NOVEL HEAVY FERMION BEHAVIOR IN PRASEODYMIUM-BASED MATERIALS:
EXPERIMENTAL STUDY OF PrOs$_4$Sb$_{12}$

By
COSTEL REMUS ROTUNDU

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by

Costel Remus Rotundu
To my parents, Constantin and Elena Rotundu,

for their sacrifices to ensure my education.
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NOVEL HEAVY FERMION BEHAVIOR IN PRASEODYMIUM-BASED MATERIALS:
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By
Costel Remus Rotundu

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Chair: Bohdan Andraka
Major Department: Physics

PrOs$_4$Sb$_{12}$ is the first discovered Pr-based heavy fermion metal and superconductor. Our high magnetic field specific heat measurements provided clear evidence for the non-magnetic singlet crystalline electric field (CEF) ground state. This CEF ground state precludes the conventional Kondo effect as the origin of the heavy fermion behavior. The superconductivity in PrOs$_4$Sb$_{12}$ is unconventional, as inferred from the double superconducting transition in the specific heat. Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ ($0 \leq x \leq 1$) crystals were synthesized and investigated in order to provide additional evidences for a postulated CEF configuration, to discriminate between different conduction electron mass enhancement ($m^*$) mechanisms proposed, and to provide insight into the nature of the superconductivity. Lanthanum doping induces anomalously small increase of the lattice constant. The specific heat results in high magnetic fields indicated that CEF scheme is unaltered between $x=0$ and at least 0.2, followed by an abrupt (but small) change somewhere between $x=0.2$ and 0.4. Magnetoresistance measurements on La-doped samples were consistent with a singlet CEF ground state of Pr. Investigation of the specific heat discontinuity at $T_c$ and of the upper critical field slope at $T_c$ indicated that the electronic effective mass, $m^*$, is strongly reduced with $x$, between $x=0$ and $x_{cr} \approx 0.2$–0.3, followed by a weak dependence on $x$ for $x>x_{cr}$. Therefore, we have postulated that single-impurity type models cannot account for the heavy fermion behavior of PrOs$_4$Sb$_{12}$. Investigation of the magnetic phase diagram and magnetoresistance provided strong correlations between
a closeness to the long-range order (antiferroquadrupolar type) and $m^*$, suggesting a possibility of fluctuations of the antiferroquadrupolar order parameter responsible for $m^*$ enhancement. Lanthanum has very weak effect on the superconducting transition temperature in a stark contrast to other known heavy fermion superconductors. The study of superconductivity provided constraints on proposed theoretical models, including the two band model.
CHAPTER 1
INTRODUCTION

In the rare earth (Ce,Yb)- and actinide (U,Np)-based alloys the electronic states have an energy orders of magnitude smaller than in ordinary metals, and since $\epsilon(k) = \hbar^2 k^2 / 2m^*$, the effective mass $m^*$ is orders of magnitude larger than the free-electron value, hence the term heavy fermion. There are several excellent experimental and theoretical reviews [1–5] on heavy fermions. One hallmark of the heavy fermion character is the large Sommerfeld coefficient $\gamma$ of the specific heat. The specific heat of metals in the normal state at low temperature is approximated by $C = \gamma T + \beta T^3$, where $\gamma T$ is the electronic specific heat and $\beta T^3$ is the lattice (Debye) contribution. For a normal metal $\gamma$ is of order of 1 mJ/K$^2$ mol, and for heavy fermion is from several hundred to several thousand mJ/K$^2$ mol. The magnetic susceptibility $\chi$ at high temperatures follows the Curie-Weiss form $\chi = C / (T + \Theta_{CW})$, where $C$ is a constant, and $\Theta_{CW}$ is the Curie-Weiss temperature. At low temperatures $\chi(0)$ ranges from $\sim 10$ to 100 memu/mol. In the majority of heavy fermion metals, the electrical resistivity $\rho$ at very low temperatures has a $T^2$ dependence: $\rho = \rho_0 + AT^2$, where $\rho_0$ is the residual resistivity and $A$ is on the order of tens of $\mu\Omega cm/K^2$, much larger than that of normal metals.

There are about 20 heavy fermion systems that are superconductors and almost all of them are Ce- or U-based (there is one Pu-based heavy fermion superconductor: PuCoGa$_5$ [6]).

The filled skutterudite PrOs$_4$Sb$_{12}$ is the first discovered Pr-based heavy fermion compound that is a superconductor [7].

In the conventional heavy fermions, the only microscopic theories somewhat successful in accounting for the effective mass enhancement ($m^*$) as measured by the specific heat are the $S=1/2$ and $S=3/2$ Kondo models. These models were initially proposed for Ce-based systems, whose effective degeneracies of $f$-electrons in crystalline electric fields are either 2 or 4. The Kondo effect in these systems is anomalous because of strong spin-orbit coupling. There is one $f$ electron per Ce atom and according to Hund’s rules
the total angular moment is $J = 5/2$, which corresponds to the degenerate 6 level case. Crystalline electric fields split this multiplet either in a) 3 doublets or b) one doublet and one quartet. Case b) can be only for cubic symmetries. Thus Ce-based heavy fermions with a doublet CEF ground state of Ce are described by the $S = 1/2$ Kondo model while those with Ce in a quartet CEF ground state are described by $S = 3/2$ Kondo model. Thus any understanding of heavy fermion behavior needs clarification of the CEF ground state. Unfortunately, CEF scheme is not known for U-based heavy fermions. Furthermore the valence of U (i.e., whether the electronic configuration is $f^2$ or $f^3$) is not known. The high temperature effective moments for $f^2$ and $f^3$ configurations that could be extracted from the high temperature susceptibility are almost identical. Studies of CEF’s done directly by inelastic neutron scattering [8, 9] are more consistent with the $f^2$ configuration, allowing for a similar CEF scheme as that for Pr. Therefore, the investigation of PrOs$_4$Sb$_{12}$ with Pr having 2 $f$-electrons might be relevant and help to the understanding of the large class of U-based heavy fermions, since CEF configurations are usually known for Pr. The non-magnetic crystalline electric field ground state (thought as either singlet or doublet [7]) excludes the conventional Kondo effect as the origin of the heavy-fermion behavior in PrOs$_4$Sb$_{12}$, which is considered to be the source of heavy fermion behavior in Ce- and U-based metals. The superconductivity in PrOs$_4$Sb$_{12}$ is unconventional, but different from that in Ce- and U-based materials. Marks of the unconventionality of superconductivity can be inferred from the double superconducting transition and power low dependence of the specific heat below the transition.

The main goals of this work are:

• to settle the crystalline electric field ground state in PrOs$_4$Sb$_{12}$,
• to bring further evidences of the heavy fermion state in PrOs$_4$Sb$_{12}$,
• to differentiate between several models proposed for the conduction electron mass enhancement ($m^*$) and to study the relationship between the correlation and the superconductivity.
The outline of the dissertation is as follows: Chapter 2 presents the theoretical framework of this thesis. This Chapter begins with the theory of crystalline electric field for the point group symmetry $T_h$, followed by a presentation of the quadrupolar Kondo effect. Other proposed models of the conduction electron mass enhancement are also discussed. Chapter 3 review the essential properties of PrOs$_4$Sb$_{12}$. Chapter 4 gives a brief description of the apparatus and experimental methods used. A characterization of the materials synthesized and measured is given in Chapter 5. The experimental data are presented and discussed in Chapters 6 and 7. Chapter 6 focus on PrOs$_4$Sb$_{12}$ itself (specific heat and resistivity in high magnetic fields). Chapter 7 presents the study of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$, $0 \leq x \leq 1$. Structural, transport, magnetic and thermodynamic measurements are discussed. Finally, Chapter 8 summarizes the main findings and contributions to the field of Pr-based heavy-fermions.
CHAPTER 2
THEORETICAL BACKGROUND

2.1 The Crystalline Electric Field (CEF) for Cubic Group

In rare earth compounds, the crystalline electric fields are responsible for a wide variety of strongly correlated electron behaviors. The 4f-electrons in a rare earth ion experience an electrostatic crystal field potential created by the surrounding electric charge distribution (of the neighbor ions). The potential reflects the local point symmetry of the site of the rare earth ion. In the point-charge ionic model the CEF potential at position \( \vec{r} \) due to the surrounding atoms is

\[
V_{CEF}(\vec{r}) = \sum_j \frac{q_j}{|\vec{r} - \vec{R}_j|},
\]

where \( q_j \) is the charge at the \( j^{th} \) neighboring ion, at \( \vec{R}_j \). If the magnetic ion has charge \( q_i \) at \( \vec{r}_i \), then the crystalline electric field Hamiltonian \( H_{CEF} \) is

\[
H_{CEF} = \sum_i \sum_j q_i \frac{q_j}{|\vec{r}_i - \vec{R}_j|}.
\]

The sum \( \sum_i \) is taken over electrons in unfilled shells [10].

The CEF potential can be evaluated in terms of Cartesian coordinates or in terms of spherical harmonics. Hutchings [10] evaluated the potential (2–1) for the simplest 3 arrangements of charges giving a cubic crystalline electric field. The three cases analyzed were when the charges are placed at the corners of an octahedron (sixfold coordination), at the corners of a cube (eightfold coordination), and at the corners of a tetrahedron (fourfold coordination). In Cartesian coordinates the potential (2–1) can be written as [10]

\[
V(x, y, z) = C_4[(x^4 + y^4 + z^4) - \frac{3}{5}r^4] + D_6[(x^6 + y^6 + z^6)
+ \frac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6],
\]

where \( d \) is the distance of the point charge \( q \) from the origin in each 3 cases. \( C_4 \) and \( D_6 \) are \(-70q/(9d^3)\) and \(-224q/(9d^7)\) for the eightfold coordination, \(+35q/(4d^5)\) and
\[-21q/(2d^7)\] for the sixfold coordination, and \[-35q/(4d^5)\] and \[-112q/(9d^7)\] for the fourfold coordination respectively.

In the spherical coordinates the same potential is written [10] as

\[V = D'_4\{Y_0^4(\theta, \phi) + \sqrt{\frac{5}{14}}[Y_4^4(\theta, \phi) + Y_4^{-4}(\theta, \phi)]\} + D'_6\{Y_0^6(\theta, \phi) - \sqrt{\frac{7}{2}}[Y_6^4(\theta, \phi) + Y_6^{-4}(\theta, \phi)]\},\] (2–4)

where \(D'_4\) and \(D'_6\) are \(-56q\sqrt{\pi}/(27d^5)\cdot r^4\) and \(+32q\sqrt{\pi}/13/(9d^7)\cdot r^6\) for the eightfold coordination, \(+7q\sqrt{\pi}/(3d^5)\cdot r^4\) and \(+3q\sqrt{\pi}/13/(2d^7)\cdot r^6\) for the sixfold coordination, and \(-28q\sqrt{\pi}/(27d^5)\cdot r^4\) and \(+16q\sqrt{\pi}/13/(9d^7)\cdot r^6\) for the eightfold coordination respectively.

The potential contains therefore terms of order 4 and 6 in coordinates. In general, the less symmetric is the site, the more potential terms occur in the expansion.

There are 2 general rules that can tell us the number of nonzero terms in the CF potential. If there is a center of inversion at the ion site there will be no odd-\(n\) terms. Secondly, if the \(z\) axis is not an \(m\)-fold axis symmetry, the potential will contain \(V^m_n\) [10].

However, calculating the potential terms in Cartesian coordinates and even in spherical coordinates is tedious. A more convenient method is the so called operator equivalent or Stevens’ operator technique [11, 12]. The Hamiltonian \((2–2)\) is of form \(H_{CEF} = -\sum_i |e|V(x_i, y_i, z_i)\). If \(f(x, y, z)\) is a Cartesian function, in order to find the equivalent operator to such terms as \(\sum_i f(x_i, y_i, z_i)\), the coordinates \(x, y, \) and \(z\) are replaced by angular momentum operators \(J_x, J_y,\) and \(J_z\) respectively, taking into account the non-commutativity of \(J_i\)'s. This is done by replacing products of \(x, y, \) and \(z\) by combinations of \(J_i\)'s divided by the total number of combinations. As an example we can consider

\[\sum_i (x_i^4 - 6x_i^2y_i^2 + y_i^4) = \sum_i [(x_i + iy_i)^4 + (x_i - iy_i)^4]/2 = \beta_J(r^4)[J_+^4 + J_-^4] = \beta_J(r^4)O_4^1,\] (2–5)

where \(J_\pm = J_x \pm iJ_y\).
The Hamiltonian is

\[
H_{CEF} = C_4[(x^4 + y^4 + z^4) - \frac{3}{5}r^4] + D_6[(x^6 + y^6 + z^6)
+ \frac{15}{4}(x^2y^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6],
\]  

(2–6)

Using the equivalent operator representation, the Hamiltonian will be [10]

\[
H_{CEF} = (C_4/20)\beta J\langle r^4 \rangle[O_4^0 + 5O_4^4] - (D_6/224)\gamma J\langle r^6 \rangle[O_6^0 - 21O_6^4],
\]  

(2–7)

or

\[
H_{CEF} = B_4^0[O_4^0 + 5O_4^4] + B_6^0[O_6^0 - 21O_6^4],
\]  

(2–8)

where \(B_4^0\) and \(B_6^0\) are \(+7|e|q\beta J\langle r^4 \rangle/(18d^5)\) and \(-|e|q\gamma J\langle r^6 \rangle/(9d^7)\) for eightfold coordination, \(-7|e|q\beta J\langle r^4 \rangle/(16d^5)\) and \(-3|e|q\gamma J\langle r^6 \rangle/(64d^7)\) for sixfold coordination, and \(+7|e|q\beta J\langle r^4 \rangle/(30d^5)\) and \(-|e|q\gamma J\langle r^6 \rangle/(18d^7)\) for fourfold coordination respectively. Also, \(\langle r^4 \rangle\) and \(\langle r^6 \rangle\) are the mean fourth and sixth power of the radii of the magnetic electrons, and the multiplicity factors \(\alpha_J\), \(\beta_J\), and \(\gamma_J\) are for \(\text{Pr}^{3+} (f^2) - 2^2 \cdot 13/(3^2 \cdot 5 \cdot 11^2), -2^2/(3^2 \cdot 5 \cdot 11^2),\) and \(-2^2 \cdot 17/(3^4 \cdot 5 \cdot 7 \cdot 11^2 \cdot 13)\) respectively [10]. Also,

\[
O_4^0 = 35J_z^4 - [30J(J + 1) - 25]J_z^2 - 6J(J + 1) + 3J^2(J + 1),
\]  

(2–9)

\[
O_4^4 = 1/2(J_+^4 + J_-^4),
\]  

(2–10)

\[
O_6^0 = 231J_z^6 - 105[3J(J + 1) - 7]J_z^4 + [105J^2(J + 1)^2 - 525J(J + 1)
+ 294]J_z^2 - 5J^3(J + 1)^3 + 40J^2(J + 1)^2 - 60J(J + 1),
\]  

(2–11)

\[
O_6^4 = 1/4[11J_z^2 - J(J + 1) - 38](J_+^4 + J_-^4) + 1/4(J_+^4 + J_-^4)
\times [11J_z^2 - J(J + 1) - 38].
\]  

(2–12)
In order to keep the eigenvalues in the same numerical range for all ratios of the fourth and sixth degree terms, $F(4)$ and $F(6)$ are introduced [13]. The Hamiltonian is written as

$$H_{CEF} = B_4^0 F(4) \frac{O_4^0 + 5O_4^4}{F(4)} + B_6^0 F(6) \frac{O_6^0 - 21O_6^4}{F(6)}.$$  \hspace{1cm} (2-13)$$

In order to cover all possible values of the ratio between the fourth and sixth degree terms are introduced the scale factor $W$ and the parameter $x$, proportional to the ratio of the two terms

$$B_4^0 F(4) = W x,$$  \hspace{1cm} (2-14)$$
$$B_6^0 F(6) = W (1 - |x|),$$  \hspace{1cm} (2-15)$$

where $-1 < x < +1$. Then, the Hamiltonian is [13]

$$H_{CEF} = W \left[ x \frac{O_4^0 + 5O_4^4}{F(4)} + (1 - |x|) \frac{O_6^0 - 21O_6^4}{F(6)} \right],$$  \hspace{1cm} (2-16)$$

The term in the square bracket is a matrix whose eigenvectors and eigenvalues (crystal field energy levels) are determined by usual diagonalization.

Praseodymium ion Pr$^{3+}$ in PrOs$_4$Sb$_{12}$ has a 4$f^2$ configuration, and then the total angular momentum is $J=4$. The site symmetry of Pr ions is $T_h$ (Fig. 2-1). This is differentiated from the cubic $O_h$ symmetry by the fact that do not contain two types of symmetry operations of $O_h$: $C_4$ (rotations through $\pi/2$ about the fourfold symmetry axis) and $C'_2$ (rotation through $\pi$ perpendicular to the principle rotation axis [14]). We recall that if the $z$ axis is not an $m$-fold axis symmetry, the potential will contain $V^m_n$ [10].

Therefore, the Hamiltonian will contain a new term:

$$H_{CEF} = W \left[ x \frac{O_4^0 + 5O_4^4}{F(4)} + (1 - |x|) \frac{O_6^0 - 21O_6^4}{F(6)} + y \frac{O_6^2 - O_6^6}{F^t(6)} \right],$$  \hspace{1cm} (2-17)$$

where the coefficients $F(4)$, $F(6)$, and $F^t(6)$ are 40, 1260, and 30 respectively [15]. The new term $O_6^2 - O_6^6$ has the following symmetry in Cartesian coordinates:

$$x^2y^2(x^2 - y^2) + y^2z^2(y^2 - z^2) + z^2x^2(z^2 - x^2).$$  \hspace{1cm} (2-18)$$
When parameter $y$ is zero, the system reduces to $O_h$ symmetry. The eigenvalues are tabulated for $x=0.6$ and several values of $y$ by Shiina et al. [15]

$$ \Gamma_1 : \frac{\sqrt{30}}{12} (|+4\rangle + |-4\rangle) + \frac{\sqrt{21}}{6} |0\rangle $$

$$ \Gamma_{23} : \sqrt{\frac{7}{24}} (|+4\rangle + |-4\rangle) - \sqrt{\frac{5}{24}} |0\rangle $$

$$ \sqrt{\frac{1}{2}} (|+2\rangle + |-2\rangle) $$

$$ \Gamma_4^{(1)} : -a_1 | -4\rangle - a_2 | -2\rangle + a_2 | +2\rangle + a_1 | +4\rangle $$

$$ b_1 | \mp 3\rangle + b_2 | \mp 1\rangle + b_3 | \pm 1\rangle + b_4 | \pm 3\rangle $$

$$ \Gamma_4^{(2)} : a_2 | -4\rangle - a_1 | -2\rangle + a_1 | +2\rangle - a_2 | +4\rangle $$

$$ b_2 | \mp 3\rangle - b_1 | \mp 1\rangle - b_4 | \pm 1\rangle + b_3 | \pm 3\rangle $$

If $y=0$, the eigenstates are those for $O_h$ symmetry [13]

$$ \Gamma_1 : \frac{\sqrt{30}}{12} (|+4\rangle + |-4\rangle) + \frac{\sqrt{21}}{6} |0\rangle $$

$$ \Gamma_3 : \sqrt{\frac{7}{24}} (|+4\rangle + |-4\rangle) - \sqrt{\frac{5}{24}} |0\rangle $$

$$ \sqrt{\frac{1}{2}} (|+2\rangle + |-2\rangle) $$

$$ \Gamma_4 : \pm \sqrt{\frac{1}{8}} | \mp 3\rangle \mp \sqrt{\frac{7}{8}} | \pm 1\rangle $$

$$ \sqrt{\frac{1}{2}} (|+4\rangle - |-4\rangle) $$

$$ \Gamma_5 : \pm \sqrt{\frac{1}{8}} | \mp 3\rangle \mp \sqrt{\frac{1}{8}} | \mp 1\rangle $$

$$ \sqrt{\frac{1}{2}} (|+2\rangle - |-2\rangle) $$
Depending on the sign of the $W$ parameter (or $E$), the ground state can be thought as either $\Gamma_{23}$ or $\Gamma_1$ (Fig. 2-2).

The eigenfunctions and eigenvalues of $\Gamma_1(T_h)$ and $\Gamma_{23}(T_h)$ are the same as those of $\Gamma_1(O_h)$ and $\Gamma_3(O_h)$, therefore are not affected by $O_6^t$ from the Hamiltonian. When $y=0$, $\Gamma_4^{(1)}(T_h)$ has the same eigenfunctions and eigenvalues as $\Gamma_4(O_h)$, and $\Gamma_4^{(2)}$ as those for $\Gamma_5(O_h)$. When $y \neq 0$, $\Gamma_4$ and $\Gamma_5$ mix resulting in two $\Gamma^{(1,2)}(T_h)$ [15]. Therefore, the eigenfunctions and eigenvalues of CEF for $T_h$ and $O_h$ are different. The $O_6^t$ term in Hamiltonian affect some eigenfunctions and eigenvalues, resulting in a change of the transition probabilities of neutron scattering in Pr$^{3+}$.

2.2 Conduction Electron Mass Enhancement ($m^*$) Mechanism in PrOs$_4$Sb$_{12}$

This Section gives a review on the mechanisms believed to be responsible for the conduction electron mass enhancement: the single-ion models, such as quadrupolar Kondo effect, or virtual CEF excitations (Fulde-Jensen model for $m^*$ enhancement in Pr metal) and comment on the cooperative model invoking proximity to the long-range order.

