shown in Figure 4.3 inset (b), which occurs around 7.5 K at all fields between 0 T and 9 T. This low value of the scaling temperature $T_0$ is consistent with the large value of $\gamma$.

The coefficient $A (= \rho_0/(T_0^2))$ of the $T^2$ term in the electrical resistivity is often found to follow the Kadowaki-Woods (KW) relation $A/\gamma^2 = 1 \times 10^{-5} \mu\Omega$ cm mol$^2$ K$^2$ mJ$^{-2}$ (where $\gamma$ is the electronic specific heat coefficient) [14]. For SmOs$_4$Sb$_{12}$, the power law fits to the electrical resistivity result in an $A/\gamma^2$ ratio of $\sim 0.5 \times 10^{-6} \mu\Omega$ cm mol$^2$ K$^2$ mJ$^{-2}$ at 0 T, which is $\sim 20$ times smaller than the value expected from the KW relation. However, Tsujii et al. recently found a different empirical relation, $A/\gamma^2 \approx 0.4 \times 10^{-6} \mu\Omega$ cm mol$^2$ K$^2$ mJ$^{-2}$, from studies of several Yb-based compounds (such as YbCu$_5$, YbAl$_3$, and YbInCu$_4$), some Ce-based compounds (CeNi$_5$Si$_4$ and CeSn$_3$), and some transition metals (such as Fe, Pd, and Os) [15]. To explain this new relation, Tsujii et al. suggested a relation to the ground state degeneracy of the system, which has been developed further by Kontani in the form of a generalized Kadowaki-Woods relation [15, 16]. The $A/\gamma^2$ value for SmOs$_4$Sb$_{12}$ seems to be in much better agreement with this new relation and, thereby, consistent with the behavior of several other heavy fermion compounds.
4.1.5 Magnetization

Inverse DC magnetic susceptibility $\chi_{dc}^{-1}$ vs $T$ data for SmOs$_4$Sb$_{12}$ are shown in Fig. 4.6. Since Sm$^{3+}$ ions have relatively low-energy angular momentum states above the Hund’s rule $J = 5/2$ ground state, a simple Curie-Weiss law was unable to describe the data. Previous work [17] has shown that $\chi(T)$ for Sm compounds can often be reasonably well described without considering CEF splitting by the equation:

$$\chi(T) = \left( \frac{N_A}{k_B} \right) \left[ \frac{\mu_{\text{eff}}^2}{3(T - \Theta_{\text{CW}})} + \frac{\mu_B^2}{\delta} \right],$$

(4.2)

where $N_A$ is Avogadro’s number, $\mu_{\text{eff}}$ is the effective magnetic moment, $\Theta_{\text{CW}}$ is the Curie-Weiss temperature, $\mu_B$ is the Bohr magneton, and $\delta = 7\Delta/20$, where $\Delta$ is...
the energy (expressed in units of K) between the Hund’s rule $J = 5/2$ ground state and the $J = 7/2$ first excited state. Equation 4.2 consists of a Curie-Weiss term due to the $J = 5/2$ ground state contribution and a temperature independent Van Vleck term due to coupling with the first excited $J = 7/2$ multiplet. The Sm$^{3+}$ free ion moment is $\mu_{\text{eff}} = g_J(J(J+1))^{1/2}\mu_B = 0.845 \mu_B$/f.u., where $g_J = 0.286$ is the Landé g-factor and $J = 5/2$. The best overall fit of Eq. 4.2 to the $\chi_{\text{dc}}^{-1}(T)$ data, shown in Fig. 4.6, results in the parameters $\Theta_{\text{CW}} = -0.99$ K, $\delta = 300$ K, and $\mu_{\text{eff}} = 0.63 \mu_B$/f.u. The value of $\mu_{\text{eff}} = 0.63 \mu_B$/f.u. is somewhat less than the Sm$^{3+}$ free ion value of $\mu_{\text{eff}} = 0.845 \mu_B$/f.u. while $\delta = 300$ K yields $\Delta = 20\delta/7 = 850$ K, which is much less than the $\Delta \sim 1500$ K value estimated for free Sm$^{3+}$ ions [18]. However, low values of $\Delta$ have previously been inferred from the fits to $\chi_{\text{dc}}(T)$ data for other Sm-based compounds such as SmRh$_4$B$_4$ [17].

The magnetic properties of SmOs$_4$Sb$_{12}$ were also characterized by mea-

Figure 4.7 $M(H)$ isotherms between $-5$ T and $5$ T for SmOs$_4$Sb$_{12}$ at 2 K, 3 K, 4 K, and 5 K. The inset displays the low field behavior of the 2 K isotherm.
suring $\chi_{\text{ac}}(T)$ and $M(H,T)$ at low temperatures. The $\chi_{\text{ac}}(T)$ data (Fig. 4.6, inset) exhibit a peak indicative of a magnetic transition at $T_C = 2.66 \, \text{K}$, where $T_C$ is defined as the temperature of the midpoint of the change in $\chi_{\text{ac}}$ on the paramagnetic side. The results of isothermal $M(H)$ measurements, made in the vicinity of the transition, are shown in Fig. 4.7. The magnetic transition can clearly be seen in the $M(H)$ isotherms where the approximately linear behavior at 5 K becomes nonlinear at lower temperatures and hysteretic at 2 K (Fig. 4.7, inset). These results reveal that some type of magnetic order with a weak ferromagnetic component occurs below 2.66 K. At 2 K, the remnant magnetization $M_R$ is $\sim 0.015 \, \mu_B/\text{f.u.}$ and the coercive field $H_C$ is $\sim 2.5 \times 10^{-3} \, \text{T}$. Even though saturation is not achieved at 2 K, which is only $\sim 0.5 \, \text{K}$ away from $T_C$, a magnetization value $M$ of $\sim 0.122 \, \mu_B/\text{f.u.}$ is obtained at 5 T which is only 17% of the theoretical value of $M_{\text{sat}} = g_J J \mu_B = 0.71 \, \mu_B/\text{f.u.}$.

![Figure 4.8 Scaling plot $|M/|t|^{\beta}$ vs $|H/|t|^{\delta}\gamma$ for SmOs$_4$Sb$_{12}$. The line is a guide to the eye.](image-url)
Figure 4.9 (a) A conventional Arrott plot for SmOs$_4$Sb$_{12}$ using the the critical exponents from the molecular field approximation ($\beta = 1/2$ and $\gamma = 1$). (b) Modified Arrott plot for SmOs$_4$Sb$_{12}$.

Arrott plots were constructed in an attempt to determine the Curie temperature $T_C$, the spontaneous magnetization $M_S$, and the initial susceptibility $\chi_0$. An Arrott plot consists of $M^2$ vs $H/M$ isotherms, where $M$ is magnetization and $H$ is the internal field. In general, the $M^2$ vs $H/M$ isotherms form a series of lines.
for a ferromagnetic compound that are parallel near $T_C$, where $T_C$ corresponds to the isotherm that passes through the origin. However, in the case of SmOs$_4$Sb$_{12}$, the $M^2$ vs $H/M$ isotherms are strongly curved, as shown in Fig. 4.9(a). To overcome this difficulty, the $M(H,T)$ data were analyzed using a modified Arrott plot, $M^{1/\beta}$ vs $(H/M)^{1/\gamma}$ (where $\beta$ and $\gamma$ are critical exponents), which is based on the Arrott-Noakes equation of state [19]. To construct the modified Arrott plot, it was necessary to determine the critical exponents $\beta$ and $\gamma$. This was accomplished by estimating the value of the critical exponent $\delta$ using the relation $m \sim h^{1/\delta}(T = T_C)$ from Section 3.1.3 and plotting $\partial \ln H/\partial \ln M$. The slope closest to zero was found to be the one for $T = 2.6$ K and the average value for $\partial \ln H/\partial \ln M$, above $H = 0.05$ T, for this isotherm gives $\delta = 1.82$. These values were then analyzed using scaling theory (Fig. 4.8), from which $|M|/|t|^\beta$ is plotted as a function of $|H|/|t|^{\beta \delta}$ where $t = (T - T_C)/T_C$; on this plot, the isotherms collapse onto two universal curves with the isotherms for $T > T_C$ on one branch and those for $T < T_C$ on the other. Based on this scaling analysis, values of $\beta = 0.73$ and $\delta = 1.82$ were determined, while $\gamma = 0.60$ was obtained from the Widom scaling relation $\delta = 1 + \gamma/\beta$ [20]. These critical exponents are very unusual, much like the exponents found earlier for Pr$_{0.87}$Fe$_4$Sb$_{12}$. Possible explanations for these critical exponents will be discussed later in Section 4.1.7. The resulting value of $T_C$ from the scaling analysis is 2.60 K, which agrees well with $T_C$ determined from $\chi_{ac}(T)$ measurements on the same crystal.

The critical exponents determined from the scaling analysis were then used to construct the modified Arrott plots, shown in Fig. 4.9(b). With the correct critical exponents for SmOs$_4$Sb$_{12}$, the isotherms in the modified Arrott plot were linear and parallel close to $T_C$, in the high field region from 0.15 T to 3 T. Linear fits to the $M^{1/\beta}$ vs $(H/M)^{1/\gamma}$ data were made in this field range as shown in Fig. 4.9(b); the intercepts of the fits were then used to determine the Curie temperature $T_C$, the initial susceptibility $\chi_0$, and the spontaneous magnetization $M_S$ for each isotherm. The value of $T_C$ from the modified Arrott plots agrees well with the scaling analysis
result of $T_C = 2.60$ K to within $\sim 0.1$ K. A Curie-Weiss fit of $\chi_0^{-1}(T)$ (Fig. 4.11(a)) resulted in $\Theta_{CW} = 2.5$ K and $\mu_{\text{eff}} = 0.4 \mu_B/\text{f.u.}$ These values are not in agreement with the earlier fit to the $\chi_0^{-1}(T)$ data using Eq. 4.2 since the $\chi_0^{-1}(T)$ data were fit from 2 K to 300 K while the $\chi_0^{-1}(T)$ data were fit only near $T_C$.

### 4.1.6 Crystalline Electric Field Effects

In the presence of a cubic crystalline electric field (CEF), the six-fold degenerate Sm$^{3+} J = 5/2$ multiplet splits into a $\Gamma_7$ doublet and a $\Gamma_8$ quartet. The best fit to the $C/T$ data for SmOs$_4$Sb$_{12}$, obtained by scaling the CEF Schottky contribution by 0.58, resulted in a $\Gamma_7$ ground state and a $\Gamma_8$ excited state separated by $\Delta E \approx 38$ K. The scaling that was necessary could imply that most of the entropy of the 4$f$ electrons in SmOs$_4$Sb$_{12}$ is associated with the Schottky-like anomaly while the rest resides within the heavy quasiparticles and magnetic ordering.

The zero-field electrical resistivity $\rho(T)$ of SmOs$_4$Sb$_{12}$ is shown in Fig. 4.10(a) (sample A). The resistivity $\rho(T)$ has an approximately linear-$T$ dependence between 50 K and 300 K and drops rapidly below $\sim 50$ K. To determine if the feature below 50 K was due to CEF splitting of the Sm$^{3+} J = 5/2$ multiplet, it was necessary to subtract a lattice contribution $\rho_{\text{lat}}$ and an impurity contribution $\rho_{\text{imp}}$ ($\sim 21 \mu\Omega \text{ cm}$) from the resistivity data, yielding an incremental resistivity $\Delta \rho$ (where $\Delta \rho = \rho - \rho_{\text{lat}} - \rho_{\text{imp}}$). Usually, $\rho_{\text{lat}}$ is estimated from an isostructural nonmagnetic reference compound; in the case of SmOs$_4$Sb$_{12}$, LaOs$_4$Sb$_{12}$ was used. However, above 100 K, $\rho(T)$ of LaOs$_4$Sb$_{12}$ exhibits a significant amount of negative curvature as discussed previously in Section 3.1.6 for LaFe$_4$Sb$_{12}$. The curvature is generally less pronounced in Y- and Lu-based compounds, which have empty and filled 4$f$-electron shells, respectively. However, since the compounds YOs$_4$Sb$_{12}$ and LuOs$_4$Sb$_{12}$ have not yet, to our knowledge, been prepared, an estimate of $\rho_{\text{lat}}$ for SmOs$_4$Sb$_{12}$ was made from 2 K to 300 K. This estimate was derived by shifting the linearly $T$-dependent resistivity of SmOs$_4$Sb$_{12}$ above 100 K, where the $T$-dependence was assumed to be completely due to electron-phonon scattering,
Figure 4.10 (a) Zero-field electrical resistivity $\rho$ and the estimated $\rho_{\text{lat}} + \rho_{\text{imp}}$ vs $T$ for SmOs$_4$Sb$_{12}$ (Sample A), where $\rho_{\text{imp}} \sim 21 \ \mu\Omega \text{cm}$. (b) $\Delta \rho$ ($= \rho - \rho_{\text{lat}} - \rho_{\text{imp}}$) vs $T$ compared with a fit of the resistivity due to $s$-$f$ exchange scattering of electrons from the $\Gamma_7$ doublet ground state and the $\Gamma_8$ quartet excited state separated by $\sim 33$ K due to the CEF (solid line). The fit gives a good description of the $\Delta \rho(T)$ data from 7 K to 300 K. The inset shows the quality of the fit at low temperatures.
such that it matched smoothly with the resistivity of LaOs$_4$Sb$_{12}$ below 100 K. These data were then combined to represent $\rho_{\text{lat}}$ from 2 K to 300 K in Fig. 4.10(a). After subtracting this estimated lattice contribution, $\Delta \rho$ was plotted as shown in Fig. 4.10(b) and compared with the calculated resistivity due solely to $s$-$f$ exchange scattering ($\rho_{\text{ex}}$) from the Sm$^{3+}$ 4$f$ energy levels in the CEF. The exchange scattering contribution $\rho_{\text{ex}}$ for SmOs$_4$Sb$_{12}$ was calculated for CEF splitting of the Hund’s rule $J = 5/2$ multiplet for Sm$^{3+}$, similar to a procedure described in Section 2.2.4. Since Sm$^{3+}$ has a magnetic ground state and, in order to simplify the analysis, a contribution to the CEF resistivity due to aspherical Coulomb scattering was not considered. The fit of the calculated $\rho_{\text{ex}}(T)$ to the $\Delta \rho(T)$ data was quite good, except below $\sim 7$ K, where the discrepancy may be due to the ferromagnetic phase transition that occurs at $\sim 2.6$ K or the development of the coherent heavy Fermi liquid ground state. Based on this fit, a splitting of $\sim 33$ K between the $\Gamma_7$ doublet ground state and $\Gamma_8$ quartet excited state was inferred. In general, the splitting that results from the CEF fit of $\rho_{\text{ex}}(T)$ to the $\Delta \rho(T)$ data is in reasonable agreement with the value (38 K) determined from specific heat measurements. However, the possibility that the drop in the resistivity below $\sim 50$ K is due to the development of the coherent heavy Fermi liquid, rather than CEF splitting of the Sm$^{3+}$ $J = 5/2$ multiplet, cannot be ruled out.

The fit of Eq. 4.2 to the $\chi_{\text{dc}}^{-1}(T)$ data yielded a good overall description of the $\chi_{\text{dc}}(T)$ data without incorporating CEF effects. Fits that considered CEF effects in addition to the splitting between the $J = 5/2$ and $J = 7/2$ multiplets (not shown) did not vary significantly from the results of Eq. 4.2. Following the modified Arrott plot analysis, it was also found that the value of $\mu_{\text{eff}}$ determined from the fit to the $\chi_0^{-1}(T)$ data is in good agreement with $\mu_{\text{eff}} = 0.41 \mu_B$/f.u. arising from a $\Gamma_7$ ground state and is less than $\mu_{\text{eff}} = 0.67 \mu_B$/f.u. associated with a $\Gamma_8$ ground state. However, a linear fit to $M_{\text{sat}}^{1/3}(T)$ (Fig. 4.11(b)) resulted in a value of 0.087 $\mu_B$/f.u. for $M_{\text{sat}}$ at $T = 0$ K, which is $\sim 37\%$ of $M_{\text{sat}} = g_J \langle J_z \rangle$ for a $\Gamma_7$ ground state at $T = 0$ K. In addition, the failure of CEF-based fits to ade-
Figure 4.11 (a) Spontaneous magnetization $M_s^{1/\beta}$ vs $T$ along with a linear fit (solid line) and extrapolation to 0 K (dashed line). (b) Inverse initial susceptibility $\chi_0(T)^{-1}$ vs $T$ along with a Curie-Weiss fit (line).

Inadequately describe the $\chi^{-1}(T)$ data may suggest that the CEF-based fit to $C/T$ is inappropriate. The Schottky-like anomaly at 10 K, taken to be a strong indicator of crystal field splitting, may conceivably be due to a complex temperature dependence of $\gamma$, which can occur when the value of $\gamma$ is greatly enhanced [21], as is observed in SmOs$_4$Sb$_{12}$.