2.2.1 Quadrupolar Kondo Effect

The quadrupolar Kondo (QK) model of HF was initially proposed by Cox to explain weak field dependence of the specific heat of UBe$_{13}$ [16, 17]. Barnes [18] found that Cu$^{2+}$ ions in the cuprate superconductors could lead to such a Kondo effect as well. Later, new evidence believed to be hallmarks of a quadrupolar Kondo effect has been found in the alloys Y$_{1-x}$U$_x$Pd$_3$ [19–22] for $x=0.1$ and 0.2.

In UBe$_{13}$, the total angular momentum of U$^{4+}$ ($5f^2$ configuration) is $J=4$. This leads [13] to a $\Gamma_3$ CEF ground state for about half the crystal field parameter range (Fig. 2-2). The $f^2$ configuration is expected also for Pr$^{3+}$ in PrOs$_4$Sb$_{12}$, and, according to CEF calculations of Lea, Leask, and Wolf [13], a $\Gamma_3$ doublet CEF ground state is very probable (Fig. 2-2). Therefore, the heavy fermion behavior in PrOs$_4$Sb$_{12}$ could be in principle due to a QK effect. Also, the physical properties of UBe$_{13}$ (and U$_{1-x}$Th$_x$Be$_{13}$) are highly
Table 2-1. The relevant states for the quadrupolar Kondo effect for U$^{4+}$. The last two columns are the projections of the magnetic and quadrupolar moments respectively (Reprinted with permission from Cox and Zavadowski [23]).

<table>
<thead>
<tr>
<th>Config.</th>
<th>State</th>
<th>$J$</th>
<th>Eigenstate</th>
<th>$\langle J_z \rangle$</th>
<th>$\langle 3J_z^2 - J(J+1) \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f^2$</td>
<td>$</td>
<td>\Gamma_3+\rangle$</td>
<td>4</td>
<td>$\sqrt{\frac{7}{24}}</td>
<td>4\rangle -</td>
</tr>
<tr>
<td>$f^2$</td>
<td>$</td>
<td>\Gamma_3-\rangle$</td>
<td>4</td>
<td>$\sqrt{\frac{1}{2}}</td>
<td>2\rangle +</td>
</tr>
<tr>
<td>$f^1$</td>
<td>$</td>
<td>\Gamma_7+\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$\sqrt{\frac{1}{6}}</td>
<td>\frac{5}{2}\rangle - \sqrt{\frac{5}{6}}</td>
</tr>
<tr>
<td>$f^1$</td>
<td>$</td>
<td>\Gamma_7-\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$\sqrt{\frac{1}{6}}</td>
<td>\frac{5}{2}\rangle - \sqrt{\frac{5}{6}}</td>
</tr>
<tr>
<td>$c^1$</td>
<td>$</td>
<td>\Gamma_8+2\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$\sqrt{\frac{5}{6}}</td>
<td>\frac{5}{2}\rangle + \sqrt{\frac{1}{6}}</td>
</tr>
<tr>
<td>$c^1$</td>
<td>$</td>
<td>\Gamma_8-2\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$\sqrt{\frac{1}{6}}</td>
<td>\frac{5}{2}\rangle - \sqrt{\frac{1}{6}}</td>
</tr>
<tr>
<td>$c^1$</td>
<td>$</td>
<td>\Gamma_8+1\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$</td>
<td>\frac{1}{2}\rangle$</td>
</tr>
<tr>
<td>$c^1$</td>
<td>$</td>
<td>\Gamma_8-1\rangle$</td>
<td>$\frac{5}{2}$</td>
<td>$</td>
<td>-\frac{1}{2}\rangle$</td>
</tr>
</tbody>
</table>

reminiscent of those of PrOs$_4$Sb$_{12}$. Thus, since the discovery of the HF state in PrOs$_4$Sb$_{12}$ its normal properties have been associated with the QK effect.

The states involved in the quadrupolar Kondo effect for U$^{4+}$ are given in Table 2-1. The doubly degenerate ground state can be treated as a two-level system (a manifold with a pseudo-spin of $\frac{1}{2}$). The projected value of the electric quadrupole moment onto the $\Gamma_3$ basis is $|Q_{zz}| = |3J_z^2 - J(J+1)| = \pm 8$ and the projected value of the magnetic dipole moment is zero, i.e. $|J_z| = 0$ (Table 2-1). Therefore, the coupling is between the electric quadrupole moment and the conduction electrons.

The Anderson model for the relevant states of the quadrupolar Kondo effect (since it considers only $\Gamma_3$, $\Gamma_7$, and $\Gamma_8$) is called the 3-7-8 model. Figure 2-3 shows a schematic representation of the Anderson model relevant for U$^{4+}$ ions in the cubic symmetry. The ground state $\Gamma_3$ ($J=4$, 4$f^2$) and first excited $\Gamma_7$ ($J=5/2$, 5$f^1$) mix only via the conduction partial waves $\Gamma_8$ ($J=5/2$, $c^1$). The transition $f^1 \rightarrow f^2$ is done by removing a conduction electron and the transition $f^2 \rightarrow f^1$ is done by emitting a conduction electron. It can
be shown that only $\Gamma_8$ conduction quartet partial waves (Table 2-1) may couple to the impurity through hybridization [23] (or, in the group theory framework, $\Gamma_3 \otimes \Gamma_7 = \Gamma_8$).

Applying a canonical transformation (Schrieffer and Wolff [24]) to the 3-7-8 model, the hybridization term can be eliminated. Also, the transformation yields to an effective exchange interaction between pseudospin-$\frac{1}{2}$ and electric quadrupole moments of the form

$$H_{\text{exchange}} = -2J_{\text{exchange}} \sigma_3 \cdot [\sigma_8(0) + \sigma_{\bar{8}}(0)], \quad (2-27)$$

where $\sigma_3$ is a pseudospin-$\frac{1}{2}$ matrix for the $\Gamma_3$ quadrupole, $\sigma_8(\sigma_{\bar{8}})$ are the pseudospins formed from the $\Gamma_8 + 2$, $\Gamma_8 + 1$ ($\Gamma_8 - 2$, $\Gamma_8 - 1$) partial waves (Table 2-1). The exchange integral $J_{\text{exchange}}$ is proportional to $\Gamma/\pi\epsilon_f N(0)$ and is negative.

The Hamiltonian has a two-channel Kondo form; two degenerate species of conduction electrons couple with identical exchange integrals $J_{\text{exchange}}$ to the local $\sigma_3 = \frac{1}{2}$ object. The channel indices are the magnetic indices of the local conduction partial wave states. Figure 2-4 shows schematically the mapping of the quadrupolar Kondo to the two-channel Kondo model. The two-channel quadrupolar form of the Hamiltonian tell us that the conduction electron orbital motion can screen the $U^{4+}$ quadrupole moment equally well for magnetic spin-up and magnetic spin-down electrons.

### 2.2.1.1 Thermodynamic Properties of the Quadrupolar Kondo Model

Figure 2-5 shows the thermodynamic properties of the quadrupolar Kondo model [25–27]. The susceptibility (Fig. 2-5, lower panel) diverges logarithmic at $T=0$, $\chi = -(e\pi T_H)^{-1} \ln(H/T_H)$, where $T_H = (\pi/e)T_K$ [28, 29]. Here, $e$ is the base of $\ln$, i.e. 2.71... In the quadrupolar Kondo model this corresponds to a divergent quadrupolar susceptibility. For $T \to 0$, the free energy in zero field is $F = -\frac{1}{2}T \ln 2$. Therefore, the zero-temperature zero-field entropy is equal to $\frac{1}{2} \ln 2$ [25]. The non-zero entropy at $T \to 0$ is consistent with the divergence in susceptibility and argues in favor of a non-singlet ground state (a singlet is the ground state for the standard Kondo model). As expected, the entropy increases monotonically with temperature and reaches asymptotically the $\ln 2$
value (free $\frac{1}{2}$ spin) at high $T$. Also, the $T=0$ entropy increases with the field. Since the $S(T = 0)$ decreases with $H$ the specific heat increases with $H$ at intermediate $T$ resulting in large values of $\gamma$, common for heavy fermion systems. At high $T$ the pseudo-spin is free, therefore $S = \ln 2$. The entropy change $\Delta S(H) = S(T = \infty, H) - S(T = 0, H)$ increases with $H$ from $\frac{1}{2} \ln 2$ to $\ln 2$ for large $H$. In the $C/T$ plots the Kondo peaks can be seen.

The initial measurements of specific heat [16] were not conclusive for a quadrupolar Kondo effect in UBe$_{13}$. Also, more recent measurements of nonlinear susceptibility [30] are inconsistent with the quadrupolar ($5f^2$) ground state of the uranium ion, indicating that the low-lying magnetic excitations of UBe$_{13}$ are predominantly dipolar in character.

2.2.1.2 Relevance for the Case of Pr$^{3+}$ Ion in PrOs$_4$Sb$_{12}$

PrOs$_4$Sb$_{12}$ has been initially reported to have a $\Gamma_3$ doublet CEF ground state [7]. Later experiments [31–33] established the crystalline electric field (CEF) ground state of the Pr$^{3+}$ ion in the cubic symmetry environment of PrOs$_4$Sb$_{12}$ ($T_h$ point group symmetry) as the non-magnetic singlet $\Gamma_1$. The consequence of this is that the original formulation of the quadrupolar Kondo effect cannot be applied to the conduction electron mass enhancement in PrOs$_4$Sb$_{12}$.

$\Gamma_1$ is nearly degenerate with the $\Gamma_4^{(2)}$ triplet. Though $\Gamma_1$ itself doesn’t carry any degrees of freedom, the pseudo-quadruplet constituted by $\Gamma_1$ and $\Gamma_4^{(2)}$ is speculated to have magnetic and quadrupolar degrees of freedom [34], and therefore a magnetic or quadrupolar Kondo effect is invoked to explain the enhancement of the effective mass of the quasi-particles.

On the other hand, the model does not seem to be relevant since the predicted properties of the quadrupolar Kondo effect are in disagreement with the measurements. But this is a single-ion model. Possibly, intersite effects are responsible for the disagreements. There is no lattice quadrupolar model.
2.2.2 Fulde-Jensen Model for $m^*$ Enhancement in Pr Metal

The mass of the conduction electrons can be enhanced by the interactions with various low-lying excitations in the solid. This explains the strong dependence of the specific heat of the Pr metal in magnetic fields found by Forgan [35].

Goremychkin et al. [32] proposed that the mass enhancement in PrOs$_4$Sb$_{12}$ can be explained by a balance between two types of interactions, magnetic dipolar and quadrupolar between conduction and the $f$ electrons of Pr. The theory of Fulde and Jensen [36] of conduction electron mass enhancement ascribes this to the inelastic scattering by crystal field transitions in a singlet ground-state system. The mass enhancement of the conduction electrons are due to their interaction with the magnetic excitations.

The relevant Hamiltonian describing the interaction between the conduction electrons and the rare-earth localized moments is [36]

$$H_{int} = -I_{sf}(g_L - 1) \sum_n \vec{\sigma}(\vec{R}_n) \cdot \vec{J}_n,$$

where $I_{sf}$ is the exchange integral, $g_L$ is the Landé factor, $\vec{J}_n$ is the total angular momentum of a rare-earth ion at site $\vec{R}_n$, and $\vec{\sigma}$ are Pauli matrices.

The mass enhancement due to the inelastic transition at energy $\Delta$ between two levels, $|i\rangle$ and $|j\rangle$, is

$$\frac{m^*}{m} = 1 + (g_J - 1)^2I_{sf}^2N(0)\frac{2}{\Delta} \left| \langle i \, | \, J \, | \, j \rangle \right|^2,$$

where $g_J$ is the Landé factor, $I_{sf}$ is the exchange integral coupling the conducting electrons to the $f$-electrons, $N(0)$ is the conduction electron density of states at the Fermi level, and $\langle i \, | \, J \, | \, j \rangle$ is the magnetic dipole matrix element calculated using the derived crystal field parameters. This formula shows that for a small excitation energy $\Delta$ leads to a large enhancement in $m^*$.

2.2.3 Fluctuations of the Quadrupolar Order Parameter

In general, models involving spin fluctuations in heavy fermions around their antiferromagnetic instability were considered by authors such as Hertz [37], Millis [38],
Moriya and Takimoto [39] (a complete review is given by Stewart [40, 41]). All these models exhibit divergence of the low temperature specific heat.

By analogy, in PrOs$_4$Sb$_{12}$, the quadrupole fluctuations of Pr ions are believed to play an important role in the HF-SC properties. Therefore, another model proposed (a collective-type model) for the mass enhancement mechanism are due to the fluctuations of the antiferroquadrupolar order parameter due to the proximity to the AFQ ordered phase.

PrOs$_4$Sb$_{12}$ exhibits an antiferroquadrupolar ordered phase in fields between about 4.5 and 14 T. For fields 5–13 T the two lowest CEF levels are sufficiently close to form a pseudo-doublet with quadrupolar and magnetic degrees of freedom, resulting in a long range order.

There is no theory (to this moment) that describes the mass enhancement due to the fluctuations of the quadrupolar order parameter. Our magnetoresistivity data of PrOs$_4$Sb$_{12}$ and La alloys presented in Chapters 6 and 7 seem to support this mass enhancement mechanism.

![Rotational symmetry $T_h$.](image)

Figure 2-1. Rotational symmetry $T_h$. In the left (a), the small bold blue segment is assimilate with the distance between two antimony atoms belonging to the same icosahedra. A $\pi$ rotation with respect to (1 0 0) and a $\frac{2\pi}{3}$ rotation with respect to (1 1 1) are allowed. The $\frac{\pi}{2}$ rotation with respect to (1 0 0) will not turn the structure into an equivalent one. Therefore, the axes $x$ (or (1 0 0)) and $y$ (or (0 1 0)) are not equivalent (Reprinted with permission from D. Vu Hung [42]).
Figure 2-2. Lea, Leask, and Wolff’s representation of CEF for $J=4$ (Redrawn with permission from Lea et al. [13]).

Figure 2-3. Representation of the $U^{4+}$ ions in cubic symmetry undergoing quadrupolar Kondo effect. The model involves a doublet ground state in each of the two electronic lowest-lying configurations: $f^2$ having the quadrupolar or non-Kramers $\Gamma_3$ doublet, and $f^1$ configuration having the magnetic or Kramers $\Gamma_7$ doublet. The conduction electrons mix the two configurations through a hybridization process. The $\Gamma_8$ conduction state couples these two doublets (Redrawn with permission from Cox and Zawadowski [23]).
Figure 2-4. Mapping of the quadrupolar Kondo Hamiltonian onto the two-channel Kondo model. a) The standard two-channel Kondo model in spin space: two conduction electrons $s_{c+}$ and $s_{c-}$ couple antiparallel to the impurity spin $S_I$. b) In the quadrupolar Kondo case, the spin is due by the quadrupolar or orbital deformations. The two channels come from the real magnetic spin of the conduction electrons. The orbital motion of the electrons produces the screening of the $U^{4+}$ orbital fluctuations (Redrawn with permission from Cox and Zavadowski [23]).

Figure 2-5. $S$, $C$, $C/T$, and $\chi$ versus $T/T_K$ of the quadrupolar Kondo model (Reprinted with permission from Sacramento and Schlottmann [27]).
CHAPTER 3
PROPERTIES REVIEW OF THE PrOs$_4$Sb$_{12}$

3.1 Crystalline Structure

PrOs$_4$Sb$_{12}$ (praseodymium osmium antimonide) is a filled skutterudite that crystalizes into a LaFe$_4$P$_{12}$-type body-centered cubic structure with the lattice parameter $a=9.3068$ Å[$^{43}$] ($a=9.30311$ Å[$^{44}$] after more recent measurements), space group $Im\bar{3}$, and $Th$ point group symmetry. The crystallographic arrangement of the atoms is given in Fig. 3-1. The mass of a mole of PrOs$_4$Sb$_{12}$ is 2363.1 g, the molar volume is $242.3 \times 10^{-6} \text{m}^3/\text{mol Pr}$ and the mass density is $9.75 \text{g/cm}^3$ [$^{45}$]. LaOs$_4$Sb$_{12}$ is the non-$f$ equivalent of PrOs$_4$Sb$_{12}$ with a similar crystal structure. All the exotic phenomena of PrOs$_4$Sb$_{12}$ are thought to be associated with its unique crystal structure. In particular, the large coordination number of Pr ions surrounded by 12 Sb and 8 Os ions leads to strong hybridization between the $4f$ and conduction electrons [$^{46}$]. This strong hybridization results in a rich variety of strongly correlated electron ground states and phenomena.

3.1.1 Rattling of Praseodymium Atom

In CoAs$_3$-type skutterudites whose name come from the cobalt arsenide mineral that was first found in Skutterud, Norway, an alkali metal, alkaline earth, rare earth, or actinide ion, occupies an atomic cage. The icosahedron shaped atomic cage made of Sb atoms accommodates a rare earth ion, and the size of this cage is bigger than the radius of the ion. Therefore, the rare earth ion will vibrate as a result of the weakly bounded rare-earth ion in the oversized cage made of Sb ions. This anharmonic oscillation is called rattling [$^{47}$]. The consequence is a reduction of the thermal conductivity. The filled skutterudites with the cage are favorable for a thermoelectric device possessing a high coefficient of merit [$^{48}$].

The amplitude of this vibration of the Pr ion in PrOs$_4$Sb$_{12}$ is about 8 times bigger than the amplitude of Os. EXAFS data [$^{49}$] supports the idea of a rattling Pr filler ion (based on the low Einstein temperature $\Theta_E \sim 75$ K) within a fairly stiff cage in this material. Besides the dynamic movement, a static displacement was detected in which
there are two equilibrium positions for the Pr ions. The Pr ions can freeze in one of these two equilibrium positions, and at low temperature they can pass from one position to another through tunnel effect. It has been estimated that this displacement is about 0.07 Å [49]. Goto et al. [50], based on a theory of Cox et al. [23], suggested that the tunnel effect between the two positions of the Pr ions could be linked to the appearance of the superconductivity.

3.1.2 Valence

At high temperature (above 150 K) the $\chi(T)$ of PrOs$_4$Sb$_{12}$ can be described by a Curie-Weiss law with an effective moment $\mu_{\text{eff}}=2.97\mu_B$ as reported by Bauer et al. [7], or $\mu_{\text{eff}}=3.5\mu_B$ as reported by Tayama et al. [51], and a Curie-Weiss temperature $\Theta_{\text{CW}}=-16$ K [7]. The effective moment found is somewhat lower than the moment of a free ion Pr$^{3+}$ which has $\mu_{\text{eff}}=3.58\mu_B$ [52].

X-ray-absorption fine-structure (XAFS) measurements [49] carried out at the Pr $L_{\text{III}}$ and Os $L_{\text{III}}$ edges on PrOs$_4$Sb$_{12}$ suggest that the Pr valence is very close to 3+. Each Pr ion has two electrons on the $f$ shell (4$f^2$ electronic structure).

3.1.3 Crystalline Electric Fields

In an ionic (localized) model, the cubic crystalline electric field of PrOs$_4$Sb$_{12}$ environment splits the $J=4$ Hund’s rule multiplet of non-Kramers Pr$^{3+}$ into a singlet ($\Gamma_1$), a doublet ($\Gamma_3$), and two triplets ($\Gamma_4$ and $\Gamma_5$) (in the $O_h$ symmetry notation). The CEF Hamiltonian in cubic symmetry was written [13] in terms of the ratio of the fourth and sixth order terms of angular momentum operator of the CEF potential, $x$, and an overall energy scale factor $W$. For more than two decades, the symmetry was thought as $O_h$, instead of $T_h$.

Bauer et al. [7] fitted the magnetic susceptibility data (see Fig. 3-2) by a CEF model in which the ground state was chosen to be either the non-magnetic $\Gamma_1$ singlet ($W>0$) or the non-magnetic $\Gamma_3$ doublet ($W<0$). The peak present in the $\chi(T)$ data was thought to be produced when the first excited state is a triplet $\Gamma_5$ with a energy <100 K above
the ground state and corresponds to a position \( x \) close to the crossing points on the LLW diagram (see Fig. 2-2) where \( \Gamma_1 \) or \( \Gamma_3 \) are degenerate with \( \Gamma_5 \). The results are presented in the upper panel of Fig. 3-2. The notation of the CEF energy levels corresponds with the initially assumed \( O_h \) symmetry by Maple et al. [53] and Bauer et al. [54].

These authors use the conventional cubic crystal field model which is applicable to the \( O, T_d \) and \( O_h \) symmetries. In the \( T_h \) symmetry, the non-Kramers doublet \( \Gamma_3 \) corresponds to the degenerate \( \Gamma_2 \) and \( \Gamma_3 \) singlet states (denoted as \( \Gamma_{23} \)) and \( \Gamma_4 \) and \( \Gamma_5 \) states coincide with \( \Gamma_4^{(1)} \) and \( \Gamma_4^{(2)} \) triplet states, respectively, when last term is zero in the crystal field Hamiltonian (2-17). The singlet state \( \Gamma_1 \) is the same for both cases.