### 4.1.7 Weak Ferromagnetism

The low value of the magnetic entropy at the transition, the lack of features in the electrical resistivity at the transition, the low non-saturating magnetization, and the unusual critical exponents seem to suggest that the ferromagnetism is either unconventional, or due to an unknown impurity phase. Although
an impurity phase may be responsible for the ferromagnetism, it should be noted that many compounds exhibit similar behavior, including the itinerant ferromagnets ZrZn$_2$, Ni$_3$Al, and Sc$_3$In [22–25], many other heavy fermion systems such as CeNi$_{0.875}$Ga$_{3.125}$, YbRhSb, and Ce$_5$Sn$_3$ [26–28], and the heavy fermion filled skutterudite SmFe$_4$P$_{12}$ [1]. For instance, the low value of the magnetic entropy at the transition ($\sim 0.016 R \ln 2$) and the small size of the feature due to magnetic ordering in $C/T$ of SmOs$_4$Sb$_{12}$ are consistent with the behavior observed in weak itinerant ferromagnets such as Sc$_3$In [29, 30]. Similar behavior is also observed in several heavy fermion systems such as CeNi$_{0.875}$Ga$_{3.125}$, YbRhSb, Ce$_5$Sn$_3$, and SmFe$_4$P$_{12}$ [1, 26–28]. These heavy fermion systems all show anomalies in $C/T$, although the magnetic entropy at the phase transitions of each of these systems ranges from (0.1 to 0.35)$R \ln 2$. The lack of features in the electrical resistivity at the transition is also consistent with the weak itinerant ferromagnets ZrZn$_2$, Ni$_3$Al, and Sc$_3$In [31–33], as well as SmFe$_4$P$_{12}$ [1]. None of these compounds show a clear indication of a phase transition in $\rho(T)$. In the case of the magnetization of SmOs$_4$Sb$_{12}$, the low non-saturating moment is similar to behavior that has been observed in the magnetization of SmFe$_4$P$_{12}$, which at 1.8 K reaches a value around 0.14 $\mu_B$/f.u. by 5 T [1]. This non-saturating moment is also observed in weak itinerant ferromagnets, such as ZrZn$_2$, Ni$_3$Al, and Sc$_3$In [22–25]. The behavior of the systems described above is not clearly understood and has been attributed to either Kondo screening or itinerant electron magnetism.

Assuming the presence of a ferromagnetic impurity phase, the percentage of this phase present in a sample of SmOs$_4$Sb$_{12}$ can be estimated from the observed magnetization. Since Sm is the only magnetic constituent in SmOs$_4$Sb$_{12}$, it is reasonable to assume a moment of $\sim 1$ $\mu_B$/f.u. for the impurity phase. In order to produce the magnetization observed at 2 K and 5 T, the impurity phase would need to constitute $\sim 1\%$ of the total mass of the crystal, assuming that the molecular weight of the impurity phase is comparable to that of Sm. Based on this, it is clear that it would be very difficult to resolve the potential impurity phase in X-ray
powder diffraction data. To check whether the unconventional magnetic behavior was due to impurities in the raw materials, single crystals were grown from ultrahigh quality materials (Sm 99.99%, Os 99.999%, Sb 99.999%). Magnetization measurements made on these crystals did not differ significantly from those made on previous crystals grown from lower quality starting materials. This finding seems to indicate that if there is an impurity phase, then a Sm compound is the most likely candidate.

The applicability of the modified Arrott analysis to SmOs$_4$Sb$_{12}$ indicates that the magnetic ordering is not described by mean field critical exponents ($\beta = 0.5, \delta = 3$, and $\gamma = 1$). Deviation from mean-field behavior is not uncommon. For instance, the magnetic interactions in a given compound may be best described by other models, such as the 3D Heisenberg model for which $\beta = 0.3639, \delta = 4.743$, and $\gamma = 1.3873$ [34]. The critical exponents determined for SmOs$_4$Sb$_{12}$ clearly do not agree with those of the 3D Heisenberg model, or any of the other standard models [20]. Other possible explanations for the unconventional critical exponents include CEF splitting [35], disorder of a single magnetic phase [36,37], or the existence of multiple magnetic phases. In the case of SmOs$_4$Sb$_{12}$, it seems that the presence of an impurity phase could lead to the unusual critical exponents that have been observed. For example, the usual mean field critical exponents of some ferromagnetic impurity could be obscured by the presence of a large paramagnetic contribution. However, it is also possible that the odd magnetic behavior is intrinsic to SmOs$_4$Sb$_{12}$ and the unexplained critical exponents may reflect some type of novel magnetic ordering, as was found for Pr$_{0.87}$Fe$_4$Sb$_{12}$ discussed in the previous chapter. The weak magnetic ordering and unusual critical exponents are common features of Pr$_{0.87}$Fe$_4$Sb$_{12}$ and SmOs$_4$Sb$_{12}$. Analysis of Pr$_{0.87}$Fe$_4$Sb$_{12}$ (Section 3.1.7) indicated that the unusual critical exponents could possibly be attributed to either a complex ferrimagnetic order or the combination of local and itinerant moments in that system. A similar scenario may explain the behavior of SmOs$_4$Sb$_{12}$ and further experiments such as neutron scattering measurements could offer insight.
into this possibility.

### 4.1.8 Summary

Measurements of $C(T)$, $\rho(T,H)$, $M(H,T)$, and $\chi_{ac}(T)$ have been performed on the filled skutterudite compound SmOs$_4$Sb$_{12}$. The $C(T)$ measurements reveal a strongly enhanced electronic specific heat coefficient $\gamma \approx 880 \text{ mJ/mol K}^2$, indicative of a large quasiparticle effective mass $m^* \approx 170 m_e$. A fit of a possible Schottky anomaly to the $C(T)$ data indicates CEF splitting of the Sm$^{3+} J = 5/2$ six-fold degenerate Hund’s rule multiplet into a $\Gamma_7$ doublet ground state and a $\Gamma_8$ quartet excited state separated by 38 K. The electrical resistivity has a strong temperature dependence below $\sim 50$ K. CEF fits to this region agree well with the specific heat measurements and yield an energy splitting of $\sim 33$ K between the $\Gamma_7$ doublet ground state and the $\Gamma_8$ quartet excited state. The resistivity of SmOs$_4$Sb$_{12}$ increases with field at all temperatures. Below $\sim 10$ K and up to 4 T, the resistivity exhibits Fermi-liquid behavior. Fits to the $\chi_{dc}^{-1}(T)$ data using a temperature independent Van Vleck term yield a value of $\mu_{\text{eff}} = 0.634 \mu_B/\text{f.u.}$ with an energy gap $\Delta = 854$ K between the $J = 5/2$ and the $J = 7/2$ multiplets. The hysteresis observed in $M(H)$ at 2 K, the low value of the ordered moment, and conformity of the $M(H,T)$ data to a modified Arrott plot are consistent with weak ferromagnetic order possibly due to an impurity phase. Analysis using scaling theory and modified Arrott plots yield the values $T_C \approx 2.60$ K and a spontaneous magnetization at 0 K of 0.087 $\mu_B$/f.u.

Chapter 4 is a reprint of the material as it appears in “Heavy-fermion behavior, crystalline electric field effects, and weak ferromagnetism in SmOs$_4$Sb$_{12}$,” W. M. Yuhasz, N. A. Frederick, P.-C. Ho, N. P. Butch, B. J. Taylor, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester, Physical Review B 71, 104402 (2005). The dissertation author was the primary investigator and author of this article.
Bibliography


Neodymium based filled skutterudites

Unlike the Pr and Sm-based filled skutterudite compounds the Nd systems display similar behavior at low temperatures, presumably due to the well localized nature of the Nd 4f electrons. Each of the Nd-based filled skutterudites that have been studied show magnetic ordering. The Nd-based compounds that have been studied in any detail include (excluding XRD) NdFe$_4$P$_{12}$, NdRu$_4$P$_{12}$, NdFe$_4$Sb$_{12}$, NdRu$_4$Sb$_{12}$, and NdOs$_4$Sb$_{12}$ with ordering temperatures of 2 K, 1.6 K, 16.5 K, 1.3 K, and 0.8 K respectively [1–7]. Of these systems only NdFe$_4$P$_{12}$ has been studied in great detail in single crystal form [1, 2]. Neutron diffraction studies of NdFe$_4$P$_{12}$ and NdFe$_4$Sb$_{12}$ (included in Chapter 3) have found ferromagnetic ordering in both cases with a Nd moment of 1.6$\mu_B$ for NdFe$_4$P$_{12}$ and a Nd moment of 2.04$\mu_B$ with a collinear Fe moment of 0.27$\mu_B$ for NdFe$_4$Sb$_{12}$ [6,8]. Curie-Weiss fits to the high temperature inverse magnetic susceptibility of NdFe$_4$P$_{12}$ and NdRu$_4$Sb$_{12}$ reveal effective moments consistent with the Nd$^{3+}$ free-ion value of 3.62$\mu_B$ [2,4], while the fit for NdFe$_4$Sb$_{12}$ indicates an extra contribution due to the Fe$_4$Sb$_{12}$ sublattice [3,6]. At low temperatures a decrease in the effective moment is associated with CEF splitting in NdFe$_4$P$_{12}$ and NdRu$_4$Sb$_{12}$ [2,4]. Further support for CEF effects comes from magnetic entropy as a function of temperature data, which is derived from specific heat measurements, that approaches values close to Rln4 for NdFe$_4$P$_{12}$, NdRu$_4$P$_{12}$, and NdRu$_4$Sb$_{12}$, which may indicate a quartet CEF split ground state for these systems [2, 4, 9, 10]. Metallic behavior is observed in
electrical resistivity $\rho$ measurements of NdFe$_4$P$_{12}$ and NdRu$_4$Sb$_{12}$. At low temperatures a minimum is found in the $\rho(T)$ data close to $\sim 30$ K for NdFe$_4$P$_{12}$ and at $\sim 6$ K for NdRu$_4$Sb$_{12}$. These minima in the $\rho(T)$ data of the two compounds are followed by a maximum at $\sim 2$ K for both systems, close to their respective ordering temperatures. Below their ordering temperatures the $\rho(T)$ data drops sharply and in the case of NdFe$_4$P$_{12}$ the $\rho(T)$ does not go as $T^2$ expected for magnon scattering, but instead goes as $T^4$ [11,12]. Much like the resistivity the specific heat of NdFe$_4$P$_{12}$ below the ordering temperature goes as $T^3$ rather the typical $T^{3/2}$ behavior observed below typical ferromagnetic transitions. The unusual behavior of the electrical resistivity and the specific heat in the ordered state warrants further study of these systems.

5.1

NdOs$_4$Sb$_{12}$

As stated in the above brief review there are many Nd-based filled skutterudites that have yet to be characterized. In order to increase our knowledge and understanding of these systems Chapter 5 reports on the characterization of NdOs$_4$Sb$_{12}$ single crystals. Just as in the previous chapters X-ray diffraction, magnetization, electrical resistivity, and specific heat measurements will be reported on. Analysis with Arrott plots and crystalline electric field fits were employed, along with detailed analysis of the electrical resistivity and specific heat measurements in order to fully characterize NdOs$_4$Sb$_{12}$.

5.1.1 Experimental Details

NdOs$_4$Sb$_{12}$ single crystals were grown with the molten metal (Sb) flux growth technique described in Section 2.1.1 using high purity Nd, Os (3.5N), and Sb (6N). Single phase NdOs$_4$Sb$_{12}$ with minor Sb impurities ($\lesssim 10\%$) was confirmed by grinding multiple single crystals and performing X-ray powder diffraction mea-
measurements using a Rigaku D/MAX B X-ray machine. The LaFe₄P₁₂-type BCC structure was confirmed [13], and a lattice parameter \( a = 9.30 \text{ Å} \) was found. Single crystal X-ray refinement was performed on two single crystals with the same procedure and experimental setup described in Section 3.1.1.

Measurements of the electrical resistivity \( \rho \) as a function of temperature \( T \) at various fields \( H \) were performed using the standard 4-wire technique in a Quantum Design PPMS system and in a \(^3\text{He}-^4\text{He} \) dilution refrigerator in fields up to 8 T. Low-temperature (0.02 K - 2.6 K) and high-field (8 T - 18 T) \( \rho(T,H) \) measurements were performed in the National High Magnetic Field Laboratory at Los Alamos National Laboratory. The field was applied perpendicular to the electrical current applied to the sample, which was along the [001] direction, in all \( \rho(T,H) \) measurements. Electrical resistivity measurements as a function of temperature at various pressures \( \rho(T,P) \) were made under hydrostatic pressures up to 28 kbar using a beryllium-copper piston-cylinder clamp in a \(^4\text{He} \) cryostat [14]. The pressure-dependent superconducting transition of a Pb manometer was measured inductively to determine the pressure.

Measurements of the DC magnetic susceptibility were performed in a Quantum Design MPMS SQUID magnetometer from 2 K to 300 K in fields up to 5.5 T. Further detailed magnetization \( M(H,T) \) measurements were carried out in a \(^3\text{He} \) Faraday magnetometer with a gradient field of \( \sim 0.05 - 0.1 \text{T/cm} \) in external magnetic fields up to 5.5 T and at temperatures between 0.4 K and 2 K. Measurements in the Faraday magnetometer required several single crystals (total mass of 21.3 mg), which were combined in a mosaic fashion such that \( H \) was applied along the [001] axis. Multiple single crystals (total mass of 42.15 mg) were also used in zero-field specific heat \( C(T) \) measurements between 0.5 K and 70 K in a \(^3\text{He} \) calorimeter using a semi-adiabatic heat-pulse technique.
5.1.2 Single-Crystal Structural Refinement

The results of a structural refinement performed on data collected from two NdOs₄Sb₁₂ single crystals are listed in Table 5.1. The refinement confirms that the lattice parameter for NdOs₄Sb₁₂ is \( a = 9.3075(2) \) Å and was able to show that

Table 5.1 Single crystal structural data for NdOs₄Sb₁₂ (LaFe₄P₁₂-type, space group Im\( \bar{3} \); No. 204) taken at \( T = 296 \) K, with scattering angles of \( 2\theta < 2\theta < 80^\circ \).

<table>
<thead>
<tr>
<th>NdOs₄Sb₁₂</th>
<th>Crystal size</th>
<th>Lattice parameter [Å]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64 × 78 × 84µm³</td>
<td>( a = 9.3075(2) )</td>
<td>( \rho = 9.745 )</td>
</tr>
</tbody>
</table>

Reflection in refinements 473 ≤ 4\( r(F₀) \) of 482

Nd in 2a (0, 0, 0); Occupancy = 1.00(1)

Os in 8c (1/4, 1/4, 1/4); Occupancy = 1.00(1)

Sb in 24g (0, y, z); Occupancy = 1.00(1)

<table>
<thead>
<tr>
<th>Nd</th>
<th>Thermal displacements [Å²]</th>
<th>Interatomic distances [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd: ( U_{11} = U_{22} = U_{33} = 0.0482(5) )</td>
<td>Nd - 12 Sb 3.4831</td>
</tr>
<tr>
<td></td>
<td>Os: ( U_{11} = U_{22} = U_{33} = 0.0025(1) )</td>
<td>Os - 6 Sb 2.6239</td>
</tr>
<tr>
<td></td>
<td>Sb: ( U_{11} = 0.0026(1) ) ( U_{22} = 0.0044(1) ) ( U_{33} = 0.0065(1) )</td>
<td>Sb - 1 Sb 2.9033 - 1 Sb 2.9752 - 2 Os 2.6239 - 1 Nd 3.4831</td>
</tr>
</tbody>
</table>

the Nd sites are fully occupied, unlike PrFe₄Sb₁₂ in Section 3.1. A feature found for the Nd atoms, which is common to the filled skutterudites, is that the thermal displacement parameters \( U_{ii} \) for the Nd atoms have large isotropic values while the \( U_{ii} \) for Os and Sb in the NdOs₄Sb₁₂ structure are much smaller. Assuming that some fraction of Nd atoms behave like Einstein oscillators, while the rest of the atoms act as a simple Debye solid, the thermal displacement and the Einstein temperature \( \Theta_E \) are related by

\[
U = \frac{\hbar^2}{2m_{Nd}k_B\Theta_E}c\coth\left(\frac{\Theta_E}{2T}\right),
\]

(5.1)

where \( m_{Nd} \) is the atomic mass of Nd. Using the room temperature Nd displacement parameter for NdOs₄Sb₁₂, \( \Theta_E \) is estimated as \( \sim 45 \) K, which is close to
the values found for thallium-filled antimony skutterudites such as Tl$_{0.22}$Co$_4$Sb$_{12}$, Tl$_{0.5}$Co$_{3.5}$Fe$_{0.5}$Sb$_{12}$, Tl$_{0.8}$Co$_3$FeSb$_{12}$, and Tl$_{0.8}$Co$_4$Sb$_{11}$Sn. [15,16]

5.1.3 Magnetization

Figure 5.1(a) displays the DC magnetic susceptibility $\chi_{dc}(T)$ data at 500 Oe for NdOs$_4$Sb$_{12}$. The inverse dc magnetic susceptibility $\chi_{dc}^{-1}(T)$ data (Fig. 5.1(b)) exhibits a change in slope that may be associated with CEF effects, as discussed in Section 2.2.2. A Curie-Weiss fit to the high-$T$ $\chi_{dc}^{-1}(T)$ data between 65 K and 300 K results in a negative Curie-Weiss temperature $\Theta_{CW} \approx -43$ K, and a effective moment $\mu_{eff}$ of $\sim 3.84 \mu_B$, which is close to the Nd$^{3+}$ free-ion value of $3.62 \mu_B$. Due to the significant change in slope of the $\chi_{dc}^{-1}(T)$ data a Curie-Weiss fit was made to the low-$T$ $\chi_{dc}^{-1}(T)$ data from 2 K to 4 K (Fig. 5.2(c)), which revealed a positive $\Theta_{CW} \sim 1$ K, and a low-$T$ $\mu_{eff}$ of $\sim 2.35 \mu_B$. The positive $\Theta_{CW}$ from the low-$T$ fit is a possible indication of ferromagnetic order developing below 1 K.