The last term of equation (2-17) is unique to the \( T_h \) symmetry of this material coming from the atomic configuration of Sb ions in the crystal [15] and is absent in the conventional cubic crystal field Hamiltonian that Maple et al. [53] and Bauer et al. [54] used. The omitting of the last term in the Hamiltonian (see equation 2-17) has implications in the interpretation of the inelastic neutron scattering data.

The above mentioned fit reproduces the overall shape of the low temperature peak, and also the value of the van Vleck paramagnetic susceptibility with an effective moment close to, but somewhat lower than that, of the free \( \text{Pr}^{3+} \) ion. Bauer et al. [7] fitted \( C \) assuming a degenerate spectrum.

Specific heat data was fitted [7] by a system with two levels of equal degeneracy split by an energy \( \delta = 6.6 \text{ K} \) (it has been assumed that the degeneracy of any level is lifted by CEF when the local site symmetry of the \( \text{Pr}^{3+} \) ions is not cubic as a result of some kind of local distortion).

The entropy in the \( \Gamma_3-\Gamma_5 \) case was found to be \( S_{\Gamma_3-\Gamma_5} = R \ln 2 \approx 7.6 \text{ J/(mol K)} \) [7]. The total entropy of the broad peak just above the transition is \( S = \int (C(T)/T) dT \approx 10.3 \text{ J/(mol K)} \). The closeness in values made Bauer et al. [7] to favor the \( \Gamma_3 \) ground state scenario.
Initial inelastic neutron scattering measurements\cite{53} considering $O_h$ symmetry suggest that $\Gamma_3$ is the CEF ground state in PrOs$_4$Sb$_{12}$. The resistivity data measurements were also interpreted in the framework of a $\Gamma_3$ CEF ground state\cite{55}.

In contrast, Tayama et al.\cite{51} obtained a somewhat better fit of the magnetic susceptibility $\chi(T)$ data by a $\Gamma_1$ CEF ground state model (Fig. 3-3 (a)). Also, the theoretical curves of $S(T)$ based on $\Gamma_1$ ground state model show increase of entropy with fields (lower panel of Fig. 3-3 (b)). This trend is confirmed by magnetic field specific heat measurements (Fig. 3-3 (c)) by Aoki et al.\cite{56}.

Therefore, zero or small magnetic fields data are contradictory, more experiments are to be done in order to establish the true CEF ground state in PrOs$_4$Sb$_{12}$.

### 3.2 Normal-State Zero-Field Properties

#### 3.2.1 Specific Heat

PrOs$_4$Sb$_{12}$ was synthesized for the first time by Jeitschko et al.\cite{43}, and then by Braun et al.\cite{57}. It was in 2002 when Bauer et al.\cite{7} discovered superconductivity in PrOs$_4$Sb$_{12}$. Since the discontinuity in specific heat is of the order of $\gamma$, this large value discontinuity $(\Delta(C/T)|_{T_c=1.85K} \sim 500 \text{ mJ/K}^2 \text{ mol}[7])$ implies the presence of heavy fermions both in the normal and superconducting states.

There is no consensus regarding the precise value of $\gamma$, but all the reported values imply heavy fermion behavior. Actually, this is perhaps the strongest evidence for HF states in PrOs$_4$Sb$_{12}$. Considering the relation $\Delta(C/\gamma T_c)=1.43$ the Sommerfeld coefficient $\gamma$ is found to be $\sim 350 \text{ mJ/K}^2 \text{ mol}$. The phonon (lattice) contribution to the specific heat $C$ data can be described by $\beta T^3$ that is identified with specific heat of LaOs$_4$Sb$_{12}$ with $\Theta_D=304 \text{ K}$. $\beta$ is related to $\Theta_D$ by $\beta=(1944\times 10^3)n/\Theta_D^3$, where $n$ is the number of atoms in the formula unit (e.g., $n=17$ in LaOs$_4$Sb$_{12}$).

#### 3.2.2 de Haas van Alphen Measurements

The Fermi surface (FS) as reconstructed by de Haas van Alphen (dHvA) measurements\cite{44} comparative with the bands structure (LDA+U method\cite{58}) are presented in
Fig. 3-5. The topology of the FS of PrOs$_4$Sb$_{12}$ is very similar to that of the reference compound LaOs$_4$Sb$_{12}$ [44] (which leaks 4$f$ electrons). This indicates that the 4$f^2$ electrons in PrOs$_4$Sb$_{12}$ are well localized. The similar topology of the FS for the two compounds is supported also by similar angular dependence of the dHvA. Three Fermi surface sheets, including two closed (practically spherical shaped) and one multi-connected, were identified in agreement with the calculations.

The effective masses measured by dHvA are between 2.4 and 7.6$m_0$ ($m_0$ is the free electron mass). These values are well below the ones reported from the specific heat measurements. These low values have been explained [59] in the framework of the two-band superconductivity model in which band 2 corresponds to the light band detected by dHvA measurements. Band 1 is a heavy band having most of the density of states. The heaviest quasiparticles are seen in thermodynamic measurements ($C$ or $H_{c2}$) only. However, the applicability of the two-band model to PrOs$_4$Sb$_{12}$ is not established. Further more, our results presented in section 7.6 sheds some doubts in the interpretation.

### 3.2.3 Resistivity

Additional evidence for heavy fermion behavior in PrOs$_4$Sb$_{12}$ is provided by an analysis of the slope of the upper critical field $H_{c2}$ near $T_c$. The upper panel of Fig. 3-2(a) shows resistivity versus $T$. From the resistivity data in small magnetic fields (data not shown, fields up to about 30 kOe) and from the fit of the linear part of $-(dH_{c2}/dH)_{T_c}$ curve, the initial slope has been measured using the BCS relations and shown to be $\sim$19 kOe/K [7]. This implies $\xi_0 \sim$116 Å, $v_F$=$1.65\times10^6$ cm/s, and $m^* \sim$50$m_0$. This calculation assumes a spherical Fermi surface.

The resistivity data between 8 and 40 K revealed a $T^2$ dependence $\rho_0+AT^2$, with $A=0.009 \mu\Omega\text{cm}/K^2$ [7]. The $A$ coefficient is about two orders of magnitude smaller than the value expected for a heavy fermion compound. Considering the Kadowaki-Woods universal relation [60] between $A$ and $\gamma$, $A/\gamma^2 = 1 \times 10^{-5}\mu\Omega\text{cm mol}^2\text{K}^2\text{mJ}^{-2}$. The $\gamma$ value
is only \(\sim 6.5 \text{ mJ/mol K}^2\) \([7]\), and this is a typical value for normal metals and is much smaller than \(\gamma\) of LaOs\(_4\)Sb\(_{12}\).

### 3.2.4 DC Magnetic Susceptibility

The \(\chi(T)\) data (Fig. 3-2(a), lower panel) exhibits a peak at \(\sim 3\) K and saturates to a value of about 0.1 emu/mol \([7]\) as \(T \to 0\). This is the hallmark of a nonmagnetic ground state. Above 150 K, \(\chi(T)\) of PrOs\(_4\)Sb\(_{12}\) can be described by a Curie-Weiss law. There is a large discrepancy between the high temperature effective moment reported by various research groups. The effective moment according to Bauer et al. \([7]\) is \(\mu_{\text{eff}} = 2.97 \mu_B\), and \(\mu_{\text{eff}} = 3.5 \mu_B\) is the value reported by Tayama et al. \([51]\) The free ion Pr\(^{3+}\) has a high temperature effective moment of 3.58\(\mu_B\) \([52]\). The Curie-Weiss temperature is \(\Theta_{\text{CW}} = -15\) K \([51]\).

From the diamagnetic onset (inset (ii), Fig. 3-4(a)) it is found that the temperature of the superconducting transition \(T_c\) is equal to the value found from the specific heat measurements.

### 3.3 The Long-Range Order in Magnetic Fields

Measurements of specific heat \([56]\) in fields up to 8 T and resistivity \([55]\) in magnetic fields up to about 10 T revealed the existence of a field induced ordered phase (FIOP) above 4.5 T. In this Chapter a discussion of the nature of the FIOP will be presented along with the specific heat data that completes the magnetic phase diagram. A similar phase diagram has been obtained later by magnetization \([51, 61]\)(see Fig. 3-6) and by thermal expansion and magnetostriction measurements \([62]\).

### 3.4 Superconductivity

Experiments on PrOs\(_4\)Sb\(_{12}\) imply the possibility of unconventional superconductivity (i.e., the existence of nodes in the gap of the Fermi surface). There is still some other evidence that suggests an isotropic SC gap. We present below experimental evidence favoring either unconventional or conventional superconductivity.
3.4.1 Unconventional Superconductivity

3.4.1.1 The Double Transition

Initial specific heat measurements [7] showed a single superconducting transition at $T_c$ of 1.85 K. Higher quality materials revealed actually two superconducting transitions (Vollmer et al. [63], Maple et al. [53], Oeschler et al. [64]). In Figure 3-7 panels (a) and (b) are shown specific heat of PrOs$_4$Sb$_{12}$ presenting two superconducting transitions, $T_{c2}$=1.75 K and $T_{c1}$=1.85 K by Vollmer et al. [63], and $T_{c2}$=1.716 K and $T_{c1}$=1.887 K by Méasson et al. [59], respectively. Two superconducting transitions at the same temperatures have been reported by Cichorek et al. [65] along with a speculation for a third superconducting transition at $\sim$0.6 K inferred from $H_{c1}$ measurements. It is believed that inclusions of the free Os in the single crystal cannot be responsible for the enhancement of $H_{c1}$, though $T_c$ of pure Os is 0.66 K [66] based on sensitive X-ray and electron microprobe studies [65].

There are two classes of explanations of the nature (intrinsic or not) of the double transition. One argues in favor of two different parts of the sample with two different superconducting phases, and therefore with different $T_c$’s. Thus, the quality of the samples is crucial. For instance it has been considered [59] that despite the sharp specific heat transitions, the samples still present spatial inhomogeneities. One possibility would be an inhomogeneous coexistence of two electronic configurations of Pr, $4f^1$ and $4f^2$. The high temperature magnetic susceptibility measurements are in favor of $4f^2$, since they have found [51] an effective moment $\mu_{eff}=3.6\mu_B$/Pr (the expected value for $4f^1$ is $2.54\mu_B$ and for $4f^2$ is $3.58\mu_B$).

Another possible scenario that is presented in this dissertation is the existence of inhomogeneities due to the closeness of the system to a long range antiferro-quadrupolar order: clusters with a short-range order would have different superconducting parameters than the remaining part of the sample.
Figure 3-7 (c) shows ac susceptibility after Méasson et al. [59]. The nature of the two transitions is not yet established. The width of the transition as measured by specific heat and ac-susceptibility is the same, about 0.2 K.

The superconducting gap structure investigated using thermal transport measurements in magnetic field rotated relative to the crystal axes by Izawa et al. [67] provides another evidence for the unconventional character of superconductivity in PrOs$_4$Sb$_{12}$. The change in the symmetry of the superconducting gap function that occurs deep inside the superconducting state gives a clear indication of the presence of two distinct superconducting phases with twofold and fourfold symmetries (Fig. 3-8). The gap functions in both phases have a point node singularity which is in contrast to the line node singularity observed in almost all unconventional superconductors. The two-band superconductivity (similar to that observed in MgB$_2$) is observed in newer thermal conductivity measurements [68].

A double transition can be seen in the thermal expansion [64] experiment (Fig. 3-9). The two transitions are at the same temperatures at which the specific heat discontinuities occur. Using the Ehrenfest equation $\frac{\partial T_c}{\partial P} = V_m T_c \Delta \beta / \Delta C$, where $V_m$ is the molar volume, calculations show that the superconducting transitions $T_{c2}$ is decreased two times faster under pressure than $T_{c1}$. This is in favor of intrinsic nature of the two superconducting transitions.

### 3.4.1.2 Temperature Dependence of Specific Heat Below $T_c$

In general, the specific heat $C$ below $T_c$ exhibits different temperature dependence according to the topology of the superconducting gap $\Delta_s(\vec{k})$. For an open gap the specific heat dependence is the well known exponential $e^{-\Delta_s/\bar{T}}$. Nodes in the gap, or zero points in the gap, will be reflected in the $T$ dependence of the specific heat as a power $T^3$ dependence. And for zero line in the gap, the temperature dependence of $C$ is $T^2$. 

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Table 3-1. The $\alpha$ values reported by different groups, extracted from fits of specific heat below $T_c$ (Reprinted with permission from Grube et al. [70]).

<table>
<thead>
<tr>
<th>Specific heat data</th>
<th>$\alpha = \Delta(0)/(k_B T_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grube et al. [70]</td>
<td>$3.7\pm0.2$</td>
</tr>
<tr>
<td>Vollmer et al. [63]</td>
<td>$2.6\pm0.2(\Gamma_3)$</td>
</tr>
<tr>
<td>Frederick et al. [71]</td>
<td>$3.1\pm0.2(\Gamma_1)$</td>
</tr>
<tr>
<td>Frederick et al. [71]</td>
<td>$3.6\pm0.2(\Gamma_3)$</td>
</tr>
</tbody>
</table>

Table 3-2. The $\alpha$ values reported by different groups from measurements other than specific heat (Reprinted with permission from Grube et al. [70]).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\alpha = \Delta(0)/(k_B T_c)$</th>
<th>Gap Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunneling spectroscopy [72]</td>
<td>1.7</td>
<td>Nearly isotropic</td>
</tr>
<tr>
<td>$\mu$SR [73]</td>
<td>2.1</td>
<td>Nearly isotropic</td>
</tr>
<tr>
<td>$\lambda(T)$ [74]</td>
<td>2.6</td>
<td>Point nodes</td>
</tr>
<tr>
<td>Sb NQR [75]</td>
<td>2.7</td>
<td>Isotropic</td>
</tr>
</tbody>
</table>

In all reported data the specific-heat measurements exhibit a rapid decrease of $C$ below the superconducting transition. This points to pronounced strong-coupling superconductivity.

The so called $\alpha$-model [69] assumes that the superconductive properties which are mainly influenced by the size of the gap and the quasiparticle-state occupancy could be approximated by simply using the temperature dependence of the weak-coupling BCS gap. The size of the gap in the Fermi surface is a freely adjustable parameter $\alpha=\Delta(0)/k_B T_c$, where $\Delta(0)$ is Fermi-surface averaged gap at $T=0$. Table 3-1 presents comparative $\alpha$ values obtained by different groups. An analysis using the $\alpha$-model results in an extremely large gap ratio of $\alpha=\Delta(0)/k_B T_c=3.7$ and a huge specific heat jump of $C/(c)\geq5$ [70].

A summary of the published superconductive gap ratios and gap anisotropy of PrOs$_4$Sb$_{12}$ from other measurements than specific heat are presented in Table 3-2.

Frederick et al. [71] succeeded in making a better fit for the specific heat data of PrOs$_4$Sb$_{12}$ using a power-law function below the superconducting temperature. The fits,
using both power-law and exponential functions, cannot be considered by themselves as proof of the superiority of one fit over the other.

3.4.1.3 **Nuclear Magnetic Resonance (Sb NQR)**

The $^{121,123}$Sb Nuclear Quadrupole Resonance (Sb NQR) experiment \[75\] in zero field shows a heavy fermion behavior and controversial conclusions regarding the nature of the superconductivity in PrOs$_4$Sb$_{12}$. In the SC state, $1/T_1$ shows neither a coherence peak just below $T_c$ nor a $T^3$-like power-law behavior observed for *anisotropic* HF superconductors with the line-node gap. The absence of the coherence peak in $1/T_1$ supports the idea of unconventional superconductivity in PrOs$_4$Sb$_{12}$ (Fig. 3-10). The *isotropic* energy gap with its size $\Delta/k_B=4.8$ K seems to open up across $T_c$ below $T^*=2.3$ K. The very large and isotropic energy gap $2\Delta/k_B T_c \sim 5.2$ indicates a new type of unconventional strong-coupling regime.

3.4.1.4 **Muon Spin Rotation ($\mu$SR)**

The broken time reversal symmetry has been reported in later muon-spin relaxation measurements. The results \[76\] reveal a spontaneous appearance of static internal magnetic fields below the superconducting transition temperature, providing unambiguous evidence for the breaking of time-reversal symmetry in the superconducting state. This will favor the multiple superconducting phase transitions observed by specific heat and thermal conductivity studies and support therefore the unconventionality of superconductivity.

Magnetic penetration depth data in single crystals of PrOs$_4$Sb$_{12}$ down to 0.1 K, with the ac field applied along the a, b, and c directions was successfully fitted \[74\] by the $^3$He A-phase-like gap with multidomains, each having two point nodes along a cube axis, and parameter $\Delta(0)/k_B T_c=2.6$, suggesting that PrOs$_4$Sb$_{12}$ is a strong-coupling superconductor with two point nodes on the Fermi surface. These measurements confirmed the two superconducting transitions at 1.75 and 1.85 K seen in other measurements.
3.4.2 Conventional Superconductivity

3.4.2.1 Nuclear Magnetic Resonance (\(\mu \text{SR}\))

The temperature \(T\) dependence of nuclear-spin-lattice-relaxation rate, \(1/T_1\), and NQR frequency unravel a low-lying CEF splitting below \(T_0 \sim 10\) K. In addition, the temperature dependence of \(1/T_1\) in PrOs\(_4\)Sb\(_{12}\) is an exponential one \([75]\) (Fig. 3-10, full symbol), which is the signature of a conventional type of superconductivity.

Figure 3-10 (open symbols) also plots the data for the conventional superconductor LaOs\(_4\)Sb\(_{12}\). For an \(s\)-wave case that is actually seen in the \(T\) dependence of \(1/T_1\) for LaOs\(_4\)Sb\(_{12}\) with \(T_c \sim 0.75\) K, in the SC state, \(1/T_1\) shows the large coherence peak just below \(T_c\), followed by an exponential dependence with the gap size of \(2\Delta/k_B T_c \sim 3.2\) at low \(T\). This is a clear evidence that LaOs\(_4\)Sb\(_{12}\) is the conventional weak-coupling BCS \(s\)-wave superconductor.

3.4.2.2 Penetration Depth Measurements (\(\lambda\)) by \(\mu \text{SR}\)

The transverse-field muon-spin rotation measurements in the vortex lattice of the heavy fermion superconductor (HFSC) PrOs\(_4\)Sb\(_{12}\) yields \([73]\) an exponential temperature dependence of the magnetic penetration depth \(\lambda\), indicative of an isotropic or nearly isotropic energy gap, indicating a conventional superconductivity mechanism.

This is not seen, to date, in any other HF superconductor and is a signature of isotropic pairing symmetry (either \(s\)- or \(p\)-wave, indistinguishable by thermodynamic or electrodynamic measurements), possibly related to a novel nonmagnetic quadrupolar Kondo HF mechanism in PrOs\(_4\)Sb\(_{12}\). Also, the estimated magnetic penetration depth \(\lambda=3440(20)\) Å \([73]\) was considerably shorter than in other HF superconductors.

3.4.2.3 Low-Temperature Tunneling Microscopy

The spectra of a direct measurement of the superconducting gap through high-resolution local tunneling spectroscopy \([72]\) in the heavy-fermion superconductor PrOs\(_4\)Sb\(_{12}\) demonstrates that the superconducting gap is well developed over a large part of the Fermi surface. The conductance has been successfully fitted by a \(s\)-wave superconductivity
model. The presence of a finite distribution of values of the superconducting gap over the Fermi surface argue in favor of isotropic BCS s-wave behavior.

Figure 3-1. Crystal structure of PrOs$_4$Sb$_{12}$ (Reprinted with permission from Aoki et al. [77])
Figure 3-2. (a) Fits of the magnetic susceptibility $\chi(T)$ of PrOs$_4$Sb$_{12}$ to CEF model with either $\Gamma_3$ (solid line) or $\Gamma_1$ (dashed line) ground state. The same symbols are used in the inset, which shows $\chi(T)$ below 30 K. In the inset, the solid line fit saturates just above $\chi=0.06$ cm$^3$/mol. (b) $C$ fitted by a two-level Schottky anomaly (Reprinted with permission from Bauer et al. [7]).
Figure 3-3. (a) Fits of the magnetic susceptibility $\chi(T)$ of PrOs$_4$Sb$_{12}$ to CEF model with either $\Gamma_3$ (dashed line) or $\Gamma_1$ (doted line) ground state. The solid lane represents the experimental data (taken from Tayama et al. [51]). (b) The calculated entropy $S(T)$ for $\vec{H} // (100)$ in both $\Gamma_3$ and $\Gamma_1$ CEF ground state models (taken from Tayama et al. [51]). (c) The measured entropy $S(T)$ for $\vec{H} // (100)$ (Reprinted with permission from Aoki et al. [56]).
Figure 3-4. (a) Resistivity $\rho(T)$ and susceptibility $\chi(T)$ of PrOs$_4$Sb$_{12}$ (b) Specific heat $C(T)$ up to 20 K [7] (Reprinted with permission from Bauer et al. [7]).
Figure 3-5. Fermi surface of PrOs$_4$Sb$_{12}$ (Reprinted with permission from Sugawara et al. [44]).
Figure 3-6. $H$-$T$ phase diagram of PrOs$_4$Sb$_{12}$ (Reprinted with permission from Tayama et al. [51]). Open and closed symbols were determined by the $dM(T)/dT$ and $dM(H)/dH$ data, respectively. Right panel, the Pr charge distributions induced in the antiferroquadrupolar ordered phase in magnetic field (Reprinted with permission from Méasson [45]).

Figure 3-7. (a) $C(T)$ of PrOs$_4$Sb$_{12}$ presenting double superconducting transition (Reprinted with permission from Vollmer et al. [63]) (b) $C(T)$ of PrOs$_4$Sb$_{12}$ presenting two superconducting transitions (Reprinted with permission from Méasson et al. [59]) (c) The real part of the ac susceptibility of PrOs$_4$Sb$_{12}$ presenting two distinct superconducting transitions (Reprinted with permission from Méasson et al. [59]).
Figure 3-8. The two superconducting phases for PrOs$_4$Sb$_{12}$ (Reprinted with permission from Izawa et al. [67]). The gap function has a fourfold symmetry in A phase and twofold symmetry in B phase. Right: The plot of the gap function with nodes for A phase and B-phase (Reprinted with permission from Maki et al. [78]).

Figure 3-9. Two superconducting transitions in the thermal expansion coefficient $\beta$ of PrOs$_4$Sb$_{12}$. The two transitions are visible for the same temperatures of the two transitions in specific heat (Reprinted with permission from Oeschler et al. [64]).
Figure 3-10. Temperature dependence of the rate $1/T_1$ at the $2\nu_Q$ transition of $^{123}$Sb for PrOs$_4$Sb$_{12}$ (closed circles) and LaOs$_4$Sb$_{12}$ (open circles) (Reprinted with permission from Kotegawa et al. [75]).

Figure 3-11. Tunneling conductance between PrOs$_4$Sb$_{12}$ and an Au tip. The gap is well developed with no low-energy excitations. The line in figure is the prediction from conventional isotropic BCS $s$-wave theory using $\Delta=270$ $\mu$eV and $T=0.19$ K (Reprinted with permission from Suderow et al. [72]).
CHAPTER 4
EXPERIMENTAL METHODS

This chapter describes the sample synthesis, characterization and the experimental procedures used: dc and ac susceptibilities, resistivity, and specific heat measurements. A brief description of the performed measurements is given.

4.1 The Samples: Synthesis and Characterization

4.1.1 Synthesis

The filled skutterudite antimonides studied in this dissertation are prepared using a molten-metal-flux growth method with an excess of Sb flux \[54, 57\]. Since the flux is one of the constituent elements of the compounds (i.e. Sb) the method is called self-flux growth. High-purity starting elements (Pr and La from AMES Laboratory, 99.99% purity powder Os from Colonial, Inc., and 99.999% purity Sb ingot from Alfa AESAR) are used in the proportion R:Os:Sb=1:4:20, when the rare-earth element R is Pr and La in various proportions. The R alloys used as components in the flux growth were synthesized eventually by melting its constituent elements in an Edmund-Bühler Arc Melter under a high purity argon atmosphere. First, small chunks of Sb were placed inside of a quartz tube. Above that were placed the Os and the R components that were pre-melted separately to eliminate any trace of oxide from the surface of the elements. The Os powder was pressed in small pellets and then melted. The quartz tube was sealed under low pressure Ar atmosphere (\(~20\) mTorr) after the tube is pumped and flushed 3 to 5 times. The tube with the mixture was placed in a Lindberg 51333 programable furnace (digital controlled, \(T_{\text{max}}=1200{\degree}\text{C}\)) using the following heat treatment sequence: temperature ramping to \(980{\degree}\text{C}\) with a rate of \(200{\degree}\text{C}/\text{h}\) followed by \(T=980{\degree}\text{C}\) for \(24\) h, then cooling at a rate of \(3{\degree}\text{C}/\text{h}\) down to \(650{\degree}\text{C}\). The last step was a fast cooling in the furnace to room temperature at a ~ \(200{\degree}\text{C}/\text{h}\) rate. The single crystals were then removed from the antimony flux excess by etching in aqua regia (\(\text{HCl}:\text{HNO}_3=1:1\)). The crystals were cubic or rectangular up to 50 mg in weight (up to ~3 mm in size) depending on the amount of the starting elements and the cooling rate. For instance, using \(~1\) g of Os and a cooling...
rate of 1°C/h the single-crystal mass was about 50 mg (Fig. 4-1). This large crystal later proved to be very useful for the dc-susceptibility measurements. In the case of \( R \) being actually an alloy, such as \( \text{Pr}_{1-x} \text{La}_x \), Pr and La are previously melted together using the arc-melter as further described.

The poly-crystalline R alloys (used as one of the starting components in the synthesis of the single crystals) were prepared by melting its constituent elements in an Edmund-Bühler Arc Melter AM under a half atmosphere high purity Ar. The apparatus consists of a stainless steel vacuum chamber which sits tight on a water cooled groove crucibles in a copper base plate and with an electrode at the top. The tungsten electrode is motor driven which can be moved freely above the crucible. The melting process can be observed through a dark glass window. All important control functions are integrated in the head of the electrode and ensure safe and convenient operation. When fed at the maximum current the temperature of the electric arc in the melter can go as high as 4000°C and melts \( \sim 500 \) g of metals. The arc melter has a flipper, a manipulator for turning the samples in situ. This gives the possibility to flip and again melt the sample, ensuring its homogeneity, without opening the chamber. Before operating, the copper base plate was thoroughly cleaned with acetone to avoid any contamination of the sample with impurities. Right at the beginning, each of the constituent elements were well cleaned to eliminate the oxide layer on the surface. The precision in mass measurements was \( \pm 0.02 \) mg. Starting with the radioactive or the hardest element we can adjust the relative masses of the other components to gain the wanted stoichiometric ratio. The total mass was from teens of milligram to \( \sim 1 \) g, the size of the sample bead was up to 1 cm. Right before the elements were melted together, a zirconium button which was also used for ignition of the arc, was melted just to ensure a even higher purity of the Ar, which was filtered through a purifier before entering into the arc chamber. Zirconium is well known as a oxygen absorber. The element with the highest vapor pressure was then placed on the copper plate right below the elements with lower vapor pressures. The aim of this
was to not strike with the arc on the element with a high vapor pressure resulting in uncontrolled vaporization of the material. The element with the lowest vapor pressure was melted first. This reduced the mass loss, and the discrepancy between predicted and actual stoichiometries of the synthesized alloys. To ensure an even better control of the temperature at which the elements were melted, the copper plate in the immediate vicinity of the place where all elements were together was first heated with a slowly increasing current. This was done until the element with the highest vapor pressure started to melt and to suck all the other elements. Then flipping the resulting bead and remelting it ensured its homogeneity. This process was repeated several times. Also, for dilute concentrations, such as Pr$_{0.98}$La$_{0.02}$Os$_4$Sb$_{12}$, Pr$_{0.98}$La$_{0.02}$ was needed first. Therefore we started with master alloys (Pr$_{0.9}$La$_{0.1}$) in order to avoid handling of very small amounts of materials.

4.1.2 X-Rays Diffraction Characterization

X-ray diffractions of the materials verified whether the arc melting plus annealing or the flux growth processes led to the formation of the desired crystal structure. From the diffraction pattern it is possible to determine the lattice constants and the presence of the secondary phases in the material (if present in a proportion greater than 5%). The measurements were performed using a Phillips XRD 3720 machine at the Major Analytical Instrumentation Center (MAIC) at the University of Florida. Single crystals and poly-crystalline samples were crushed and ground out into a fine powder using a ceramic mortar. On a glass slide, about 1 cm$^2$ of powder was glued using 7:1 amyl acetate-collodion mixture. The machine uses two wavelengths in the measurements: Cu $K_{\alpha_1}=1.54056$ Å and Cu $K_{\alpha_2}=1.54439$ Å. The intensity of the $\alpha_1$ beam is twice as great as the $\alpha_2$ beam. All the measurements were taken in a 2$\theta$ angle range from 20° and 120° with a 0.02° step and a scan speed of 6°/min, the machine recording 1000 counts/sec. 2$\theta$ is the angle between the incident beam and the reflected one. All measurements were performed at room temperature. The computer controlled X-ray machine records the
relative intensities of the peaks which will be plotted/displayed (X-ray pattern) when the scan is completed. Also, the precise angles corresponding to specific peaks were listed. The angles corresponding to the peaks were found from Bragg’s law:

\[ n\lambda = 2d \sin \theta, \quad (4-1) \]

where \( \theta \) is half of the reflection angle, \( n \) is an integer (\( n = 1 \) for the first order spectrum), \( d \) is the inter-plane distance, and \( \lambda \) is the wavelength of the incident radiation. The lattice constants are then calculated from \( d \) and the intersection points of the lattice planes from the desired space group number is given in terms of the Miller indices \((hkl)\). For a cubic symmetry the same Bragg equation can be rewritten as

\[ \sin^2 \theta = \frac{\lambda^2}{4(h^2 + k^2 + l^2)}, \quad (4-2) \]

which is derived from \( d(hkl) = a/\sqrt{h^2 + k^2 + l^2} \), where \( a \) is the lattice parameter. Using a least-squares fitting program with the wavelength, structure type, \((hkl)\) indices and the angles \( 2\theta \) of the narrowest intensity lines as input, the lattice constant can be found. All the X-ray diffractions were taken at room temperature.

4.2 Specific Heat Measurements

4.2.1 Equipment

4.2.1.1 Cryogenics

This sub-section describes the probes used in the specific heat, in house resistivity and ac-susceptibility measurements.

In house (Stewart Lab., Physics Department at University of Florida) measurements of specific heat were performed in the temperature range of 0.3 to 2 K usually, and in some cases up to 10 K. A home made \(^3\)He cryostat was used. The schematic drawing is given in Fig. 4-3. This probe was used for the measurements of specific heat in magnetic fields as well. A specially designed dewar from Cryogenic Consultants Limited was also used. The superconducting magnet reached 14 T at 4.2 K bath temperature. For the ac
susceptibility and resistivity measurements, another $^3$He cryostat was used. The resistivity was measured between the lowest temperature of 0.3 K and the room temperature, while the ac-susceptibility was measured between 0.3 K and about 2 K. The difference from the one used for specific heat measurements is that this probe has no $^4$He pot, the pumping being performed on the Dewar in order to reach 1.1 K for the use of the $^3$He cooling system.

Specific heat measurements at lower temperature and higher magnetic fields were performed at the Millikelvin Facility (Superconducting Magnet 1–SCM 1), High Magnetic Field National Laboratory, Tallahassee, Florida using a top loading dilution refrigerator which is permanently installed in a 18/20 T superconducting magnet. The measurement temperature range was 20 mK to 2 K combined with a magnetic field of up to 20 T. The small home made calorimeter (Fig. 4-5) was connected to the general purpose sample mount provided by the facility. Resistivity measurements performed at the same facility were done in the temperature range of 20 mK to 0.9 K. Another sample holder, a so-called 16 pin ample rotator, was used. This allows the change of orientation of the sample in field during the experiment. This holder has 16 pins (16 connection wires to the top of the probe) that allows up to a maximum of four different samples to be measured without pulling out the probe from the dilution refrigerator, saving precious time. Takes up to 6 hours to insert the probe into the refrigerator and cool the sample to 20 mK. Specific heat measurements in magnetic fields up to 32 T were performed at the 33 T, 32 mm bore resistive magnet (Cell 9), at the same National Laboratory. Another home made $^3$He probe similar to the one mentioned earlier but with slightly different dimensions in order to fit into the magnet and also to accommodate the sample in the maximum field strength region was used. Right before the insertion of the probe into the magnet an electrical check was done on wire connections. The quality of vacuum and sealing was checked also using an Alcatel ASM 10 Leak Detector. For both 33 T and 45 T measurements, a special positioning system made it possible to center the probe inside the magnet such that it did
not touch the inner walls of the magnet. The probe was to be perfectly centered into the maximum strength field region.

Because of the large amount of heat that had to be removed, the probe was cooled in liquid nitrogen (LN) down to the boiling point (77.35 K). After about 2 hours, when the probe was at thermal equilibrium with the liquid nitrogen, it was transferred quickly into a dewar in which it fits tight. The dewar was cooled in advance in LN as well. The dewar (with the probe inside) was filled with liquid $^4\text{He}$ (LHe) and after several hours (depending on the volume of the can) the temperature of the probe reached 4.2 K. After 4.2 K was attained following the procedure described above, the $^4\text{He}$ pot was filled with LHe from the bath by opening the needle valve, and $^3\text{He}$ gas (a lighter isotope of He) was transferred into the $^3\text{He}$ pot+probe line using a home-made $^3\text{He}$ handling system. The handling system consists of a tank filled with $^3\text{He}$, a pump which helps to transfer to and back from the $^3\text{He}$ pot line, and pressure gauges to display the amount of $^3\text{He}$ left in the tank and in the transfer lines. After closing the needle valve and pumping in the $^4\text{He}$ line a temperature between 1 and 2 K was obtained. It was necessary to refill the $^4\text{He}$ pot by opening the needle valve once in several hours. In order to attain 0.3 K a completely contained $^3\text{He}$ cooling part using a sorption pump was required. When cooled, gases generally adsorb to solid surfaces. The sorption pump is based on the idea that at $\sim 10$ K almost all of the $^3\text{He}$ gas molecules are adsorbed, whereas at $\sim 35$ K all of the molecules desorb. The sorption pump consists of a Cu cylinder that contains activated charcoal, which has an enormous surface area (tens of square meters per gram). The cylinder is attached to the lower end of a metallic rod. The whole system, rod+cylinder with charcoal, was placed inside the $^3\text{He}$-gas enclosure. As the charcoal was lowered toward the $^3\text{He}$ pot, the $^3\text{He}$ was absorbed by the charcoal reducing the vapor pressure and lowering the temperature of the $^3\text{He}$ pot. After the charcoal became saturated with $^3\text{He}$, the charcoal was warmed up (by raising the rod with the charcoal), and the gas was
released. In about 15 minutes the gas condensed and dripped into the $^3$He pot again. Then the whole process was repeated.

### 4.2.1.2 Sample Platform

The sapphire platform is attached to the bottom of the probes to the $^3$He or $^4$He pot, depending on the probe used (Fig. 4-5 (a)). The sample is attached to a small piece of sapphire disc using H31LV silver epoxy cured at 150°C for 1/2 h. The new assembly of sample+sapphire sitting on the sapphire platform and attached by Wakefield grease is shown in Fig. 4-5 (b). This ensured a good thermal contact between the sample and the platform. The platform is thermally linked to a copper ring (silver in the case of the platform of the calorimeter used at the SCM1 - NHMFL) as schematically drawn in Fig. 4-5. Two types of platforms were used. Each platform has four wires soldered to silver pads attached to the ring by thermally-conductive Stycast. The two pairs of wires are connected to the platform heater and thermometer, respectively, using EpoTek H31LV silver epoxy. The wires ensure the mechanical support of the platform and the thermal contact with the ring and the $^3$He or $^4$He pot by the case. They also provide the electrical contact to a heater and a thermometer on the platform. The platform heater is an evaporated layer of 7%Ti-Cr alloy. For measurements between 1–10 K, the platform thermometer used was an elongated piece of doped Ge, and the platform wires were made of a Au-7%Cu alloy. A thin piece of Speer carbon resistor and Pt-10%Rh platform wires (more mechanical resistant than the ones made from the Au-alloy) were used for measurements between 0.4 and 2 K.

### 4.2.2 Thermal Relaxation Method

The specific heat was measured using the probes described earlier, employing the thermal relaxation method [79–81]. The thermal relaxation method consists of measuring the time constant of the temperature decay of the sample connected to the heat bath by a small thermal link. A power $P$ is applied (Fig. 4-6) (thermal power by a small current of the order of $\mu$A) to the platform-sample system. The temperature of the sample, initially
at \( T_0 \), increases by a small amount, \( \Delta T \). When the current is turned off, the system temperature \( T(t) \) decays exponentially to the base temperature \( T_0 \):

\[
T(t) = T_0 + \Delta T \exp\left(-t/\tau_1\right).
\]  

(4–3)

The time constant \( \tau_1 \) is proportional to the \( C_{\text{total}} \) (sample+platform):

\[
\tau_1 = \frac{C_{\text{total}}}{\kappa},
\]

(4–4)

where \( \kappa \) is the thermal conductance of the wires linking the sample+platform at \( T=T_0+\Delta T \) and the ring at \( T=T_0 \). The block temperature is regulated by a block heater (a bundle of manganin wire) and measured by a thermometer attached to the block. The time constant is obtained by measuring the time decay of the off-balance voltage signal from a Wheatstone bridge using a lock-in amplifier. Two arms of the Wheatstone bridge are a variable resistance box and the platform thermometer. The bridge is balanced by adjusting the resistance of the resistance box. This made it possible to find the resistance of the thermometer. From an initial calibration of the thermometer \( R \) versus \( T \):

\[
\frac{1}{T} = \sum_{i=0}^{n} A_i (\ln R)^i,
\]

(4–5)

it is possible to find the temperature corresponding to the platform thermometer resistance. The thermal conductance is given by:

\[
\kappa = \frac{P}{\Delta T},
\]

(4–6)

where \( P=IV \) is the power applied to the platform heater. Equation (4–3) is valid if the thermal contact between sample and platform is ideal (i.e., \( \kappa_{\text{sample}} \sim \infty \)). If the contact is poor (i.e., \( \kappa_{\text{sample}} \sim \kappa \)), then

\[
T(t) = T_0 + A \exp\left(-t/\tau_1\right) + B \exp\left(-t/\tau_2\right),
\]

(4–7)
where $A$ and $B$ are measurement parameters and $\tau_2$ is the time constant between sample and platform temperatures. $C_{total}$ can be calculated from $\tau_1$, $\tau_2$, and $\kappa$. The thermal conductivity is measured by applying a power $P=IV$ and calculating the $\Delta T$ as a result of the power applied to the heater. The specific heat of the sample can be calculated by subtracting the addenda contribution from the $C_{total}$. The result is multiplied by the molecular weight and divided by the mass of the sample.

4.3 Magnetic Measurements

Magnetic susceptibility measurements were made in order to characterize the magnetic properties of PrOs$_4$Sb$_{12}$ and its La alloys. The direct current (dc) magnetic susceptibility was measured using a Superconducting Quantum Interference Device (SQUID) made by Quantum Design which can perform measurements in magnetic fields up to 5 T, and a temperature range from 1.8 K to 300 K (350 K with special preparations). The alternating current (ac) susceptibility was measured using a home made apparatus. The temperature range can run from about 0.3 K to 10 K, although normally all the measurements were done up to 2 K. Both dc- and ac-magnetic susceptibility methods are discussed in the next subsection.

4.3.1 DC Susceptibility

All the measurements were performed in 1 or 5 kOe magnetic fields. For small samples (mass approximately a few mg), 1 T magnetic field was used since the signal of the sample was comparable with the signal of the plastic straw holder. In any case, in order to avoid the straws signal subtraction, the samples were kept tightly between two drinking straws. The principle behind the magnetic susceptibility measurements is the Lenz’s law. The magnetic moment is measured by induction: the sample moves 4 cm through a set of superconducting pickup coils and the SQUID instrument measure the current induced in the pickup coils. The SQUID voltage is proportional to the change in flux detected by the pickup coils. In order to get the magnetization data curve a set of 48 points are taken during the movement of the sample. At a given temperature this
is repeated 4 times and the signals are averaged for a better accuracy. The magnetic susceptibility for a fixed field is \( \chi = M/H \) (in emu/mol), where \( M \) is the magnetic moment, and \( H \) is the magnetic field. This is obtained from the signal measured at a fixed field by multiplying with molecular weight of the alloy, and dividing by mass and the applied field. Beside the magnetization at fixed field and various temperatures the SQUID can perform measurements of magnetization in different magnetic fields at constant temperature.

### 4.3.2 AC Susceptibility

The apparatus consists of a primary coil of NbTi superconducting wire, 90/10 CuNi of 0.004” with insulation, 185 turns \([82]\) and two secondary coils made from copper wire, wound in both sides in opposite directions of 2700 turns. The coils are attached to the Cu block (which is in thermal contact with the \(^3\)He pot). The apparatus uses the mutual inductance principle. The sample is subject to an alternating magnetic field of 0.1 Oe produced by the primary coil (and also the Earth’s magnetic field). The resulting electromotive force (EMF) induced in the secondary coil is detected. The background signal is nulled by the identical secondary coil, connected in series opposition. For the same reason the two screws are identically built. The sample is glued to one screw with General Electric (GE) varnish 7031 which ensures a good thermal and mechanical contact at low temperature and also can be removed easily using acetone. The ac susceptibility measurements were performed at two different frequencies: 27 Hertz (Hz) and 273 Hz. It was deliberately used these frequencies (not integer multiples of 60 Hz) in order to avoid the noise coming from the common electrical outlet. In general, \( B=\mu_0(H+M_V)\mu_0H(1+\chi) \), with \( H \) the magnetic field, \( M_V \) the volume magnetization and \( \chi=M_V/H \) is the magnetic susceptibility. If the applied field \( H \) has a sinusoidal form, the time dependent magnetization \( M_V(t) \) can be expressed as a Fourier series of the non-linear complex ac susceptibility. Applying the inverse Fourier transform to \( M_V(t) \) it can be found the \( n^{th} \) harmonic of both real and imaginary ac susceptibility. The fundamental real component
is associated with the dispersive magnetic response which is in phase with the ac applied magnetic field, and the fundamental imaginary component is associated with absorptive or irreversible components which arise from energy dissipation within the sample, or in other words the energy absorbed by the sample from the ac field. The induced EMF in coils $V(t) = -d\Phi(t)/dt$ (complex, i.e. $V = V' + iV''$) is proportional to the $\chi = \chi' + i\chi''$. Therefore, if the reference signal of the lock-in amplifier is derived from the primary driving signal, then $V' \propto \chi''$, and $V'' \propto \chi'$. The superconducting transition temperature is determined by a midpoint of the inductive signal deviation associated with the superconduction transition.