Given the significant change in slope of the $\chi_{dc}^{-1}(T)$ data, CEF analysis of the magnetic susceptibility of NdOs$_4$Sb$_{12}$ was performed. In an ionic (localized) model assuming cubic symmetry, the Nd$^{3+}$ ten-fold degenerate $J = 9/2$ Hund’s rule ground state multiplet splits into a $\Gamma_6$ doublet and two $\Gamma_8$ ($\Gamma_8^{(1)}, \Gamma_8^{(2)}$) quartet states. The $\chi_{dc}^{-1}(T)$ data for NdOs$_4$Sb$_{12}$ was fit to the form $\chi^{-1} = \chi_{CEF}^{-1} - \Lambda$, where the molecular field constant $\Lambda$ is included to account for the magnetic order in NdOs$_4$Sb$_{12}$ and the CEF term $\chi_{CEF}^{-1}$ follows from Section 2.2.2.

The ground state $\mu_{eff}$ (2.35$\mu_B$) estimated from the low-$T$ fit to the $\chi_{dc}^{-1}(T)$ data for NdOs$_4$Sb$_{12}$ limits the possible Nd$^{3+}$ ground state to either the $\Gamma_6$ doublet or $\Gamma_8^{(2)}$ quartet. Satisfactory fits to the $\chi(T)$ data assuming a $\Gamma_6$ ground state occurred with $x_{LLW}$ ranging from $-1$ to 0.1. While for a $\Gamma_8$ ground state acceptable fits were only found for $x_{LLW} \approx -0.4$. The various CEF fits to the $\chi(T)$ data result in an energy level splitting greater than 120 K between the ground and first excited states for the two possible ground state scenarios. The best CEF fits to the $\chi(T)$ data (Figs. 5.1(a) and (b)) were determined by comparison with CEF
Figure 5.1 (a) DC magnetic susceptibility $\chi_{dc}$ vs temperature $T$ from 0 K to 10 K measured at 500 Oe. Fits of $\chi_{dc}(T)$ to a CEF model in which the ground state is either $\Gamma_6$ (dashed line) or $\Gamma_8^{(2)}$ (solid line). (b) The $\chi_{dc}^{-1}(T)$ data plotted from 0 K to 300 K. Fits of $\chi_{dc}(T)$ and $\chi_{dc}^{-1}(T)$ to a CEF model assuming either a $\Gamma_6$ (dashed line) or $\Gamma_8^{(2)}$ (solid line) ground state.

fits to the $\rho(T)$ data (Section 5.1.4). The best fits are (1) $x_{LLW} = -0.1$, $W = 3.9$, and (2) $x_{LLW} = -0.4$, $W = -7.2$, corresponding to the following level schemes: (1) $\Gamma_6$ (0 K), $\Gamma_8^{(1)}$ (180 K), $\Gamma_8^{(2)}$ (420 K) and (2) $\Gamma_8^{(2)}$ (0 K), $\Gamma_8^{(1)}$ (220 K), $\Gamma_6$ (600 K),
with $\Lambda = 1.39 \text{ Nd-mol/cm}^3$ and an effective ground state moment of $\sim 2.31 \mu_B$ for both schemes.

Figure 5.2 (a) Magnetization $M$ vs magnetic field $H$ isotherms and the saturation magnetization $M_{\text{sat}}$ extrapolated the $M(H)$ isotherms below the Curie temperature $T_C$. (b) $M^2$ vs $H/M$ isotherms (Arrott plot) for NdOs$_4$Sb$_{12}$. (c) Inverse initial magnetic susceptibility (open circles) determined from $M^2 = 0$ intercepts of $M^2$ vs $H/M$ isotherms, compared to the $\chi^{-1}_{dc}(T)$ data (pluses). The line is a Curie-Weiss fit. (d) $H/M = 0$ intercepts of $M^2$ vs $H/M$ isotherms plotted versus $T$. Positive values correspond to the spontaneous magnetization $M_{\text{sp}}$.

Measurements of the magnetization as a function of magnetic field $M(H)$ between 0.4 K and 3 K are plotted in Fig. 5.2(a). A Brillouin function with an effective $J = 2.7$ and a temperature shift of 1 K (due to ferromagnetic ordering) fit the $M(H)$ isotherms between 2 K and 5 K in the paramagnetic state. An Arrott plot ($M^2$ vs $H/M$) of the magnetization isotherms around the ordering temperature are shown in Fig. 5.2(b). The Arrott plot indicates that NdOs$_4$Sb$_{12}$ is a mean-field ferromagnet since the magnetization isotherms in the vicinity of $T_C$ are linear and parallel for $H \leq 1$ T. Linear fits to the Arrott plot isotherms below 1 T (solid
lines) are included in Fig. 5.2(b). The \((H/M)\)-axis intercepts of these linear fits (\(\equiv\) the inverse initial magnetic susceptibility) are consistent with the low-\(T\) \(\chi_{dc}^{-1}(T)\) data as indicated in Fig. 5.2(c). Displayed in Fig. 5.2(d) are the intercepts of the linear fits to the \(M^2\)-axis of the Arrott plot and from this the Curie temperature is defined as the temperature where \(M^2\) is zero \((T_C = 0.93 \text{ K})\). The intercepts of the linear fits to the \(M^2\)-axis, below \(T_C\), correspond to the square of the spontaneous magnetization \(M_{sp}^2\), which levels off at the low value of \(M_{sp} \sim 0.7 \mu_B/\text{f.u.}\). However, a linear extrapolation of the negative \(M^2\)-axis intercepts (above \(T_C\)) back to zero temperature yield a much larger value of \(\sim 1.76 \mu_B/\text{f.u.}\), which is comparable to the saturation magnetization \(M_{sat}\) of \(\sim 1.73 \mu_B/\text{f.u.}\) determined directly from the \(M(H)\) data of NdOs\(_4\)Sb\(_{12}\) (Fig. 5.2(a)). The value of \(M_{sat}\) is also consistent with the saturation magnetization found in NdFe\(_4\)P\(_{12}\) \((1.72 \mu_B/\text{f.u.}) [2]\).

### 5.1.4 Electrical Resistivity

In Figs. 5.3(a) and (b) the low-\(T\) \(\rho(T)\) data for NdOs\(_4\)Sb\(_{12}\) are displayed for \(H\) between 0 T and 18 T. The good quality of the single crystal studied is confirmed by the zero-field residual resistivity ratio RRR \(\equiv \rho(300 \text{ K})/\rho(0.02 \text{ K})\) of \(\sim 45\) (Fig. 5.3(a) and (d)). In zero-field the \(\rho(T)\) data display a shoulder at \(\sim 1.2 \text{ K}\) and drops sharply as the temperature is decreased below the onset of magnetic order. The point where linear fits to the data above and below the transition intersect is used to define \(T_d\) the temperature at which the \(\rho(T)\) drop occurs. The points midway between \(T_d\) and the temperatures at which the linear fits deviate from the data define the upper and lower limits of transition. In Fig. 5.3(c) \(T_d\) as a function of \(H\) is found to increase with increasing \(H\) up to 6 T, above which it can not be observed in the \(\rho(T)\) data. The onset of magnetic ordering \((0.9 \text{ K})\) determined from magnetization and specific heat measurements correlates with \(T_d\). The high-\(T\) \(\rho(T)\) data for NdOs\(_4\)Sb\(_{12}\) from 0 T to 9 T, shown in Fig. 5.3(d), feature a slight increase in \(\rho(T)\) with increasing field.