### 4.4 Resistivity

The resistivity measurements used the same probe used for the ac susceptibility. The sample was mounted to a sapphire disk. Four platinum wires (0.002'' diameter) were attached to the sample using silver paint (whose resistivity is much lower than that of the sample itself) and then for a good mechanical contact with EPO-TEK H31LV silver epoxy. The extra resistance introduced by the silver-epoxy contacts is avoided by the use of the silver paint for electrical contacts and the epoxy just only for a good mechanical contact between the wires and the sapphire disk. Then, the disk with the sample was glued to the $^3$He block using GE varnish 7031 ensuring a good thermal contact. At each temperature, the resistivity was obtained by averaging both absolute values for each polarity of the current. The temperatures between 77.4 K and room temperature were covered by measurements in liquid nitrogen (LN). The probe was immersed in LN and the program starts collecting data, while the sample cooled towards 77.4 K. Thereafter, as described in the previous section, the LN was removed, and liquid He was transferred. The temperature dropped further toward 4.2 K. Further down, the resistivity was measured to approximately 0.3 K, making use of $^3$He gas as described.
Figure 4-1. PrOs$_4$Sb$_{12}$ large crystal, about 50 mg (right). In the left, an Os ball with PrOs$_4$Sb$_{12}$ single crystals attached, waiting to be etched out.

Figure 4-2. PrOs$_4$Sb$_{12}$ samples prepared for (left panel) resistivity and (right panel) specific heat measurements.
Figure 4-3. Schematic view of the $^3$He cryostat used in the measurements performed at University of Florida.
Figure 4-4. Schematic view of the calorimeter used in the Superconducting Magnet 1 (SCM 1), National High Magnetic Field Laboratory.
Figure 4-5. (a) Top view of the sample-platform/Cu-ring assembly. (b) Lateral view of the sapphire platform and sample.
Figure 4-6. Specific heat C measurement process using the relaxation time method (Redrawn with permission from Mixson [83]).
CHAPTER 5
MATERIALS CHARACTERIZATION

All samples were synthesized using the self-flux growth method, described in Chapter 4. The samples are cubic shaped and of sizes ranging from 1/2 mm to 3 mm and weighting from 1 mg to about 50 mg. X-ray diffraction was performed to verify the desired crystal structure. From the diffraction pattern it was also possible to determine the lattice constants. In addition to this, the X-rays confirmed that the samples were single-phase within an accuracy of 5%.

The quality of the sample is also given by the sharpness of the transition in the specific heat. A more quantitatively measure of the quality of the sample is the residual resistivity ratio $RRR=\rho(300K)/\rho(T\rightarrow0)$. This ratio ranges from 50 to about 170 (PrOs$_4$Sb$_{12}$ samples studied by M´easson et al. [59] have $RRR\approx40$.)

Due to the very small size of the samples used, the susceptibilities measured for all concentrations and the background (susceptibility of the sample holder consisting from a plastic drinking straw) were comparable at 10 K. At room temperature the susceptibility was even smaller than the background, especially for dilute concentrations. In order to avoid this background contribution, magnetic susceptibility were remeasured (for $x=0$, 0.05, 0.3, 0.67, 0.8 and 0.95) using bigger samples. Also, in these measurements, the material was pressed in between two long concentric tubes such that no background subtraction was needed.

All these additional measurements yielded to a Curie-Weiss temperature dependence above 150 K, corresponding to an effective magnetic moment close to the one expected for Pr$^{3+}$ (Fig. 5-1), much closer to the expected value for Pr$^{3+}$ than the initially reported $\mu_{eff}=2.97\mu_B$ [7] for PrOs$_4$Sb$_{12}$. The effective moment of the free Pr$^{3+}$ is $\mu_{eff}=3.58\mu_B$ [52]. New measurements by Tayama et al. [51] revealed an effective moment close to this value. This supports the notion of an essentially trivalent state of Pr in all Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ alloys.
Figure 5-1. $\chi(T)$ of PrOs$_4$Sb$_{12}$. In the inset is the Curie-Weiss fit of high temperature ($T>150$ K). The high temperature effective moment is $\mu_{\text{eff}}=3.65\mu_B$, very close to the one corresponding to free Pr$^{3+}$, which is $3.58\mu_B$.

Figure 5-2. $\chi(T)$ of the non-$f$ equivalent LaOs$_4$Sb$_{12}$. 
CHAPTER 6
PrOs$_4$Sb$_{12}$

Any understanding of heavy fermion (HF) behavior requires knowledge of the crystalline electric field (CEF) configuration. Therefore, one of the main objectives of this thesis was to establish the CEF scheme for PrOs$_4$Sb$_{12}$ and to see how the CEF ground state is reflected in low temperature properties of this material. The Chapter starts with results on the specific heat of PrOs$_4$Sb$_{12}$ in high magnetic fields. The magnetic phase diagram (i.e. phases that exist at a given temperature and field) will allow us to determine the CEF scheme of Pr. High magnetic field low temperature resistivity measurements will be used to argue for a HF state in PrOs$_4$Sb$_{12}$.

6.1 Investigation of CEF Configuration by Specific Heat in High Magnetic Fields

The initially proposed CEF schemes [7] (either $\Gamma_3$ or $\Gamma_1$ CEF ground state) for PrOs$_4$Sb$_{12}$ imply non-magnetic ground states and exclude a conventional Kondo effect, believed to be the source of HF behavior in Ce- and some U-based metals.

The controversy between the two schemes was brought about by different experiments that seem to favor either configuration.

As presented in Chapter 3, the first published results such as the zero field specific heat, magnetic susceptibility data [7], resistivity in small magnetic fields [55], inelastic neutron scattering data interpreted using $O_h$ symmetry [53] favored the $\Gamma_3$ doublet as the CEF ground state.

On the other hand, magnetic susceptibility data of Tayama et al. [51] and entropy changes in small magnetic fields measured by Aoki et al. [56] were better fitted by a $\Gamma_1$ CEF ground state model.

The zero field Schottky anomaly occurring at 3.1 K can be related to the $\Gamma_3$-$\Gamma_5$ model, assuming these two levels are split by 6.5 K, or $\Gamma_1$-$\Gamma_5$ model with the splitting of 8.4 K. The difficulty in interpreting these low temperature, low field results is related to a strong hybridization of 4$f$ and conduction electrons, inferred from the large electronic
specific heat coefficient and the size of the discontinuity in the specific heat $C$ at $T_c$.

The idea behind specific heat measurements in high magnetic fields was to suppress this coupling between $f$ and conduction electrons to reveal the ionic character of Pr.

In order to present our results in a proper perspective we start from recalling the specific heat data for fields smaller than 8 T obtained by Aoki et al. [56]

Figure 6-1, upper panel, shows the low temperature specific heat to 8 T obtained by Aoki et al. [56], the lower panel a comprehensive phase diagram known before our measurements. 4.5 T is the lowest field at which a signature of FIOP is detectable as a small kink (at $\sim$0.7 K). This kink evolves into a sharp peak at 0.98 K in 6 T. The $C(T)$ peak grows and moves also to higher temperatures for higher fields.

The FIOP was confirmed by specific heat of Vollmer et al. [63] and magnetization study of Tayama et al. [51].

A number of observations brought forward the interpretation of FIOP in terms of antiferroquadrupolar (AFQ) order. These observations included a large anomaly in the specific heat (corresponding to a large entropy removed by the transition) and the very small value of the ordered (antiferromagnetic) moment (about 0.025$\mu_B$ at 0.25 K in 8 T [84]) measured by neutron diffraction, and also similarities to systems displaying quadrupolar order (e.g., PrPb$_3$ [85]).

Figures 6-2, 6-3, and 6-4 show the specific heat in fields ranging from 10 to 32 T. The specific heat measurements in fields up to 14 T were done using Cryogenic Consultant Limited superconducting magnet at the University of Florida. Measurements in fields larger than 14 T were carried out at the National High Magnetic Field Laboratory, Tallahassee, Florida using a resistive Bitter magnet. The field was applied along the crystallographic (100) direction.

The specific heat data in all three figures are after subtracting the phonon background ($\beta T^3$ with $\beta=(1944 \times 10^3)n/\Theta_D^3$ [1]) corresponding to a Debye temperature ($\Theta_D$) of 165 K, proposed by Vollmer et al. [63] This value of $\Theta_D$ obtained from the temperature
dependence of the specific heat of PrOs$_4$Sb$_{12}$ is somewhat controversial. Other estimates of the Debye temperature: 304 K (Bauer et al. [7]), 320 K (Aoki et al. [56]), and 259 K (Maple et al. [53]) are based on specific heat measurements of LaOs$_4$Sb$_{12}$.

The lowest temperature of the heat capacity measurements, actual value, is chosen relatively high in order to avoid complications associated with a nuclear contribution of Pr. This contribution is strongly enhanced by coupling with orbital moments of f electrons [86, 87]. It is difficult to measure specific heat by a conventional relaxation method at temperatures where nuclear degrees of freedom dominate because of additional the time scale entering the experiment, nuclear spin-lattice relaxation time $T_1$ [88]. Strongly non-exponential temperature decays at the lowest temperatures (e.g., below 0.5 K in the field of 10 T and bellow 1.5 K in the field of 32 T) indicate the importance of nuclear degrees of freedom and cannot be analyzed using the so-called $\tau_2$ correction. Therefore, these lowest temperature points carry large uncertainty. When the magnetic field applied along the (1 0 0) crystallographic direction is 10 T, the temperature of the sharp FIOP peak appears at 1 K (Fig. 6-2). When increasing the field from 10 T field to 12 and 13 T (Figs. 6-2 and 6-3) the ordering temperature $T_x$ decreases only slightly but $C(T_x)$ is suppressed in a strong manner.

The results presented here [31] combined with those of Aoki et al. [56] and Vollmer et al. [63] show that $T_x$ (peak position in $C$) reaches a maximum value around 9 T. Also, $C$ at $T_x$ is maximum somewhere between 8 and 10 T.

In 13 T a shoulder appears on the high temperature side of the FIOP anomaly. The specific heat value at this shoulder is about 3400 mJ/K mol. This shoulder evolves into a broad maximum for $H=13.5$ T. Above 13.5 T the FIOP cannot be observed anymore in the specific heat. Thus, these results strongly imply the disappearance of FIOP before $T_x$ reaches 0.

The broad maximum that appears in 13 T exists at all fields studied up to at least 32 T. The temperature of the maximum increases with the strength of the field (Fig. 6-4).
The magnitude of this anomaly, in fields of 13 T and larger, stays between 3300 and 3500 mJ/K mol and it is field independent. These values are within about 10% of the maximum value for a Schottky anomaly of a two level system with identical degeneracies [89]. The uncertainty of the specific heat measurements in these fields (and at temperatures where nuclear contribution is small) is about 10%. Increasing Θ_D from 165 K, used in the subtraction of the phonon term, to the other extremal value proposed, 320 K would raise the estimate of the electronic part of C by about 290 mJ/K mol at 3.5 K. Thus, the extracted values at the maximum are well within the realistic error bar of the theoretical 3650 mJ/K mol for the two-level Schottky anomaly. The highest field used of 32 T is large enough to split any degenerate levels, therefore the observed Schottky anomaly is due to the excitations between two singlets. T_m is related to the energy separation of the two levels δ by T_m=0.417δ [89]. An extrapolation of T_m to T=0 (Fig. 6-5) determines the field at which the two levels cross, which is somewhere between 8 and 9 T.

These result can be used to infer new information regarding the plausible crystal field configuration of Pr. Pr can be modeled by the following single-site mean-field Hamiltonian [84]:

\[ H = H_{CEF} - g_J \mu_B \mathbf{J} \cdot \mathbf{H} - \mathbf{J} \langle \mathbf{J}' \rangle \cdot \mathbf{J} - \sum_i Q_i \langle O_i' \rangle O_i, \]  

(6–1)

where \( H_{CEF} \), \( \mathbf{J} \) and \( O_i \) represent the CEF Hamiltonian for the cubic \( T_h \) symmetry, the total angular momentum, and the \( i \)-th quadrupole moment of Pr in a sublattice, respectively, where there are five types of quadrupolar moment operators: \( O_0^0 \), \( O_2^2 \), \( O_{xy} \), \( O_{yz} \), and \( O_{zx} \). \( \mathbf{J} \) and \( Q_i \) are the inter-sublattice molecular field coupling constants of spin (exchange) and quadrupolar interactions, respectively. The thermal averages of the angular momentum and quadrupole moment of the Pr in the counterpart sublattice are \( \langle J' \rangle \) and \( \langle O_i' \rangle \).

Using the CEF parameters proposed by Kohgi [84] for the \( \Gamma_1-\Gamma_5 \) CEF configuration, \( T_m \) (with \( Q_i=0 \)) and the \( O_{yz} \)-type quadrupolar ordering temperature \( T_x \) were calculated for \( (1\,0\,0) \) direction by Aoki et al. [90] As it is demonstrated in Fig. 6-5, the measured
phase diagram and the theoretical one (in the insets) expected for the \( \Gamma_1 - \Gamma_5 \) model for \( \vec{H}/(100) \) are in very good agreement. In both diagrams, the crossing field is very close to the one at which the transition temperature of the FIOP becomes maximum. Thus, the observed correlation between the two characteristic fields constitutes a very strong argument for the \( \Gamma_1 \) singlet being the lowest CEF level.

However, the level crossing for field \((100)\) direction is also expected for \( \Gamma_3-\Gamma_4 \) model, although at somewhat different field, as demonstrated by Vollmer et al. [63].

More conclusive arguments regarding the CEF configuration can be obtained from the study of the anisotropy of the Zeeman effect. Results of our calculations for the Zeeman effect for \( \vec{H}/(100) \), \( \vec{H}/(110) \), and \( \vec{H}/(111) \) are shown in Fig. 6-6 for \( \Gamma_1 \) CEF ground state. The plots show only the four lowest CEF levels. The higher levels are at above 100 K and 200 K from the ground state, and therefore play no role in the low temperature properties. The calculations were done neglecting exchange and quadrupolar interactions and considering the \( T_h \) symmetry. Neglecting or retaining the last two terms in (6–1) for the \((100)\) direction lead to almost identical results for eigenvalues (Aoki et al. [90] and our results).

There is a crossing between \( \Gamma_1 \) and the lowest \( \Gamma_5 \) level (split by magnetic field) at about 9 T when \( \vec{H}/(100) \) or \( \vec{H}/(111) \) and anti-crossing when \( \vec{H}/(110) \) around the same field. Therefore, the crossing field, extrapolated from the temperature of the Schottky anomaly at high fields should be independent of the field direction.

Figure 6-7 shows the same calculations for the \( \Gamma_3 \) CEF ground state model. For \( \vec{H}/(100) \) there is a crossing between the two lowest CEF levels, although at a field somewhat larger than the one expected for the \( \Gamma_1 \) CEF ground state. However, there is no crossing expected involving the lowest CEF levels when the field is applied along the \((110)\) or \((111)\) direction in the \( \Gamma_3-\Gamma_5 \) model (Fig. 6-7). Therefore, measurements of specific heat when magnetic field is applied in any direction different than \((100)\) differentiate between the two scenarios. Measurements of the specific heat in fields to 14
T were done for $\vec{H}/(110)$ and are presented in Fig. 6-8. The inset to Fig. 6-8 shows the specific heat in fields between 8 and 11 T around the AFQ transition. The specific heat at the AFQ transition and the temperature at which AFQ occurs are maximum for 9 T. Figure 6-10 and the inset to Fig. 6-8 suggest that between 9 and 12 T both the specific heat maximum and the temperature at which this maximum occurs decrease. In $H=12$ T both the AFQ transition and Schottky anomaly are visible. In fields higher than 12 T the AFQ transition is completely suppressed. The broad anomalies from Figure 6-8 at 12, 13, and 14 T are Schottky type.

The $H$-$T$ phase diagram is presented in Figure 6-10. For $\vec{H}/(110)$ direction we observe a decrease of $T_x$ values with respect to the $(100)$ direction for the corresponding fields, consistent with the previous magnetization measurements [51] (Fig. 3-6). On the other hand, within the uncertainty of the measurement, there is no change in the position of the Schottky anomaly at 13 and 14 T, as expected for the $\Gamma_1$ CEF ground state and inconsistent with the $\Gamma_3$ scenario. Moreover, for the $(110)$ orientation the Schottky anomaly can be clearly seen already at 12 T. This lower field limit for the Schottky maximum is probably due to competition between the two types of anomalies and lower values of $T_x$ for the $(110)$ direction (Fig. 6-9).

A straight line fit for the three $T_m$ points results in the crossing field value of 9±1 T. This value agrees, within the error bar, with the estimate for the $(100)$ direction. The existence of the crossing field for the $(110)$ direction provides an unambiguous evidence for the $\Gamma_1$-$\Gamma_5$ model. A small misalignment of the sample with respect to the field in either of the measurements cannot explain essentially identical crossing fields for both directions. In fact, the measured difference in $T_x$ values for $(100)$ and $(110)$ directions provides an additional check of the alignment. Similar to the $(100)$ direction, there seems to be a close correlation between the crossing field and the field corresponding to $T_x$ maximum.

Figures 6-5 and 6-10 imply a strong competition between the field-induced order and the Schottky peak. The FIOP transition in the specific heat abruptly disappears before
$T_x$ reaches zero. Precise magnetization measurements \cite{44, 51}, on the other hand, were able to map $T_x$ as a function of the magnetic field all the way to $T_x \approx 0$. This apparent contradiction can be explained by a very small entropy available for the FIOP transition above 13 and 12 T for fields parallel to the (1 0 0) and (1 1 0) directions, respectively.

Specific heat, being a bulk measurement, can be less sensitive than magnetization techniques in this situation. A strong competition is to be expected in the $\Gamma_1-\Gamma_5$ scenario. The ground state pseudo-doublet formed at the level crossing carries both magnetic and quadrupolar moments. Since a quadrupolar moment operator does not commute with a dipolar one, the quadrupolar interactions leading to FIOP compete with the magnetic Zeeman effect.

Therefore, the high magnetic fields measurements of specific heat \cite{31} provided the first unambiguous evidence for the singlet CEF ground state of Pr in PrOs$_4$Sb$_{12}$. This result was confirmed by recent inelastic neutron scattering experiments \cite{32} analyzed in the $T_h$ symmetry, and our magnetoresistivity results described in Sections 6.2 and 7.2.

6.2 Magnetoresistance of PrOs$_4$Sb$_{12}$

Magnetoresistance of PrOs$_4$Sb$_{12}$ was measured to search for further experimental evidences of the proposed CEF scheme and for possible signatures of heavy-fermion behavior.

The main indication of heavy electrons in PrOs$_4$Sb$_{12}$ is the large discontinuity in $C/T$ at $T_c$. The mass enhancement inferred from specific heat measurements is of the order of 50 \cite{7}. This value is an estimate and there is no consensus on a precise value. An uncertainty exists in evaluation of the effective mass directly from the low temperature zero-field specific heat, because there is no straightforward method of accounting for the CEF specific heat. The corresponding Schottky anomaly is strongly modified because of the hybridization between the $f$ and conduction electrons. The zero-field specific heat just above $T_c$ is dominated by CEF effects.

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Several other estimates of $m^*$ have been proposed. For instance, Goremychkin et al. [32] suggested $m^*$ enhancement to be about 20. However, their estimate was based on the Fulde-Jensen model, which we do not believe is relevant to PrOs$_4$Sb$_{12}$. This enhancement is 3–7, according to the de Haas-van Alphen measurements [44]. However, dHvA effect was analyzed over a wide range of fields 3–17 T and did not take into account $m^*$ being dependent of $H$ [44].

The residual resistivity ratio $RRR = \rho(300K)/\rho(T\to0)$ of the investigated sample was about 150. This value is among the highest reported, implying high quality of our sample. Both the current and the magnetic field were parallel to the (1 0 0) direction (longitudinal magnetoresistance). The measurements were done using the 18 T/20 T superconducting magnet at the Millikelvin Facility, National High Magnetic Field Laboratory, Tallahassee, Florida. The temperature range was 20 mK to $\approx$0.9 K, the maximum field used 20 T. Measurements at the University of Florida were done in fields up to 14 T down to 0.35 K.

The zero-field electrical resistivity, another important characteristics of heavy fermion metals, does not provide a straightforward support for the presence of heavy electrons. Maple et al. [91] found that the resistivity, between 8 and 40 K, follows a fermi-liquid temperature dependence ($\rho = \rho_0 + AT^2$). Our resistivity data between 8 and 16 K follows the above mentioned dependence (Fig. 6-11) with $A \approx 0.009 \Omega\text{cm/K}^2$ (in agreement with $A$ found by Maple et al. [91]). As inferred from Kadowaki-Woods (KW) relation ($A/\gamma^2 \approx 1 \times 10^{-5} \Omega\text{cm(mol K/mJ)}^2$) [60] this value of $A$ implies a small electronic specific-heat coefficient $\gamma \approx 30 \text{ mJ/K}^2 \text{ mol}$, comparable to the one measured for LaOs$_4$Sb$_{12}$. So, evidently there is an upper temperature limit (less than 8 K) for the heavy fermion behavior.

Figure 6-12 shows the resistivity of PrOs$_4$Sb$_{12}$ in $H=3, 10, 15, 16, 17$ and 18 T in a temperature range of 20 mK to 0.9 K. The resistivity below 200 mK saturates for all fields. This temperature dependence at the lowest temperature was also observed by other groups [91, 92]. Therefore, the resistivity for all other intermediate fields was measured to
350 mK. Figure 6-13 shows the resistivity between 350 mK and about 1.3 K for several relevant fields (3.5, 5.5, 7, 10, and 13 T).

Maple et al. [91] proposed the following temperature dependence for fixed magnetic field: $\rho = \rho_0 + aT^n$, with $n > 2$. In their study (transversal magnetoresistivity) $n$ was $\sim 3$ for 3 T and 2.6 for 8 T. In our longitudinal case these exponents are slightly larger (e.g., 3.9 for 3 T). The exponents depend on the temperature range of the fit, i.e., $n$ becomes smaller when the upper temperature limit of the fit decreases. The residual resistivity $\rho_0$ values resulted from the fit on different temperature ranges (included in the 350 mK and 0.9 K interval) were close to $\rho$ at 20 mK. The residual resistivity $\rho_0$ attains a maximum near $H=10$ T, field corresponding to the crossing between the two lowest-energy CEF levels of Pr (Fig. 6-14, lower panel). In this region (around 9–10 T) the lowest two singlets form a quasidoublet possessing quadrupolar degree of freedom. These electric quadrupoles order at sufficiently low temperatures [56] with the ordering temperature having maximum in the crossing field [31, 56]. Resistivity is dominated therefore by the CEF effects or the quadrupolar ordering. This ordering is completely suppressed by fields higher than 15 T. As it can be noticed from Figs. 6-12 and 6-14 the residual resistivity $\rho_0$ does not change substantially in fields higher than 15 T. In fact, it can be seen than the residual resistivity $\rho_0$ versus $H$ field can map the boundary of the AFQ phase, i.e. a sharp increase of $\rho_0$ indeed coincides with the AFQ boundary, indicated by arrows in Fig. 6-14, lower panel.

The same conclusion can be drawn from resistivity measurements for high magnetic fields perpendicular to the current [55]. The rate of the increase of the resistivity with temperature is still changing above 15 T (Fig. 6-12). It can be concluded that the reduction of the temperature rate correlates with an increase of the energy between the lowest CEF levels. A precise accounting of these changes is difficult since neither of the functions checked out describe accurately the variation $\rho(T)$ in a fixed field.

A linear dependence of $\rho$ on $T^2$ is accounted by resistivity ($\rho = \rho_0 + aT^2$) in different temperature ranges (above 0.4 and 0.5 K), as seen in Figs. 6-13. Using the KW ratio [60]
(however, there is no experimental or theoretical studies on $A/\gamma^2$ for Pr-based systems) the electronic specific heat coefficients for $H=3$, 10, and 18 T are about 200, 400, and 200 mJ/K$^2$ respectively. The A coefficient deduced from the narrow range of temperature (Fig. 6-15) increases sharply with the magnetic field and reaches a maximum near 6 T. After a plateau between 6 and 12 T, a strong decrease is encountered. This establishes a correlation between $A$ and both AFQ order and CEFs with a strong increase when approaching the AFQ boundary.

A characteristic field dependence of the residual resistivity (Fig. 6-14, low panel) was associated both to CEF effects and long range AFQ order. The CEF effect on the resistivity was considered by Frederick and Maple [93] using the following expression:

$$\rho_{CEF} = \alpha \left[ Tr(PQ^M) + Tr(PQ^A) \right]. \quad (6-2)$$

The first term represents a contribution due to exchange scattering, and the second term is the contribution due to aspherical (or quadrupolar) scattering. The aspherical Coulomb scattering is due to the quadrupolar charge distribution of the Pr$^{3+}$. Matrices $P_{ij}$, $Q_{ij}^M$ and $Q_{ij}^A$ are defined as follows:

$$P_{ij} = \frac{e^{-\beta E_i}}{\sum_k e^{-\beta E_k}} \frac{\beta (E_k - E_j)}{1 - e^{-\beta (E_i - E_j)}}, \quad (6-3)$$

$$Q_{ij}^M = |\langle i|J_2|j\rangle|^2 + \frac{1}{2}|\langle i|J_+|j\rangle|^2 + \frac{1}{2}|\langle i|J_-|j\rangle|^2, \quad (6-4)$$

$$Q_{ij}^A = \sum_{m=-2}^{+2} |\langle i|y_2^m|j\rangle|^2. \quad (6-5)$$

In the above relations $E_i$ are the eigenvalue of the CEF eigenstates, the $|i\rangle$’s are the CEF eigenstates, $\beta=1/(k_BT)$, and the $y_2^m$’s are the operator equivalents of the spherical harmonics for $L=2$ (i.e., quadrupolar terms) [94]. The $Q_{ij}$-matrices are normalized to each other [95] such that

$$\sum_{i,j} Q_{ij}^M = \sum_{i,j} Q_{ij}^A = (2J+1)J(J+1)|_{J=4} = 180. \quad (6-6)$$
The most intriguing conclusion is a strong enhancement of the $A$ coefficient with the magnetic field between 2 and 6 T. This could imply an enhancement of $m^*$ for fields in this range. Low temperature resistivity calculation for $\Gamma_3$ and $\Gamma_1$ CEF ground state are shown in Fig. 6-16 (upper and lower panel, respectively). Our residual resistivity (at $T=20$ mK) seems to be in a better agreement with calculations for $\Gamma_3$ than for $\Gamma_1$ ground state. Thus, CEF cannot account for the magnetoresistance of PrOs$_4$Sb$_{12}$. We will return to this interesting problem while describing the magnetoresistivity of La-doped crystals.

Furthermore $A$ seems to have a maximum value near the field separating ordered and non-ordered phases. Note that this is not the crossing field for the lowest CEF levels. Thus, these results suggest a possibility of $m^*$ enhancement due to strong fluctuation of the AFQ order parameter.
Figure 6-1. Specific heat $C$ of PrOs$_4$Sb$_{12}$ in fields up to 8 T for $\vec{H}/\langle100\rangle$ (upper panel). The magnetic field phase diagram $H-T$ of PrOs$_4$Sb$_{12}$ in fields up to 8 T for $\vec{H}/\langle100\rangle$ (lower panel) (Reprinted with permission from Aoki et al. [56]).
Figure 6-2. Specific heat $C$ of PrOs$_4$Sb$_{12}$ in 10 and 12 T in the vicinity of FIOP transition for $\vec{H}//(100)$ (Reprinted with permission from Rotundu et al. [31]).
Figure 6-3. Specific heat $C$ of PrOs$_4$Sb$_{12}$ in 13, 13.5, and 14 T, for $\vec{H}/(100)$. A shoulder appears at about 1.2–1.3 K at 13 T and the FIOP transition is suppressed at 13.5 T.
Figure 6-4. Specific heat $C$ of PrOs$_4$Sb$_{12}$ in magnetic fields of 16, 20, and 32 T, for $\vec{H}/|(010)$. 
Figure 6-5. Magnetic field phase diagram H-T of PrOs$_4$Sb$_{12}$ for $\vec{H} // (1 0 0)$ ($H > 8$ T). Filled squares represent the FIOP transition. Open squares correspond to the Schottky anomaly. The inset is the model calculation of the Schottky anomaly assuming the singlet as the ground state [90]. The solid line represents the FIOP boundary; the dashed line corresponds to a maximum in $C$ (Reprinted with permission from Rotundu et al. [31]).
Figure 6-6. Zeeman effect calculations for PrOs₄Sb₁₂ in the Γ₁ CEF ground state scenario. There is crossing of the two lowest levels for $\vec{H} // (100)$ or $\vec{H} // (111)$ at around 9 T and anti-crossing at the same field for $\vec{H} // (110)$. The figure shows only the two lowest levels, i.e. the singlet $\Gamma_1$ and the triplet $\Gamma_5$. 
Figure 6-7. Zeeman effect for PrOs₄Sb₁₂ in the Γ₃ CEF ground state scenario. The effect in strongly anisotropic. There is no crossing of the two lowest CEF levels for \( \vec{H} // (110) \) or \( \vec{H} // (111) \). The figure shows only the two lowest levels, i.e. the doublet \( \Gamma₃ \) and the triplet \( \Gamma₅ \).
Figure 6-8. Specific heat $C$ of PrOs$_4$Sb$_{12}$ for $\vec{H}///(1 1 0)$, $H=10, 12, 13, \text{ and } 14$ T. The inset shows $C$ versus $T$ neat $T_x$ for 8, 9, 9.5, 10, 10.5, and 11 T.
Figure 6-9. Specific heat $C$ of PrOs$_4$Sb$_{12}$ in $H=12$ T, for $\vec{H}//(100)$ (upper panel), and $\vec{H}//(110)$ (lower panel). The arrow indicates the AFQ transition.
Figure 6-10. The magnetic field phase diagram $H$-$T$ of PrOs$_4$Sb$_{12}$ for $\vec{H} \parallel (110)$ ($H>8$ T). The inset shows the specific heat $C_{\text{max}}$ of AFQ versus $H$. For a definition of symbols see Fig. 6.5.

Figure 6-11. Electrical resistivity $\rho$ versus $T^2$ for PrOs$_4$Sb$_{12}$. In the inset is $\rho$ versus $T$ showing the superconducting transition at $T_c=1.85$ K.
Figure 6-12. Resistivity $\rho(T)$ between 20 mK and about 0.9 K of PrOs$_4$Sb$_{12}$ in 3, 10, 15, 16, 17, and 18 T (Reprinted with permission from Rotundu and Andraka [96]).
Figure 6-13. Resistivity $\rho$ versus $T^2$ of PrOs$_4$Sb$_{12}$ for 3.5, 5.5, 7, 10, and 13 T.
Figure 6-14. Coefficient $a$ ($\rho=\rho_0+aT^n$) versus $H$ for $\text{PrOs}_4\text{Sb}_{12}$ fields up to 18 T is in upper panel. The residual resistivity $\rho_0(H)$ is shown in lower panel.
Figure 6-15. Coefficient $A$ ($\rho = \rho_0 + AT^2$) versus $H$. 
Figure 6-16. The calculated $\rho(H)$ of PrOs$_4$Sb$_{12}$, for both $\Gamma_3$ and $\Gamma_1$ scenarios. The vertical line indicates the field crossing of the two lowest CEF levels. Note that the crossing field for the $\Gamma_1$ ground state was assumed at 3 T (lower panel) (Reprinted with permission from Frederick and Maple [93]).
CHAPTER 7
Pr\textsubscript{1−x}La\textsubscript{x}Os\textsubscript{4}Sb\textsubscript{12}

In this Chapter the La-alloying study of PrOs\textsubscript{4}Sb\textsubscript{12} by dc and ac susceptibility, specific heat and resistivity is presented. One of main objectives of this work was to differentiate between different proposed models of the conduction electron mass enhancement in PrOs\textsubscript{4}Sb\textsubscript{12}. Mechanisms that have been considered range from single-ion models, such as the quadrupolar Kondo effect \cite{7,16} or virtual CEF excitations \cite{32,36}, to cooperative models invoking proximity to a long-range order (proximity to the low temperature state of AFQ order) \cite{56}. While investigating the applicability of these models, close attention was paid to whether the single-ion parameters such as the CEF spectrum and hybridization parameters vary with the alloying.

7.1 Lattice Constant

The room temperature X-ray diffraction patterns for several La concentration are given in Fig. 7-1. The results of the X-ray diffraction analysis were consistent with single phase materials. A very small and monotonic increase of the lattice constant, \(a\), with the La content is detected (Fig. 7-2). The lattice constant is calculated from the high index line (8 2 2) of the X-ray diffraction pattern. Calculations from smaller angle lines result in the same dependence of \(a\) on \(x\), but had a much larger scatter. These small changes (about 0.03\%) between the end compounds is in agreement with previously reported \cite{57} and almost non-existent lanthanide contraction in ternary skutterudites containing Sb, of a general form LnT\textsubscript{4}Sb\textsubscript{12}, where T and Ln are transition element and light lanthanide, respectively.

To present this change in a proper perspective we recall that the change of the lattice constant across Pr(Os\textsubscript{1−x}Ru\textsubscript{x})\textsubscript{4}Sb\textsubscript{12} \cite{97} is 10 times larger. This is despite the fact that the atomic radii of Os and Ru are almost identical (1.35 and 1.35 Å for Os and Ru respectively), while La is much larger than Pr (1.88 versus 1.82 Å). In Pr(Os\textsubscript{1−x}Ru\textsubscript{x})\textsubscript{4}Sb\textsubscript{12} the CEF parameters increase monotonically with \(x\). Very small changes in lattice constant in Pr\textsubscript{1−x}La\textsubscript{x}Os\textsubscript{4}Sb\textsubscript{12} suggest small, if any, changes in the CEF parameters.
and hybridization. These parameters depend on the position of ligand atoms with respect to Pr. These small changes of the lattice constant in $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ provide a unique opportunity for the alloying study of superconductivity and other phenomena that are strongly influenced by microscopic inhomogeneities associated with the lattice constants’ mismatch.

### 7.2 DC Magnetic Susceptibility

Susceptibility measurements were done on single-crystal samples of masses ranging between a few mg to 50 mg belonging to different batches. Specific heat measurements were performed as well on samples characterized by the susceptibility.

Figure 7-3 shows the susceptibilities only in the range 1.85 to 10 K. All data are normalized to a Pr mole. Due to the very small size of the samples used in the initial measurements, the measured moment of most of the samples and the background (the magnetic moment of the sample holder consisting of a piece of a plastic drinking straw) were comparable at 10 K. At room temperature the magnetic moment of the samples was even smaller than the background, especially for dilute concentrations. In order to avoid this background contribution, the magnetic susceptibilities were remeasured (for $x=0, 0.05, 0.3, 0.8$ and 0.95) using several crystals and holding them between two long concentric straws. No background subtraction was needed this time. The Curie-Weiss temperature was found above 150 K and the effective magnetic moment in the range $3.2–3.6\mu_B$/Pr atom. The values are in the range of moments reported for pure PrOs$_4$Sb$_{12}$. Some discrepancy between these values and that expected for Pr$^{3+}$, $3.58\mu_B$ [52], can be due to an error in mass determination. Because of the very fragile nature of these crystals, some of them broke off during the measurement and small fractions moved in between the two tubes. A further check of the magnetic moment was performed on one large crystal for $x=0.67$ ($\sim$20 mg each). Figure 7-4 shows the susceptibility and the inverse of susceptibility for $x=0.67$. From the Curie-Weiss fit the high temperature effective moment is found to be $3.62\mu_B$/Pr mol, close to the value expected for Pr$^{3+}$. 

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All low temperature susceptibility data (Fig. 7-3) exhibit a broad maximum at 3–5 K due to excitations between the lowest CEF states. Our high magnetic field specific heat study [31], and neutron [32, 84] measurements established $\Gamma_1$ singlet as the CEF ground state separated by about 8 K from the first excited $\Gamma_5$ triplet. Very small changes in the position of these maxima in the susceptibility are the first indication that CEF are essentially unaltered by the doping as expected from the measurement of the lattice constant.

Another interesting aspect of the susceptibility is a strong initial reduction of the low-temperature values of $\chi$ (normalized to a mole of Pr) by La. The reduction of the maximum susceptibility from approximately 100 for $x=0$ to about 50 memu/Pr mol for $x=0.4$ is clearly outside the error bar. The aforementioned measurements on assemblies of crystals for $x=0.8$ and 0.95 also resulted in a 4 K value of about 50±5 memu/Pr mol for both compositions. Some broadening and decrease in magnitude of the CEF susceptibility are expected in mixed alloys due to increased atomic disorder. However, the very large initial drop in the susceptibility and lack of variation above $x=0.4$ might indicate that some characteristic electronic energy (analogous to a Kondo temperature) increases sharply upon substituting La for Pr. A similar suppression of the corresponding maximum is observed in the specific heat data discussed in the next section.

7.3 Zero Field Specific Heat

7.3.1 Specific Heat of PrOs$_4$Sb$_{12}$: Sample Dependence

The main evidence for heavy fermion behavior in PrOs$_4$Sb$_{12}$ comes from a large discontinuity of the specific heat at $T_c$. Specific heat provides evidence for unconventional superconductivity. The evidence includes a power low dependence of $C$ below $T_c$, and the presence of two distinct superconducting transition. PrOs$_4$Sb$_{12}$ was initially reported to have a single superconducting transition at $T_c=1.85$ K [7]. More recent specific heat measurements revealed two superconducting transitions (Vollmer et al. [63], Maple et al. [53], Oeschler et al. [64], Cichorek et al. [65]).
Before discussing zero field specific heat measurements of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ we need to comment on the sample dependence of the specific heat of PrOs$_4$Sb$_{12}$. This is in order to distinguish La-induced changes from variation related to sample quality. In Fig. 7-5 we present the specific heat near $T_c$ for three representative samples from three different batches. All three samples were obtained in an identical way. All three samples have pronounced lower temperature transitions. The upper temperature transition is less distinct and sample dependent. Our convention of defining $T_{c1}$ and $T_{c2}$ (by local maxima or shoulders in $C/T$ versus $T$) is illustrated in Fig. 7-5. The upper transition temperature $T_{c1}$ is identical for all three samples. There seems to be some sample dependence for the lower transition temperature $T_{c2}$. However, the variation is very small considering that each $C/T$ at a given $T$ in Fig. 7-5 was obtained by integrating the specific heat over 0.04T interval. The width of the transition defined, for comparison reason, by $T_3 - T_c$ (Fig. 7-5) is large and approximately equal for all the samples. Finally, $\Delta(C/T)$ defined as the difference between $C/T$ at $T_{c2}$ and $T_3$ is about 800 mJ/K$^2$ mol.

Our observations are consistent with other, particularly more recent, reports. Almost all recent investigations find two superconducting anomalies, more pronounced at $T_{c2}$ and less defined at $T_{c1}$. An exception to this rule are unpublished data by Aoki et al. [98] that show a sharp peak at $T_{c1}$, and only a change of slope in $C/T$ at $T_{c2}$. The width of the transition, $\sim$0.2 K, defined above, is quite similar for all published data. There is a large distribution of reported $\Delta(C/T)$ at $T_c$, from 500 to 1000 mJ/K$^2$ mol. A usual determination of $\Delta(C/T)$ by an equal area (conservation of entropy) construction cannot be applied due to the presence of two superconducting transitions. Applying our method, $C/T(T_{c2}) - C/T(T_3)$, results in an average $\Delta(C/T)$ of 800 mJ/K$^2$ mol for the most recent results.

7.3.2 Zero Field Specific Heat of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$

In order to account for normal-electron and phonon contributions to the specific heat of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ alloys, the specific heat of LaOs$_4$Sb$_{12}$ was measured. The normal state
specific heat between 1 and 10 K is shown in Fig. 7-6 in the format of $C/T$ versus $T^2$.
The results can be expressed by the following equation

$$
C/T = 56 + 1.003 T^2 + 0.081 T^4 - 4.260 \times 10^{-4} T^6,
$$

where $C/T$ is expressed in mJ/(K$^2$ mol) and $T$ in K (Fig. 7-6). A significant nonlinearity in $C/T$ versus $T^2$ is probably due to the rattling motion of loosely bound La atoms [99].

Values of $\gamma$ and $\beta$ for LaOs$_4$Sb$_{12}$ reported by other research groups are: $\gamma$ of 36 [54], 55 mJ/K$^2$ mol [100], 56 [44] and $\beta$=0.98 mJ/K$^3$ mol [101].

Figures 7-7 and 7-8 present the f-electron specific heat of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ alloys, i.e. the specific heat of LaOs$_4$Sb$_{12}$ and, normalizing to a mole of Pr. Note that the phonon specific heat of pure PrOs$_4$Sb$_{12}$ in Chapter 6 was taken from Vollmer et al. [63], which was derived by fitting the total specific heat $C$ to a function representing phonon, conduction electrons, and Schottky contributions. However, using the LaOs$_4$Sb$_{12}$ specific heat seems to be more justifiable for moderately and strongly La-doped alloys and therefore this way of accounting for phonons is consistently used in this chapter on La alloying.

### 7.3.2.1 Evolution of $T_c$ with the La Doping

Figure 7-7 shows the specific heat for $x=0$, 0.05, 0.1, and 0.2 near the superconducting transition temperature. As already discussed, the pure compound has two superconducting anomalies in the specific heat. The specific heat data for $x=0.05$ exhibit a shoulder which seems to correspond to the anomaly at $T_{c1}$ for $x=0$. The width of the transition ($T_3-T_{c2}$) for $x=0$ is about 0.2 K. This width becomes slightly smaller for $x=0.05$. The specific heat for $x\geq0.3$ alloys (Fig. 7-8) exhibits one superconducting transition only. The width of the transition for this group of materials is about a half of the width of the pure material.