The \(\rho(T)\) data in the ordered state below \(T_C\) were fit with a power-law
Figure 5.3 (a) and (b) The low-\textit{T} electrical resistivity \( \rho \) vs temperature \( T \) at various magnetic field \( H \) for \text{NdOs}_4\text{Sb}_{12}. (a) For \( H \) between 0 T and 6 T. (b) For \( H \) between 8 T and 18 T. (c) Position of the shoulder \( T_d \) in \( \rho(T) \) (which corresponds to \( T_C \)) vs \( H \), with vertical bars indicating the width of the transition at \( T_d \) as described in the text. (d) High-\textit{T} resistivity \( \rho \) vs \( T \) at \( H = 0 \text{T}, 0.5 \text{T}, 1 \text{T}, 2 \text{T}, 4 \text{T}, 6 \text{T}, 8 \text{T}, 9 \text{T} \).

of the form \( \rho(T) = \rho_0 + BT^n \) and displayed in Fig. 5.4(a) as dashed lines. From these fits it is found that the residual resistivity \( \rho_0 \) increases with increasing field
Figure 5.4 (a) Low-T electrical resistivity $\rho$ vs temperature $T$ with power-law (dashed line) and spin-wave (solid line) fits at various magnetic fields for NdOs$_4$Sb$_{12}$. (b) Residual resistivity $\rho_0$ vs $H$. (c) Exponent $n$ of the power-law fit vs $H$. (d) Energy gap $\Delta$ from the spin-wave fit vs $H$.

and has a linear $H$-dependence above 8 T (Fig. 5.4(b)). The variation of the exponent $n$ from 3 to 4 for NdOs$_4$Sb$_{12}$ (Fig. 5.4(c)), between 0 T and 18 T, is not an indication of typical Fermi-liquid ($n \sim 2$) or typical non-Fermi-liquid ($n < 2$) behavior, though the value of 4 is consistent with similar fits to the $\rho(T)$ data for NdFe$_4$P$_{12}$ [11, 12]. Electron-spin wave scattering was considered, due to the likely hood of ferromagnetic ordering below $T_C$, with the following form [17]

$$\rho(T) = \rho_0 + b \frac{T}{\Delta} \left(1 + 2 \frac{T}{\Delta}\right) e^{-\Delta/T},$$

(5.2)

where $\Delta$ is the spin wave energy gap, which can be a result of magnetic anisotropy or broken symmetry due to a CEF. The fits represented by the solid lines in Fig. 5.4(a) indicate that the $\rho(T, H)$ data are fit well by this formula. The spin-wave energy gap $\Delta$, derived from these fits, is $\sim 0.75$ K at 0 T, linearly increases to $\sim 4.5$ K as the field increases to 12 T, and then drops to $\sim 3.4$ K at 18 T (Fig. 5.4(d)).
Figure 5.5 (a) Zero-field electrical resistivity $\rho$ and the combined estimates for the lattice and impurity contributions ($\rho_{\text{lat}} + \rho_{\text{imp}}$) vs temperature $T$ for NdOs$_4$Sb$_{12}$, where $\rho_{\text{imp}} \sim 9.4 \mu\Omega$-cm. (b) Temperature dependence of the incremental resistivity $\Delta \rho = \rho - \rho_{\text{lat}} - \rho_{\text{imp}}$ and CEF fits for two different ground states: $\Gamma_6$ (dashed line) and $\Gamma_8^{(2)}$ (solid line), where $x/(1-x)$ is the ratio of $s$-$f$ exchange to aspherical Coulomb scattering for NdOs$_4$Sb$_{12}$.

The high-$T$ $\rho(T)$ data displayed in Fig. 5.5(a) exhibits metallic behavior
and features a slight negative curvature around 130 K, which may be an indication of CEF effects. The CEF contribution is determined by first subtracting an impurity $\rho_{\text{imp}}$ ($\sim 9.4 \mu\Omega\cdot\text{cm}$) and lattice contribution $\rho_{\text{lat}}(T)$ from the $\rho(T)$ data for NdOs$_4$Sb$_{12}$. As stated in previous chapters an isostructural nonmagnetic reference compound is usually used as an estimate of $\rho_{\text{lat}}(T)$. As previously found for SmOs$_4$Sb$_{12}$ in Chapter 4 the $\rho(T)$ data for the nonmagnetic reference compound LaOs$_4$Sb$_{12}$ exhibits substantial negative curvature above 100 K. Due to this behavior the $\rho_{\text{lat}}$ contribution to the $\rho(T)$ data for NdOs$_4$Sb$_{12}$ above 100 K was estimated from the $\rho(T)$ data for SmOs$_4$Sb$_{12}$, since SmOs$_4$Sb$_{12}$ has an approximately linear-$T$ dependence between 100 K and 300 K (see Section 4.1.4). Also, the contribution due to $s$-$f$ exchange scattering in the $\rho(T)$ data for SmOs$_4$Sb$_{12}$ only appears below 80 K due to the small energy splitting ($\sim 35$ K) between the
ground and the first excited states in that compound (see Section 4.1.6). Therefore, \( \rho_{\text{lat}}(T) \) for NdOs\(_4\)Sb\(_{12}\) above 100 K can be derived from the SmOs\(_4\)Sb\(_{12}\) \( \rho(T) \) data, since the temperature dependence of the electrical resistivity for SmOs\(_4\)Sb\(_{12}\) between 100 K and 300 K is primarily due to electron-phonon scattering.

In Fig. 5.5(b) the incremental resistivity \( \Delta \rho(T) = \rho(T) - \rho_{\text{lat}}(T) - \rho_{\text{imp}} \) can be fit by two CEF energy level schemes consistent with the previous CEF analysis of \( \chi(T) \). An initial CEF analysis found that \( s-f \) exchange scattering could not alone account for the behavior of \( \Delta \rho(T) \), unless an unphysical negative \( \rho_{\text{imp}} \) was included in the fit. To correct for this, a term due to aspherical Coulomb scattering, was included [18–20]. During the CEF analysis, the contributions due to \( s-f \) exchange scattering and the aspherical Coulomb scattering were weighted by \( x \) and \( 1-x \), respectively. The CEF energy splitting schemes associated with the two best fits are displayed along with \( \Delta \rho(T) \) in Fig. 5.5(b). The \( \Delta \rho(T) \) data above 40 K is well described by these two schemes. The deviation of the CEF fits from \( \Delta \rho(T) \) below 40 K could be the result of reduced electron scattering, due to the development of a coherent heavy-fermion ground state in NdOs\(_4\)Sb\(_{12}\) with decreasing temperature. In Fig. 5.6 the \( \rho(H) \) data for NdOs\(_4\)Sb\(_{12}\) are displayed (Fig. 5.6(a)) along with \( \rho(H) \) isotherms derived from the two CEF energy level splitting schemes derived from the analysis of the \( \Delta \rho(T) \) data (Fig. 5.6(b) and (c)).

Figure 5.7 displays the pressure dependence of the \( \rho(T) \) data for 0 kbar \( \leq P \leq 28 \) kbar. At high-\( T \) the shift in the \( \rho(T) \) due to an applied pressure is much more significant than the magnetic field induced shift observed in Fig. 5.3(c). Inset (a) to Fig. 5.7 features the pressure dependence of the \( \rho(T) \) data for NdOs\(_4\)Sb\(_{12}\) around \( T_C \), from which \( T_d \) as a function of pressure is derived and displayed in Fig. 5.7 inset (b). Clearly, from figures Fig. 5.3(c) and Fig. 5.7 inset (b) the field dependence of \( T_d \) is much stronger than than the dependence on pressure.
Figure 5.7 Electrical resistivity $\rho$ vs temperature $T$ for NdOs$_4$Sb$_{12}$ at various pressures $P$ up to 28 kbar. Inset (a) shows an expanded view around the magnetic transitions. Inset (b) displays the estimated onset of magnetic order $T_d$ (approximately corresponding to the Curie temperature $T_C$) vs $P$ with vertical bars indicating the width of the transition.

5.1.5 Specific Heat

In Fig. 5.8(a) the specific heat divided by temperature $C/T$ vs $T$ data for NdOs$_4$Sb$_{12}$ are displayed. Below 20 K the only feature in the $C/T$ vs $T$ data is a pronounced peak at $\sim 0.8$ K, that agrees well with the magnetic ordering temperature $T_C$ derived from the Arrott analysis, with no obvious indication of a Schottky anomaly. The lack of a clear Schottky anomaly is consistent with the CEF splitting of 120 K between the ground and first excited states estimated from fits to the DC magnetic susceptibility. The Schottky anomaly that would result from the calculated 120 K splitting would peak at $\sim 40$ K with no significant contribution below 20 K. In this temperature range the anomaly would be difficult to separate from the large lattice contribution to the specific heat.
Figure 5.8 (a) The zero-field \( C(T) \) data for NdOs\(_4\)Sb\(_{12}\) and LaOs\(_4\)Sb\(_{12}\) below 20 K. The inset displays \( \delta C/T \) vs \( T^2 \) below 20 K, where \( \delta C \equiv C(\text{NdOs}_4\text{Sb}_{12}) - C(\text{LaOs}_4\text{Sb}_{12}) \). The extrapolated values of the two dashed lines at 0 K set the lower and upper limits of \( \gamma(\text{NdOs}_4\text{Sb}_{12}) - \gamma(\text{LaOs}_4\text{Sb}_{12}) \).

(b) A comparison between \( C(T) \) for NdOs\(_4\)Sb\(_{12}\) and a fit with \( C_{el}(T) + C_{lat}(T) \), where \( C_{el}(T) = \gamma T \) and \( C_{lat} \) is composed of \( C_{Deb}(T) \) and \( C_{Ein}(T) \) as described in the text. The electronic specific heat coefficient \( \gamma \), the Debye temperature \( (\Theta_D) \), Einstein temperature \( (\Theta_E) \), and coupling constant \( r \) for the Einstein oscillator are estimated as 520 mJ/mol-K\(^2\), 255 K, 39 K, and 0.48 respectively. Shown in the inset is \( C/T \) vs \( T^2 \) for NdOs\(_4\)Sb\(_{12}\) below 20 K.
The $C(T)$ data for NdOs$_4$Sb$_{12}$ are displayed in Fig. 5.8(a) along with $C(T)$ data for LaOs$_4$Sb$_{12}$ as a comparison. The lattice subtracted specific heat $\delta C(T)$ is derived by subtracting the $C(T)$ data for the nonmagnetic reference compound LaOs$_4$Sb$_{12}$ from the $C(T)$ data for NdOs$_4$Sb$_{12}$. In the inset of Fig. 5.8(a) is displayed $\delta C/T$ vs $T^2$, from which the electronic contribution to the specific heat $\gamma$ for NdOs$_4$Sb$_{12}$ can be estimated. From this figure estimates for $\gamma$ range from $\sim 436$ mJ/mol-K$^2$ to $\sim 530$ mJ/mol-K$^2$. The variation in $\delta C/T$ vs $T^2$ below 13 K may be due to a discrepancy between the actual lattice contribution to $C(T)$ for NdOs$_4$Sb$_{12}$ and the contribution estimated from LaOs$_4$Sb$_{12}$. The significant curvature in $\delta C/T$ vs $T^2$, and the magnetic ordering around 1 K complicate the $C(T)$ analysis with the formula $C/T = \gamma + \beta T^2$. Assuming the Schottky contribution to the $C(T)$ data for NdOs$_4$Sb$_{12}$ is negligible below 20 K, the source of the curvature of $\delta C/T$ vs $T^2$ may be due to a narrow peak in the electronic density of states near the Fermi energy, such as a Kondo resonance, or rattling of the Nd atoms [21]. The first of these possibilities is excluded due to the lack of an obvious Kondo effect in the $\rho(T)$ data and the conformity of the magnetization data above $T_C$ for NdOs$_4$Sb$_{12}$ to a Brillouin function. The specific heat contribution due to rattling in the filled skutterudite compounds has been considered previously by Sales et al. [15]. Their study found that the difference in the heat capacity between the partially filled Tl$_{0.22}$Co$_4$Sb$_{12}$ and the unfilled CoSb$_3$ can be accounted for by treating the Tl atoms as localized harmonic oscillators (Einstein oscillators) with an Einstein temperature ($\Theta_E$) of 55 K. For NdOs$_4$Sb$_{12}$ the structural refinement of the room temperature XRD data indicates a small $\Theta_E$ of $\sim 45$ K, associated with the rattling of the Nd atoms. The full lattice contribution to the specific heat $C_{\text{lat}}(T)$ can then be estimated as being due to a portion of the Nd atoms acting as Einstein oscillators $C_{\text{Ein}}(T)$ and the rest of the atoms which act as a debye solid $C_{\text{Deb}}(T)$ with the final form $C_{\text{lat}}(T) = C_{\text{Ein}}(T) + C_{\text{Deb}}(T)$.

$$C_{\text{Ein}}(T) = r \left[ 3R \frac{(\Theta_E/T)^2 e^{(\Theta_E/T)}}{[e^{(\Theta_E/T)} - 1]^2} \right],$$ (5.3)
\[ C_{\text{Deb}}(T) = (17 - r) \cdot \frac{12\pi^4}{5} R \left( \frac{T}{\Theta_D} \right)^3, \]  

(5.4)

where \( R \) is the universal gas constant, \( \Theta_D \) represents the Debye temperature, and \( r \leq 1 \). Since the majority of the atoms in the unit cell act as a Debye solid, the effective Debye contribution is \((17 - r)/r\) times bigger than that of the Einstein-like rattling motion of the Nd atoms. A least squares fit of \( C(T) = C_{\text{el}}(T) + C_{\text{lat}}(T) \) to the NdOs\(_4\)Sb\(_{12}\) data was performed below 20 K, where \( C_{\text{el}}(T) = \gamma T \) is the electronic specific heat, from which estimated values of \( \gamma, \Theta_D, \Theta_E, \) and \( r \) were derived. In Fig. 5.8(b) the fitting curve is plotted along with the \( C(T) \) data for NdOs\(_4\)Sb\(_{12}\) as a comparison. The values obtained from the fit for \( \gamma, \Theta_D, \Theta_E, \) and \( r \) are 520 mJ/mol-K\(^2\), 255 K, 39 K, and 0.48, respectively. The value of \( \Theta_D \) from the least squares fit is close to the Debye temperature of LaOs\(_4\)Sb\(_{12}\) (\( \sim 280 \) K), the value of \( \Theta_E \) is comparable to that determined from the X-ray data, and the value of \( \gamma \) is close to that estimated from the simple subtraction of the LaOs\(_4\)Sb\(_{12}\) specific heat data, suggesting that NdOs\(_4\)Sb\(_{12}\) displays heavy fermion behavior.

Integration of \( \Delta C/T \) vs \( T \), where \( \Delta C(T) \equiv C(T) - C_{\text{el}}(T) - C_{\text{lat}}(T) \), results in the magnetic entropy \( S_{\text{mag}} \) as a function of temperature displayed in Fig. 5.9(a). The temperature dependence of \( S_{\text{mag}}(T) \) for NdOs\(_4\)Sb\(_{12}\) reaches Rln2 at 0.85 K and levels off at a value of Rln3. At \( T_C \) the magnetic entropy reaches \( \sim 74\% \) with a noticeable magnetic contribution remaining up to \( \sim 3 \) K. This contribution may indicate the presence of magnetic fluctuations that persist above \( T_C \). One may then argue that short range magnetic correlations near \( T_C \) contribute to the enhanced specific heat observed in NdOs\(_4\)Sb\(_{12}\) [22–24]. Since, in other compounds, such as the antiferromagnetic system Gd\(_{1-x}\)Y\(_x\)Ni\(_2\)Si\(_2\), magnetic fluctuations can contribute to \( C(T) \) at temperatures up to 5 times the Néel temperature [22]. However, when considering the magnitude of the electronic specific heat enhancement it seems unlikely that magnetic fluctuations could account entirely for this since: (1) The \( M(H) \) isotherms in the paramagnetic state \((2 - 5 \) K\) scale with a Brillouin function. No evidence of magnetic fluctuations can be observed above 2 K in the 2 K and 3 K \( M(H) \) data, the \( \chi_{\text{dc}}^{-1}(T) \) data, and the initial \( \chi^{-1}(T) \)
Figure 5.9 (a) Incremental specific heat $\Delta C$ ($\Delta C(T) \equiv C(T) - C_{el}(T) - C_{lat}(T)$) (left axis) and the magnetic entropy $S_{mag}$ (right axis) vs temperature $T$. (b) Logarithmic plot of the power-law fit (dotted line) and the anisotropic-spin-wave fit (dashed line) to the incremental specific heat $\Delta C(T)$ after the electronic and lattice contributions have been removed (in a very limited measuring range below $T_C$).

from the Arrott Plot analysis for NdOs$_4$Sb$_{12}$ (displayed in Fig. 5.2 (a) and (b)).

(2) The value of $\gamma$ (520 mJ/mol-K$^2$) is well within the range of 436 – 530 mJ/mol-
$K^2$ estimated from an earlier analysis, in which the specific heat of NdOs$_4$Sb$_{12}$ is compared to the nonmagnetic compound LaOs$_4$Sb$_{12}$.  (3) The lower limit (4 K) of the fitting range used to determine $\gamma$ from the formula $C(T) = C_{\text{el}}(T) + C_{\text{lat}}(T)$ is four times the Curie temperature, which is safely higher than the temperature at which the calculated $S_{\text{mag}}(T)$ saturates.  (4) The neighboring compounds to NdOs$_4$Sb$_{12}$ also exhibit heavy fermion behavior, such as PrOs$_4$Sb$_{12}$ with $\gamma \sim 600$ mJ/mol-K$^2$ [25], SmOs$_4$Sb$_{12}$ [26], and with $\gamma \approx 880$ mJ/mol-K$^2$ along with earlier studies of the related compound NdFe$_4$Sb$_{12}$ which also reported evidence for an enhanced electron mass [2, 27]. These combined points reinforce the notion that the enhanced specific heat of NdOs$_4$Sb$_{12}$ is due to heavy fermion behavior.