This reduction cannot be accounted for by the reduction of $T_c$ itself. A similar conclusion about a drastic reduction of the width of the transition can be derived from graphs in which $T$ is replaced by a reduced temperature $T/T_c$. The reduction is probably related to a disappearance of one superconducting transition (at $T_{c1}$).
Open symbols in Fig. 7-9 denote the lower temperature superconducting transition, and the filled squares symbolize the higher temperature superconducting transition $T_{c2}$. Lanthanum doping has a surprisingly weak impact on $T_c$. This weak dependence (approximately linear) of $T_c$ on $x$ in Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ is unusual for heavy fermion alloys. For instance, heavy fermion superconductivity in UBe$_{13}$ is completely suppressed by only 3% La [102] substituted for U. Furthermore, since PrOs$_4$Sb$_{12}$ is clearly an unconventional superconductor (e.g., time reversal symmetry breaking) while La$_x$Os$_4$Sb$_{12}$ is presumably a conventional superconductor we would expect, while varying $x$, a suppression of one type of superconductivity before the other type emerges. Figure 7-10 shows that there is smooth evolution of $T_c$ (and superconductivity) between the end-compounds. A somewhat stronger suppression is observed in the case of Ru replacing Os [71, 97]. But even in this case, the $T_c$ reduction rate is small if compared with the majority of Ce- and U-based heavy fermions and considering the fact that Ru alloying drastically affects CEF energies and hybridization parameters.

### 7.3.2.2 The Discontinuity in $C/T$ at $T_c$

Existence of two distinct superconducting transitions in PrOs$_4$Sb$_{12}$ makes the determination of the discontinuity in $C/T$ somewhat arbitrary. Furthermore, it also complicates the interpretation of this discontinuity. Despite a substantial recent improvement in sample quality, the question whether the two transitions correspond to different regions of the sample becoming superconducting at different temperatures or whether the lower transition corresponds to the change of the symmetry of the superconducting order parameter in a homogeneous medium is not completely settled. The comparable magnitude (equal as argued by Vollmer et al. [63]) of the anomalies at $T_{c1}$ and $T_{c2}$ precludes a popular speculation that one of these transitions is associated with surface superconductivity.

As it was already stressed, this $\Delta(C/T)$ is currently the main evidence for the presence of heavy electrons. The presence of a modified Schottky anomaly near $T_c$ makes
a direct determination of the electronic specific heat coefficient unreliable. In a BCS-type superconductor, $\Delta C/T_c$ is related to the electronic specific heat coefficient $\gamma$. In general, $\Delta C/T_c$ and $\gamma$ are affected by the coupling strength of the Cooper pairs and can vary by a factor of order of 2–3. Nevertheless, for lack of any other measure, we use this quantity as an indication of heaviness of electrons in Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$.

We recall that LaOs$_4$Sb$_{12}$ is also a superconductor, therefore for dilute Pr concentrations the normalization of $C/T$ to Pr mole (used in Figs 7-7 and 7-8) has no meaning. Therefore, Fig. 7-10 shows the total $\Delta(C/T)$ per formula unit. There is a drastic decrease of $\Delta(C/T)$ with $x$ for $0 \leq x \leq 0.2$ (Fig. 7-7). The discontinuity of $C/T$ is suppressed from 800 for $x=0$ to 280 for $x=0.2$ and further to about 160 mJ/(K$^2$ Pr mol) for $x=0.3$ ($C/T$ is seven fold reduced with $x$, for $x$ between 0 and 0.3). $\Delta(C/T)$ stays approximately constant with $x$ for $0.3 < x < 1$ (Fig. 7-8) and is approximately equal to $C/T$ at $T_c$ of LaOs$_4$Sb$_{12}$. Therefore, these results suggest that the heavy fermion character disappears above $x=0.3$. Therefore, there is a lack of strong correlation between the heavy-fermion character as measured by $\Delta(C/T)$ at $T_c$ or $\Delta C/T_c$ and the average $T_c$. Thus, the results argue also for different mechanisms responsible for the heavy fermion state and enhanced value of $T_c$ in PrOs$_4$Sb$_{12}$.

7.3.2.3 The Schottky Anomaly

The evolution of Schottky-like anomaly in pure PrOs$_4$Sb$_{12}$ near 3 K with magnetic fields provided important information on the CEF configuration of Pr. The discrepancy between the theoretically predicted temperature dependence and the observed one has been explained by mixing of $f$- and conduction-electrons degrees of freedom, reducing the entropy associated with the pure Schottky anomaly. The results on the discontinuity of $C/T$ at $T_c$, presented in the previous section, suggest that the heavy fermion character is strongly suppressed by the La alloying. Thus, one would expect the mixing to be reduced for strongly La-doped samples and the Schottky anomaly to approach the theoretically predicted temperature dependence. Recall that the maximum value of the specific heat
in PrOs$_4$Sb$_{12}$ is about 7100 mJ/K mol, smaller than the theoretical value of 8500 for singlet to triplet excitations. However, as it can be inferred from Figs. 8.7 and 8.8 the specific heat at the Schottky-like maximum decreases noticeably with the alloying. Some reduction and broadening of such a maximum due to CEF excitations can be explained by disorder effects induced by the alloying. However, this effect should be small. La does not change the local symmetry of Pr nor the distances between Pr and its nearest neighbors. Furthermore, the main reduction takes place between $x=0$ and $x=0.2$ and, within our error bars, there is no appreciable change beyond $x=0.3$. This reduction, by a factor of 2, is about the same as the decrease of the low temperature magnetic susceptibility, discussed in Section 7.2.

In order to study further this specific heat reduction, a large crystal of Pr$_{0.33}$La$_{0.67}$Os$_4$Sb$_{12}$, for which addenda heat capacity is negligible below 6 K, was investigated. First of all, the effective magnetic moment measured at room temperature for this particular crystal is very close to the expected value for Pr$^{3+}$. Thus, the reduced specific heat cannot be explained by incorrect Pr stoichiometry, nor by some Pr ions being in a mixed-valent state. The results, after subtracting the specific heat of LaOs$_4$Sb$_{12}$ and dividing by 0.33, are shown in Fig. 7-11 in the form of $C/T$. This graph shows also a fit to the function describing a Schottky specific heat for a singlet-triplet excitations, scaled by a factor $a=0.44$. A similar scaling was used by Frederick et al. [71] to account for the specific heat data of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ in terms of the singlet CEF ground state. A necessity to use such a small scaling factor for this model of CEF (of about 0.5) was used by Frederick et al. [71] to argue for a doublet CEF ground state. However, as can be seen from Fig. 7-12, a reasonable fit to the doublet CEF model also requires a scaling factor, although somewhat larger ($a=0.73$). Finally, a fit to the singlet-to-singlet scattering requires no scaling at all. The fit shown in Fig. 7-13 obtained with $a$ as an adjustable parameter, resulted in $a=1.009$ (within 1%).
These results pose two important questions. What is the origin of a two-fold decrease in the specific heat values upon La doping? Is the agreement between the measured specific heat and that predicted for a singlet-singlet Schottky anomaly meaningful or accidental? This apparent agreement seems to suggest that the first excited CEF state is not a triplet but a singlet. Can La alloying lead to such strong, non-cubic, modification of CEF potential?

7.4 Specific Heat in Large Fields

To answer the above stated questions, low temperature specific heat measurements of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ for $x=0.02, 0.1, 0.2,$ and $0.6$ have been conducted in magnetic fields up to 14 T. Other goals of this study were to determine the critical concentration for which the field-induced antiferroquadrupolar (AFQ) ordered phase is suppressed and to search for possible correlations between the existence of this field-induced ordered phase and heavy fermion behavior. The effect of small amounts of La on the field-induced AFQ transition is illustrated in Fig 7-14. This figure shows the specific heat for $x=0$ and 0.02 for fields (applied in the (1 0 0) crystallographic direction) in which this transition exhibits strongest anomalies. Recall that for $x=0$, $T_x$ (filled circles in Fig. 7-14) and $C(T_x)$ reach maximum values between 8 and 10 T. We estimate about 25-30% reduction of the size of the anomaly in 10 T between $x=0$ and 0.02. Also, $T_x$ itself is reduced by about 20% in this field. This suppression of the AFQ order is relatively mild in comparison with other systems exhibiting this type of long-range order, although in zero field. For instance, 2% of La suppresses completely the AFQ order in another well-studied Pr compound, PrPb$_3$. We believe that remnants of this field-induced transition can be detected in much more dilute Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ alloys. For instance, the anomalies seen in $x=0.1$ in fields 10 and 12 T (Fig. 7-15) are too sharp to be associated with Schottky maxima only. On the other hand, we could not resolve these field-induced AFQ transitions in $x=0.2$ alloy (Fig. 7-16). However, Yonezawa et al. [103] suggest presence of the field induced AFQ order for much higher La-concentrations, as high 0.3.
Broad anomalies seen in fields of 6, 12, and 14 T for $x=0.1$ (Fig. 7-15) are reminiscent of Schottky maxima, and are due to excitations between lowest CEF levels. Figure 7-18 shows the magnetic field phase diagram for $x=0$, 0.02, 0.1, and 0.2. Open symbols stand for AFQ anomalies while closed symbols for Schottky maxima (or for a superposition of these two types of anomalies as discussed for $x=0.1$). There is no change, within our experimental uncertainty, of the temperature of the high field (13 T and 14 T) Schottky maximum between $x=0$ and 0.2. A straight line drawn for 13 and 14 T points ($x=0$, 0.1 and 0.2) would intercept the field axis at about 9 T, a value of the crossing field.

Thus, these results, together with previously discussed evolution of zero field properties, particularly weak sensitivity of the temperature of the magnetic susceptibility maximum, provide strong arguments for CEF energies and eigenstates being unaffected by La alloying, at least to $x=0.2$. On the other hand, the temperatures of the Schottky anomaly in 13 and 14 T for $x=0.6$ are about 0.3 K lower than those for $x\leq0.2$, suggesting a possibility that the CEF energies and the crossing field for $x=0.4$ increase by approximately 20%. Very recent results of the high field specific heat study of $x=0.67$ by Andraka [116] also imply the CEF energies to be 20–25% larger than in the undoped material. Thus, there is a possibility of an abrupt (but small) change of CEF energies somewhere between $x=0.2$ and 0.67. However, to within our experimental uncertainty, we claim CEF energies (and eigenstates) to be identical between $x=0$ and 0.2, thus in the concentration range where dramatic changes of $m^*$ are anticipated based on measurements of $\Delta(C/T)$.

These high field results allow us to comment on whether the agreement between the magnitude of the zero field anomaly in moderately and strongly ($x=0.67$) diluted alloys and the Schottky specific heat corresponding to singlet-singlet excitations is accidental or meaningful. The specific heat maximum for $x=0.4$ in 14 T is approximately 1500 mJ/K mol ($\pm200$ mJ/K mol). This value is significantly smaller than the theoretical value for the Schottky maximum (3650 mJ/K mol). Similarly the specific heat of Pr$_{0.33}$La$_{0.67}$Os$_4$Sb$_{12}$ in magnetic fields as high as 18 T shows a maximum whose value
is only about a half of the expected one for the singlet-singlet Schottky maximum. These and zero field specific heat data suggest that only a fraction (roughly 1/2) of Pr ions in $x=0.4$ and 0.67 alloys contribute to the specific heat maximum. Thus, there is a possibility of the existence of two crystallographic inequivalent Pr sites with different CEF configuration in these alloys. Very recently, the group of Sato has found high temperature anomalies in the specific heat of strongly diluted Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ that cannot be accounted by a single set of CEF energies [103].

7.5 Magnetoresistance of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$

The magnetoresistance of pure PrOs$_4$Sb$_{12}$ posed several important questions that we tried to answer by investigating Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ alloys. Among the questions to be answered is the unusual shape of the magnetoresistance versus magnetic field, more consistent with the doublet CEF ground state than with the now established singlet. What is the effect of the AFQ ordering on magnetoresistance? Is the procedure of extracting the $T^2$ coefficient from the resistivity over a finite temperature range away from $T=0$ justifiable? Otherwise, does the La alloying expand the $T^2$ temperature regime (to both lower and higher temperature values) in the resistivity?

The resistivities of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ for $x=0.05$, 0.3 and 0.7 in fields up to 18 T were measured in temperature down to 20 mK. The uncertainty in the determination of the absolute value of the resistivity was up to 30%. The room temperature resistivity was approximately equal for all three crystals. Therefore, we assumed that the resistivity at room temperature is 300 $\mu$Ωcm for all crystals, consistent with the published value for both end compounds, PrOs$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$ [92]. The ratio of the room temperature resistance to the resistance extrapolated to $T=0$ ($RRR$) was 50, 180, and 170 for $x=0.05$, 0.3, and 0.7, respectively. With the exception with the result for $x=0.05$, these values belong to the highest ever reported for pure and doped PrOs$_4$Sb$_{12}$, suggesting good qualities of our samples. The $x=0.05$ crystal was from the same batch whose results of specific heat and susceptibility were described in previous Sections.
Figure 7-19 shows the resistivity versus magnetic field for Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ at 20 mK for $\vec{H} \parallel I$ and $\vec{H} \perp I$, respectively. The current was applied in the (100) direction. Superconductivity was suppressed by 2 T. Above this field, the shape of the graphs is a distorted dome with the low field side (around 6 T) more abrupt. The high field side (around 14 T) shows a moderate variation with the field.

Longitudinal magnetoresistance for $x=0.05$ at two temperatures, 20 and 300 mK, is shown in Fig. 7-20. The transverse magnetoresistance for the same alloy at for temperatures 20, 310, and 660 mK is shown in Fig. 7-21. The two curves in Fig. 7-20 show excellent overlap, implying an absence of temperature dependence of the resistivity below 300 mK for any field between 2 and 18 T. This overlap is consistent with our resistivity measurements of the pure compound (Fig. 6-12) for which the resistivity was flat below 300 mK for all fields between 3 and 18 T.

Thus, the 20 mK resistivity above the critical field is essentially identical to the residual resistivity, $\rho_0$. $\rho_0$ for $x=0.05$ increases by a factor of 2 between 2 and 10 T (Fig. 7-21). This increase is significantly larger than the corresponding increase for $x=0$ which was about 25%. This larger increase in $\rho_0$ for $x=0.05$ coincides with some suppression of the AFQ order with La, as demonstrated by specific heat measurement in magnetic fields. A larger $\rho_0$ at 10 T for $x=0.05$ is due to a smaller degree of the AFQ order. The drop in $\rho_0$ above 10 T, on the other hand, is less pronounced for $x=0.05$ than $x=0$. These trends continue with further La doping, $x=0.3$.

The electrical resistivity for $x=0.3$ in zero field, just above $T_c$, is proportional to the square of temperature, with $A=0.16 \mu\Omega cm/K^2$ (Fig. 7-22, upper panel). By applying the Kadowaki-Woods formula, $A/\gamma^2=10^{-5}$ (with $A$ in $\mu\Omega cm/K^2$ and $\gamma$ in $mJ/K^2$ mol), we arrive at $\gamma$ of order 100 $mJ/K^2$ mol. However, the application of just 0.5 T (approximately $H_{c2}$ for this concentration) again reveals the saturation of resistivity at the lowest temperatures which was seen in the pure compound (Fig. 6-12). In higher magnetic fields, the linear variation in $T^2$ is gradually restrained to narrower temperature intervals
such that it is lost for $H=9$ T (Fig. 7-23, upper panel). This dependence is recovered in 13 T, but again, above a certain temperature (Fig. 7-23, lower panel).

Figure 7-24 shows the resistivity at 20 mK for $x=0.3$ up to 18 T for fields parallel to (0 0 1), (0 1 1), and (0 1 0) and $I//\langle001\rangle$. All three isotherms exhibit a step centered near 9–10 T superimposed on a linear background. In the investigated field range we do not find the dome structure characteristic of $x=0$ or 0.05. Note the approximately equal slopes of the curves below 3 T and above 14 T. Interestingly, Sugawara et al. [92] found that the magnetoresistance of LaOs$_4$Sb$_{12}$ at 0.36 K is approximately linear in magnetic field and has a similar orientation as that shown in Fig. 7-24. The larger magnetoresistance of LaOs$_4$Sb$_{12}$ for (0 1 1) than for the (0 0 1) direction correlates with the larger magnetoresistance of $x=0.3$ for (0 1 1) than for (001) direction (Fig. 7-24). Therefore, we can assume that the approximately linear in $H$ magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ below 3 T and above 14 T is due to normal (non-$f$) electrons. Subtracting such linear contributions results in identical curves, almost flat below 6 T and above 13 T (inset to Fig. 7-24). Furthermore, the resulting curves are identical for all three directions, arguing for very isotropic $f$-electron magnetoresistance. This isotropic behavior is consistent with the singlet and inconsistent with the doublet CEF ground state of Pr.

The field variation of the resistivity shown in the inset to Fig. 7-24 is consistent with model calculations of the resistivity for the $\Gamma_1-\Gamma_5$ model by Frederick and Maple [93]. According to these calculations that take into account magnetic and quadrupolar degrees of freedom, the resistivity should exhibit a sharp jump at the crossing field. The independence of the crossing field on the crystallographic direction is also consistent with the $\Gamma_1-\Gamma_5$ CEF model (Fig. 6-6). Recall that CEF level crossing in the $\Gamma_3-\Gamma_5$ CEF model occurs for the (1 0 0) direction only (Fig. 6-7).

Figure 7-25 shows raw data for the same sample when $\vec{H}//I//\langle100\rangle$ for several temperatures, 20, 310, 660, and 1100 mK. No background subtraction has been done.
The data exhibit the very similar step-shaped curves, although somewhat less pronounced and broadened, particularly for 1.1 K. This evolution in temperature is also in general agreement with model calculations of the resistivity for the $\Gamma_1-\Gamma_5$ model by Frederick and Maple [93].

The more dilute concentration, $x=0.67$ was investigated to about 0.35 K in temperature and in fields up to 14 T. Its resistivity at the lowest temperatures exhibits a similar magnetic field dependence to that for $x=0.3$ (Fig. 7-26).

The presented resistivity data show that there is no sign of FIOP ordered phase in the $x=0.3$ material. Our previous specific heat measurements indicated that the FIOP phase disappears somewhere near $x=0.2$. However, the main effect of the La doping on the AFQ anomaly is the suppression of its size, with a somewhat smaller effect on the transition temperature itself. Thus, it is possible that this field-induced AFQ order persists to concentrations larger than $x=0.2$, but its signatures in the specific heat are undetectable due to small entropies involved. The calculations of the resistivity predicting the step in the magnetoresistance were performed in a single impurity limit, i.e., assuming independent scattering from each Pr ion. For PrOs$_4$Sb$_{12}$ the scattering in both small and large fields should be coherent; i.e., one might expect small contribution from $f$ ions away from the crossing field of about 9 T. At the crossing field, the Pr lattice loses its coherence since some of the ions will be in the excited state; i.e., the translational periodicity is lost. We believe, this coherence mechanism is responsible for the dome shape of $\rho(H)$ in PrOs$_4$Sb$_{12}$ and the difference between pure and La-doped alloys.

The unchanged field value for the step in the resistivity between $x=0.3$ and 0.67 suggests that CEF energies are not significantly altered by the La doping. This is in agreement with the almost unchanged temperature position of the maximum in the magnetic susceptibility and specific heat believed to be due excitations between the lowest CEF levels.
Therefore, the main finding of this study is the isotropic behavior of the f-electron magnetoresistance in La-doped samples. This provides another support for the singlet CEF ground state (consistent also with our previous result of isotropic behavior in high field specific heat data). The strong increase of the magnetoresistance between 7 and 11 T seems to be related to the (near) crossing of the lowest CEF levels.

### 7.6 Upper Critical Field $H_{c2}$

#### 7.6.1 AC Susceptibility

The ac-susceptibility measurements were performed on the same samples used in zero and high field specific heat measurements. Figure 7-27 shows the ac susceptibility (in arbitrary units) of $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ for $x=0$, 0.05, 0.4, 0.8, and 1 versus reduced temperature $T/T_c$, where $T_c$ was determined by the diamagnetic onset. The measurements were done in the Earth’s magnetic field. No significant differences were noted when we used different frequencies, 27 and 273 Hz. The ac susceptibility and specific heat, presented in the next Section, are sample dependent. Two samples from different batches were measured for $x=0$. The diamagnetic onset is the same for the two samples, about 1.85 K. While sample No. 1 has one superconducting transition, sample No. 2 have two. The transition of sample No. 1 is slightly wider than the combined transition of sample No. 2. However, the widths are in agreement with the values of about 0.2 K previously reported [59, 65, 104]. The temperature separation between the two steps in ac susceptibility for $x=0$ is about 0.14 K and is approximately equal to that between the peaks in the specific heat. The field cooled dc magnetization of samples performed by Méasson et al. [59] showed a Meissner effect of 50%, indicating (like specific heat) bulk superconductivity. Therefore, there is a possibility that the two transitions are due to inhomogeneous coexistence of two superconducting phases in $\text{PrOs}_4\text{Sb}_{12}$. For $x=0.05$ both transitions are visible and the overall width of the transition is about 0.13 K. The onset temperature is approximately the same as for $x=0$. From $x=0.2$ to 0.8 the ac susceptibility data are similar. There is an increase of the transition width (in the reduced
temperature scale) for $x=0.8$ followed by a drastic decrease for $x=1$ (Fig. 7-27). The width of the transition of LaOs$_4$Sb$_{12}$ ($T_c=0.78$ K) is about 0.02 K. The strong reduction of the width at $T_c$ in the ac susceptibility with small $x$ correlates with the strong reduction of the width in specific heat between $x=0$ and $x_{cr} \approx 0.2-0.3$.