Attempts to use $S_{\text{mag}}(T)$ to determine the CEF ground state were hindered. Since, unlike several other Nd-based filled skutterudites discussed earlier, the $S_{\text{mag}}(T)$ for NdOs$_4$Sb$_{12}$ saturates at a value between Rln2 and Rln4. Which makes it difficult to determine conclusively whether the $\Gamma_6$ doublet or $\Gamma^{(2)}_8$ quartet is the Nd$^{3+}$ ground state. A $\Gamma_6$ doublet ground state would imply an excess of entropy could result from another degree of freedom, such as a tunnelling mode or off-center mode associated with the Nd$^{3+}$ ion rattling in an Sb-cage [28]. While a $\Gamma^{(2)}_8$ quartet ground implies a smaller than expected entropy possibly due to overestimating the lattice contribution to the specific heat or entropy transfer to the conduction electrons.

The incremental specific heat $\Delta C(T)$ ($\Delta C(T) \equiv C(T) - C_{\text{el}}(T) - C_{\text{lat}}(T)$) as a function of temperature is displayed in Fig. 5.9(b). In the limited range of $\Delta C(T)$ data below $T_C$, the data were fit with spin-wave formulas $\Delta C(T) \propto T^n$ for magnetically isotropic metals and $\Delta C(T) \propto T^{3/2} \exp(-\Delta/T)$ for magnetically anisotropic metals [29]. From the first formula, the value of the exponent $n \approx 2.3$ is higher than the value of 1.5 expected from a spin wave in an isotropic metal and lower than the $n = 3$ value found for NdFe$_4$P$_{12}$ [11,12]. The spin-wave energy gap $\Delta$ determined from the second formula is $\sim 0.54$ K, consistent with the value of 0.75 K determined from the zero-field $\rho(T)$ data for NdOs$_4$Sb$_{12}$. 
5.1.6 Summary

Strongly correlated electron behavior has been identified in NdOs$_4$Sb$_{12}$ single crystals through X-ray diffraction, electrical resistivity, magnetization, and specific heat measurements. The full occupancy of the Nd site in NdOs$_4$Sb$_{12}$ has been found through structural refinement of X-ray diffraction data. Arrott plot analysis revealed mean-field-type ferromagnetism in NdOs$_4$Sb$_{12}$ with $T_C \sim 0.9$ K. A thorough specific heat analysis found a value of $\gamma \sim 520$ mJ/mol-K$^2$ ($m^* \sim 98$ $m_e$), which indicates that NdOs$_4$Sb$_{12}$ is a possible heavy fermion compound. CEF analysis suggests two best-fit energy level schemes: (1) $\Gamma_6$ (0 K), $\Gamma_8^{(1)}$ (180 K), $\Gamma_8^{(2)}$ (420 K); (2) $\Gamma_8^{(2)}$ (0 K), $\Gamma_8^{(1)}$ (220 K), $\Gamma_6$ (600 K). The CEF analysis of the electrical resistivity data implied that both s-f exchange and aspherical Coulomb scattering are present in NdOs$_4$Sb$_{12}$. Fits to the Low-$T \rho(T)$ data, below $T_C$, suggest the possible existence of spin-wave excitations. Further experiments such as neutron scattering should be able to resolve the uncertainty in the CEF energy level scheme and the possibility of spin-wave excitations in NdOs$_4$Sb$_{12}$.

A portion of the text and data of Chapter 5 is a reprint of the material as it appears in “Ferromagnetism and possible heavy-fermion behavior in single crystals of NdOs$_4$Sb$_{12}$,” P.-C. Ho, W. M. Yuhasz, N. P. Butch, N. A. Frederick, T. A. Sayles, J. R. Jeffries, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester, Physical Review B 72, 094410 (2005). The dissertation author was second author in this article and contributed to the single crystal growth, magnetization and electrical resistivity measurements.

Bibliography


Concluding remarks

The properties of the filled skutterudite compounds Pr\textsubscript{0.87}Fe\textsubscript{4}Sb\textsubscript{12}, PrOs\textsubscript{4}As\textsubscript{12}, PrOs\textsubscript{4}P\textsubscript{12}, SmOs\textsubscript{4}Sb\textsubscript{12}, and NdOs\textsubscript{4}Sb\textsubscript{12} were studied in detail. Overall single crystal structural refinement indicates large mean square atomic displacement factors for the rare earth ions, consistent with rattling behavior of the filling ion. Crystalline electric field effects were predominant in all the systems studied. The crystalline electric field acting on the rare earth ion determines the ground state of the rare earth and the resulting strongly correlated electron phenomena. The most prominent features associated with crystalline electric fields were Schottky anomalies in specific heat as a function of temperature of PrOs\textsubscript{4}P\textsubscript{12} and SmOs\textsubscript{4}Sb\textsubscript{12}. The Schottky anomalies emerged at temperatures of the order of the splitting between the ground state and first excited state of the rare earth ion. In these two systems, the CEF schemes could be well defined, while only ranges for possible CEF schemes could be determined for Pr\textsubscript{0.87}Fe\textsubscript{4}Sb\textsubscript{12}, PrOs\textsubscript{4}As\textsubscript{12}, and NdOs\textsubscript{4}Sb\textsubscript{12}.

The filled skutterudite systems Pr\textsubscript{0.87}Fe\textsubscript{4}Sb\textsubscript{12}, PrOs\textsubscript{4}As\textsubscript{12}, SmOs\textsubscript{4}Sb\textsubscript{12}, and NdOs\textsubscript{4}Sb\textsubscript{12} all seem to display an enhanced electron effective mass along with magnetic phase transitions below 4.1 K, 2.3 K, 2.6 K, and 0.9 K, respectively. The heavy fermion behavior observed in these systems could be due to the high coordination of the rare earth ion by the twelve surrounding pnictogen ions. The high coordination may result in strong hybridization between the 4f- and conduction electrons, which could lead to the observed heavy fermion behavior. Recently, an-
other proposal has been made by Hattori et al. implying that interactions between conduction electrons and rare earth ions that tunnel between multiple off-center sites may result in the unconventional superconductivity of PrOs$_4$Sb$_{12}$ as well as the observed heavy fermion behavior [1]. Since SmOs$_4$Sb$_{12}$ and NdOs$_4$Sb$_{12}$ are both structurally similar to PrOs$_4$Sb$_{12}$, with almost identical lattice parameters, the same interactions may lead to the enhanced effective masses in these systems as well.

The magnetic ordering observed in PrOs$_4$As$_{12}$ below 2.3 K was found to be mean field type antiferromagnetic ordering based on neutron diffraction experiments. The ordering of NdOs$_4$Sb$_{12}$ below 0.9 K was found to be consistent with mean field ferromagnetism based on an Arrott plot that was constructed. The magnetic ordering observed in Pr$_{0.87}$Fe$_4$Sb$_{12}$ and SmOs$_4$Sb$_{12}$ has several features consistent with itinerant magnetism such as nonsaturating $M(H)$ isotherms, weak ordered moments, and very low entropy at the ordering temperature. The unusual critical exponents that were derived from the modified Arrott plots for these systems are comparable, which may imply similar behavior. Indications from neutron diffraction experiments of local moment in Pr$_{0.87}$Fe$_4$Sb$_{12}$ may imply the presence of both local and itinerant moments in these systems. This combination of local and itinerant behavior may result in the unusual critical exponents determined for these systems.

In order to gain a better understanding of the magnetic ordering and heavy fermion behavior observed in several of these systems further research is necessary. These include neutron diffraction experiments performed NdOs$_4$Sb$_{12}$ as well as PrOs$_4$As$_{12}$ in field to conclusively determine the magnetic ordering in the ordered state of NdOs$_4$Sb$_{12}$ and the multiple ordered phases of PrOs$_4$As$_{12}$. Further work improving the quality of Pr$_{0.87}$Fe$_4$Sb$_{12}$ single crystals may improve the quality of the neutron diffraction results.

The phenomena exhibited by the group of filled skutterudites in this study represent a small sample of the interesting properties displayed by this family of
compounds. Although many of these systems have been studied several other filled skutterudite compounds, especially the arsenic based systems, have yet to be characterized and represent a fertile area of future research.

Bibliography