The most probable origin of the wide superconducting transitions is inhomogeneities, whose origin is not clear. PrOs$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$ are isostructural, but LaOs$_4$Sb$_{12}$ exhibits a very sharp transition. Therefore, the inhomogeneities seem to be associated rather with 4$f$ electrons of Pr. One plausible scenario is a mixture of two electronic configurations of Pr, 4$f^1$ and 4$f^2$. However, high temperature magnetic susceptibility data were in general consistent with 4$f^2$ configuration of Pr. Also, the $L_{III}$ absorption [49] and inelastic neutron scattering [32, 105] results agree with a valence of Pr close to +3.

Another scenario for the existence of inhomogeneities is the closeness of the system to a long range antiferroquadrupolar order [56]. This means that clusters with a short-range order would have different superconducting parameters than the remaining part of the sample.

### 7.6.2 Determination of $H_{c2}(T)$ by Specific Heat Measurements in Small Magnetic Fields

Similar to the ac susceptibility, the specific heat of PrOs$_4$Sb$_{12}$ is sample dependent. This sample dependence has been discussed already in Section 7.3 on crystal No. 1 (Fig. 7-27, the upper panel) which shows a single wide transition in ac susceptibility exhibits two transitions in $C/T$ at $T_{c1}$ and $T_{c2}$ (Fig. 7-28, upper panel). Crystal No. 2, from another batch, that showed two distinct transitions in ac susceptibility, has a pronounced anomaly at $T_{c2}$, and only a shoulder that might correspond to a different transition at $T_{c1}$. We determine $T_{c1}$ ($T_{c2}$ or $T_c$ in the case of a single transition) by a maximum in $C/T$. Despite the aforementioned differences, both samples have the same $T_{c2}$ and $T_{c1}$, within the experimental uncertainty, and the same width of the combined transition.
The response of the specific heat of the two crystals to magnetic field is also shown in Fig. 7-27. For both samples the field was oriented approximately in the (1 0 0) crystallographic direction. For sample No. 1 the magnetic field, concomitant with a steady lowering of both transition temperatures, suppresses $C/T$ values at $T_{c1}$ and $T_{c2}$, but in a different manner. The anomaly at $T_{c2}$ is much more rapidly reduced than that at $T_{c1}$. For instance, 0.5 T suppresses completely the $T_{c2}$ peak, while $T_{c1}$ peak is still visible. The negative slope of $C/T$ versus $T$ between $T_{c2}$ and $T_{c1}$ in $H=0$ T becomes approximately zero for 0.2 T and positive in the field of 0.5 T. For sample No. 2 the low temperature anomaly is still visible up to 1.2 T. Similar behaviors in zero and magnetic field specific heat has been observed by Frederick et al. [71]. If these two peaks in $C/T$ are related to two different superconducting phases, then crystal No. 1 has a relatively large fraction corresponding to the higher $T_c$ phase. The evolution of these specific heat peaks in magnetic fields indicates that there is a correlation between these two phases.

The two insets to Fig. 7-28 show the critical field versus $T$ determined by specific heat for both samples. For sample No.1 both superconducting transitions are visible in fields up to 0.5 T. Open symbols mark the higher transition temperature $T_{c1}$ and the closed circles mark $T_{c2}$. The lines representing the two transitions remain approximately parallel, with a temperature separation of about 0.12 K. The most interesting feature is a positive curvature in $H_{c2}$ versus $T$ for $H<2000$ Oe. The initial slope of $H_{c2}$ versus $T$ is $-dH_{c2}/dT=1$ T/K. However, for $H>2000$ Oe the $H_{c2}$ is linear in $T$ (inset to upper panel of Fig. 7-28) and the slope is about twice as large, i.e. $-dH_{c2}/dT=2.1$ T/K. A positive curvature in $H_{c2}$ versus $T$ near $T_c$, was also detected in measurements of electrical resistivity, magnetic susceptibility, and specific heat [7, 55, 63, 67]. This consistency was used to argue for intrinsic property, and not due to some artifact of transport measurements or coming from inhomogeneities in the samples. Méasson et al. [59] considered this positive curvature to be a hallmark of the two-band superconductivity. The two-band superconductivity description, in which two different bands correspond
to light and heavy quasiparticles, is consistent with the results of thermal conductance measurements [106] in magnetic fields.

In sample No. 2 we were unable to determine the evolution of $T_c$ in fields, therefore only one line is presented in the inset to lower panel. Within the resolution of our measurements, there is no curvature in $H_{c2}$ versus $T$ near $T_{c2}$, and the slope is found equal to that of sample No. 1 for fields higher than 2000 Oe, i.e. 2.1 T/K. To our knowledge, this is the only measurement of $H_{c2}(T)$ near $T_c$ that does not find this positive curvature.

For all concentrations other than $x=0$ only a single superconducting anomaly in the specific heat measurements could be clearly detected (most probably corresponding to $T_{c2}$ in $x=0$). Our $x=0.02$ and 0.05 alloys exhibit a small but detectable curvature (inset to Fig. 7-29 for $x=0.05$). For $x=0.05$, the initial slope determined for fields smaller than 1000 Oe is about 0.9 T/K. For fields higher than 1000 Oe the slope is 1.6 T/K. Quite possibly there is a small curvature in $H_c(T)$ for $x=0.1$, but it cannot be clearly resolved (inset to Fig 7-30). For $x=0.3$ (Fig. 7-31) and alloys with $x>0.3$ we have a conventional variation of $H_{c2}(T)$, i.e., with no positive curvature near $T_c$. For $x=0.3$, $-dH_{c2}/dT=0.5$ T/K.

The evolution of $-dH_{c2}/dT$ is of great interest since the slope of $H_{c2}$ versus $T$ at $T_{c2}$ is related to the effective mass of Cooper pairs. Figure 7-32 shows the $-dH_{c2}/dT$ versus La concentration. For concentrations $x=0$, 0.02, and 0.05 two sets of $-dH_{c2}/dT$ values have been determined: the initial slope (open circles) and that for sufficiently large fields, for which $H_{c2}$ is clearly linear in $T$ ($H>2000$ Oe for $x=0$ and $H>1000$ Oe for $x=0.02$ and 0.05) (filled circles). This $-dH_{c2}/dT$, marked by closed circles, is about 2.1 T/K for $x=0$ and decreases rapidly with $x$, with most of the reduction taking place for small values of $x$. This implies that the effective mass of carriers is rapidly reduced by small amount of La.

In the clean limit of superconductivity ($l\gg\xi$), which is the case for PrOs$_4$Sb$_{12}$ and La alloys, the effective mass depends on $\sqrt{-dH_{c2}/dT/T_c}$. Figure 7-33 shows the dependence of this quantity on $x$. Most of the reduction takes place between $x=0$ and $x=0.2-0.3$. 

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When $\sqrt{-dH_{c2}/dT/T_c}$ is extrapolated from high values of $x$ to $x=0$, a slope close to the one obtained from the initial $-dH_{c2}/dT$ for PrOs$_4$Sb$_{12}$ is obtained.

Both $\sqrt{-dH_{c2}/dT/T_c}$ and $\Delta C/T_c$ quantities exhibit a crossover concentration $x_{cr} \approx 0.2$–0.3. There is a rapid reduction of both those quantities with $x$ for $x<x_{cr} \approx 0.2$–0.3, followed by a moderate or small one for $x>x_{cr}$. This crossover concentration has been previously identified in $\Delta(C/T)$ (Section 7.3), which is also related to $m^*$. We believe that this crossover concentration shows up also in crystalline electric fields (discussed in Section 7.4).

Using the two band superconductivity framework, the two slopes in $H_{c2}(T)$ (Fig. 7-32) for $x<x_{cr}$ can be related to two different conduction electron bands. The smaller initial slope suggests that the transition at $T_{c1}$ is dominated by lighter electrons. Heavier electrons contribute to the lower temperature transition. Since the ratio of the slopes is about 2, it can be inferred that the ratio of the effective electron masses is also of order of 2. This may explain why the discontinuities in specific heat at $T_{c1}$ and $T_{c2}$ are of similar magnitude.

Interpretation of the $-dH_{c2}(T)/dT$ results is hampered by the uncertainty as to the nature of the two superconducting transitions: a homogeneous coexistence of two superconducting order parameters or different parts of a sample undergoing a superconducting transition at different temperatures. Both scenarios can be argued based on the presented data. The two-step transition in ac susceptibility is consistent with inhomogeneities. However, we recall that the first evidence for a double superconducting anomaly in UPt$_3$ was obtained for samples exhibiting two-step transition in ac susceptibility [107]. Subsequent measurements on samples with a single step in the ac susceptibility confirmed the double superconducting transition. The evolution of the two peaks in fields (Fig. 7-28, upper panel) suggests that there is some coupling between the two superconducting phases, consistent with intrinsic nature of the transition. A Josephson coupling between the two superconducting order parameters was argued based on the
penetration depth experiments[59, 108]. However, in such a case only the upper transition should show up in the specific heat. Another possibility, not yet considered in literature, is that the upper superconducting transition is related to the phase transition with an order higher than 2 [109–111]. A two-step transition is expected in this case. A higher order phase transition (such as the third order) would be very susceptible to impurities and imperfections leading to a second order transition in sufficiently imperfect crystals. The expulsion of magnetic flux would be weak when lowering $T$ from $T_{c1}$ to $T_{c2}$, followed by a more rapid expulsion below $T_{c2}$. This scenario may account for the different magnetic field response in magnetic fields of the two samples. The possibility of the third order phase transition remains speculative since few materials were reported to exhibit phase transitions with an order higher than 2 [109–111].
Figure 7-1. X-ray diffraction patterns of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ versus La content $x$ for $x=0$, 0.1, 0.2, 0.4, and 1. The intensities are normalized to the highest peak.
Figure 7-2. Lattice constant $a$ of $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ versus La content $x$. The solid line is a linear least-squares fit to $a$ versus $x$.

Figure 7-3. Magnetic susceptibility $\chi(T)$ of $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ normalized to Pr mole between 1.8 and 10 K, measured in the field of 0.5 T. The measurements were performed on individual crystals with masses ranging between 1 and 5 mg. Large uncertainty are due to large background (Reprinted with permission from Rotundu et al. [112]).
Figure 7-4. Magnetic susceptibility $\chi(T)$ of Pr$_{0.33}$La$_{0.67}$OsSb$_{12}$ versus temperature $T$. In the inset is the Curie-Weiss fit of the high temperature data ($T>150$ K) from which an effective moment of $3.62\mu_B$/Pr mole has been calculated.
Figure 7-5. $C/T$ versus $T$ for three different PrOs$_4$Sb$_{12}$ samples from different batches. The arrow indicates the higher temperature superconducting transition.
Figure 7-6. $C/T$ versus $T^2$ above $T_c$ of LaOs$_4$Sb$_{12}$.  

\[ C/T = 56.0 + 1.003T^2 + 0.081T^4 - 4.260 \times 10^{-4}T^6 \]
Figure 7-7. $C/T$ versus $T$ near $T_c$ for Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ for $x=0$, 0.05, 0.1, and 0.2. The grey band highlights the width of the superconducting transition which for $x=0$ is $\approx 0.2$ K (Reprinted with permission from Rotundu et al. [112]).
Figure 7-8. $C/T$ versus $T$ near $T_c$ of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ for $x \geq 0.3$ (Reprinted with permission from Rotundu et al. [112]).
Figure 7-9. Superconducting transition temperature $T_c$ versus $x$ of $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ (Reprinted with permission from Rotundu et al. [112]).

Figure 7-10. Total $C/T$ discontinuity at $T_c$ and $\chi_0$ versus $x$ of $\text{Pr}_{1-x}\text{La}_x\text{Os}_4\text{Sb}_{12}$ for $0 \geq x \geq 1$ (Reprinted with permission from Rotundu et al. [112]).
Figure 7-11. $C/T$ versus $T$ of $\text{Pr}_{0.33}\text{La}_{0.67}\text{Os}_4\text{Sb}_{12}$ fitted by $\Gamma_1 - \Gamma_5$ Schottky.

Figure 7-12. $C/T$ versus $T$ of $\text{Pr}_{0.33}\text{La}_{0.67}\text{Os}_4\text{Sb}_{12}$ fitted by $\Gamma_3 - \Gamma_5$ Schottky.
Figure 7-13. $C/T$ versus $T$ of Pr$_{0.33}$La$_{0.67}$Os$_4$Sb$_{12}$ fitted by singlet-singlet Schottky.

$C_{Sn} = 8.315^*a^*(g_s^*g_\parallel)(\delta/\Theta)^2e^{(\delta/\Theta)}(g_\parallel^2 + g_\perp^2 e^{(\delta/\Theta)^2})$

$g_\parallel = 1$, $g_\perp = 1$ (singlet-singlet)

$a = 1.009$

$\delta = 8.686$ (K)

Figure 7-14. $C$ of PrOs$_4$Sb$_{12}$ in 10 T and Pr$_{0.98}$La$_{0.02}$Os$_4$Sb$_{12}$ in 8 and 9.5 T.
Figure 7-15. $f$-electron specific heat of Pr$_{0.9}$La$_{0.1}$Os$_4$Sb$_{12}$ in magnetic fields (Reprinted with permission from Rotundu and Andraka [113]).

Figure 7-16. $f$-electron specific heat of Pr$_{0.8}$La$_{0.2}$Os$_4$Sb$_{12}$ in magnetic fields. No AFQ is detected (Reprinted with permission from Rotundu and Andraka [113]).
Figure 7-17. $f$-electron specific heat of Pr$_{0.4}$La$_{0.6}$Os$_4$Sb$_{12}$ in magnetic fields. No AFQ is detected.

Figure 7-18. $H$-$T$ phase diagram from $C$ measurements for $x=0$, 0.02, 0.1, and 0.2.
Figure 7-19. $\rho(H)$ of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ at $T=20$ mK for $\mathbf{H} \parallel I$ and $\mathbf{H} \perp I$. The current was parallel with (0 0 1).

Figure 7-20. $\rho(H)$ of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ for $\mathbf{H} \perp I // (0 0 1)$ at $T=20$ and 300 mK.
Figure 7-21. ρ(H) of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ for $\vec{H} \parallel I // (0 0 1)$ at $T=20$, 310, and 660 mK (Reprinted with permission from Rotundu and Andraka [114]).
Figure 7-22. $\rho$ versus $T^2$ of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ in 0 and 0.5 T (Reprinted with permission from Rotundu and Andraka [114]).
Figure 7-23. $\rho$ versus $T^2$ of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ in 9 and 13 T.
Figure 7-24. $\rho(H)$ of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ for $\vec{H}$ parallel with all three crystallographic directions and $I// (001)$. The inset shows the same data after the linear background subtraction as explained in text.

Figure 7-25. $\rho(H)$ of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ when $\vec{H}//I// (001)$ at 20, 310, 660, and 1100 mK.
Figure 7-26. $\rho(H)$ of Pr$_{0.33}$La$_{0.67}$Os$_4$Sb$_{12}$ at 0.35 K (Reprinted with permission from Rotundu and Andraka [114]).
Figure 7-27. AC susceptibility versus $T/T_c$ of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$, for $x=0$, 0.05, 0.4, 0.8, and 1. Sample No. 1 exhibit one superconducting transition while sample No. 2 have two (Reprinted with permission from Rotundu et al. [115]).
Figure 7-28. $C/T$ versus $T$ near $T_c$ for two PrOs$_4$Sb$_{12}$ samples from two different batches in low magnetic fields, No. 1 in the upper panel and No. 2 in the lower panel. The insets show $H_{c2}$ versus $T$ (Reprinted with permission from Rotundu et al. [115]).
Figure 7-29. $C/T$ versus $T$, near $T_c$, of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ in low magnetic fields (Reprinted with permission from Rotundu et al. [115]).

Figure 7-30. $C/T$ versus $T$, near $T_c$, of Pr$_{0.9}$La$_{0.1}$Os$_4$Sb$_{12}$ in small magnetic fields (Reprinted with permission from Rotundu et al. [115]).
Figure 7-31. $C/T$ versus $T$, near $T_c$, of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ in magnetic fields (Reprinted with permission from Rotundu et al. [115]).

Figure 7-32. $-\frac{dH_c}{dT}$ versus $x$. For sufficiently large fields, for which $H_{c2}$ is linear in $T$ (for $H>2000$ Oe for $x=0$ and $H>1000$ Oe for $x=0.02$ and 0.05) $-\frac{dH_c}{dT}$ is represented by the full circle symbols, for fields smaller than 1000 Oe with open symbols (Reprinted with permission from Rotundu et al. [115]).
Figure 7-33. $\sqrt{-dH_{c2}/dT/T_c}$ versus $x$ with the critical $x_{cr} \approx 0.25$. The inset shows $\Delta(C/T)$ at $T_c$ with $x_{cr} \approx 0.25–0.3$ (Reprinted with permission from Rotundu et al. [115]).
CHAPTER 8
CONCLUSION

This chapter summarizes the results of thermodynamic measurements on Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ (0 ≤ $x$ ≤ 1) as a function of lanthanum concentration ($x$), temperature, and magnetic field. Specific heat measurements in fields between 8 and 32 T of PrOs$_4$Sb$_{12}$ extended the previously measured $H$-$T$ phase diagram up to 8 T [56]. The Schottky anomaly, due to excitations between two lowest crystalline electric field (CEF) levels, was found for both $\vec{H}$$\parallel$(1 0 0) and $\vec{H}$$\parallel$(1 1 0) above the field where the field-induced ordered phase (FIOP) (identified with an antiferroquadrupolar ordered phase [56]) is completely suppressed. The H-T phase diagram shows weak magnetic anisotropy and implies a crossing of the two CEF levels at about 9–10 T for both field directions. Calculations of the Zeeman effect in the $\Gamma_1$ CEF ground state scenario predict a crossing between $\Gamma_1$ and the lowest $\Gamma_5$ energy level, between between 9 and 10 T, which is almost independent on the field direction Similar calculations for the $\Gamma_3$ CEF ground state model predict both strong anisotropy of the phase diagram and no crossing for the (1 1 0) direction. Thus, this work has established the non-magnetic $\Gamma_1$ singlet being the CEF ground state. Furthermore, our investigation of the field-induced ordered phase (FIOP) has provided evidences for the (near) level crossing as the driving mechanism of FIOP. The non-magnetic singlet $\Gamma_1$ CEF ground state contradicts the idea of a quadrupolar Kondo effect, at least in the present formulation, as the origin of the heavy fermion behavior in PrOs$_4$Sb$_{12}$.

The La-alloy study was performed to provide insight on the origin of the electronic mass enhancement. Zero field specific heat of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ showed that the total $\Delta(C/T)$ at $T_c$ is reduced more than sevenfold from about 800 mJ/K$^2$ mol between $x=0$ and 0.3 and stays approximately constant and about equal to that of LaOs$_4$Sb$_{12}$, which is a conventional superconductor, for $x>0.3$. Similarly, measurements of the upper critical field suggested the existence of a crossover concentration, $x_{cr} \approx 0.2–0.3$. The upper critical field slope near $T_c$ decreases rapidly with $x$ for $x<x_{cr}$, followed by a weak concentration
dependence for $x > x_{cr}$. Thus, measurements of $\Delta(C/T)$ and $dH_{c2}/dT$ indicate that the heavy fermion character is rapidly reduced by the La doping, suggesting a non-single impurity origin of the electronic mass enhancement.

In order to verify that single-ion parameters, such as hybridization and CEF spectrum (considered by single impurity models), are not severely affected the alloying, measurements of the lattice constant and high field specific heat were performed. X-ray powder diffraction of Pr$_{1 - x}$La$_x$Os$_4$Sb$_{12}$ revealed an anomalously small increase of lattice constant with $x$ (0.04% between the end compounds). The low-temperature magnetic susceptibility showed almost nonexistent concentration dependence of the low temperature maximum, believed to be due to excitations between the lowest CEF levels. Specific heat in magnetic fields up to 14 T for $x=0, 0.02, 0.1, and 0.2$ showed that the temperature of the Schottky anomaly has a similar field dependence for all these concentrations. Therefore, CEF energies and eigenstates of Pr are unchanged between $x=0$ and at least 0.2, i.e., in the alloy parameter range where a large change of the electron effective mass is observed. These results reinforce our conclusion of a non-single impurity origin of the heavy fermion behavior of PrOs$_4$Sb$_{12}$. In particular, they are inconsistent with the currently prevailing Fulde-Jensen model.

Our results imply a strong correlation between the parameters characterizing the field-induced antiferroquadrupolar order, such as the transition temperature, the size of the corresponding specific heat anomaly, and $m^*$, suggesting a possibility that the heavy fermion state is due to fluctuations of the quadrupolar order parameter. This possibility is consistent with our magnetoresistance results, suggesting that $m^*$ increases with the magnetic field up the the field value for which the long-range order is observed.

The study of the magnetoresistance on La-doped samples confirmed the singlet CEF ground state. Furthermore, they provided an explanation for a few-year old puzzle of an unusual magnetoresistance of the pure compound, previously used to argue for a doublet CEF ground state.
Measurements were also performed to shed light on the origin of the two superconducting transitions in the specific heat of PrOs$_4$Sb$_{12}$. Substitution of small amounts of La results in a single superconducting transition. This anti-correlation between atomic disorder and presence of two superconducting transition argues for a homogeneous coexistence of two superconducting order parameters. On the other hand, a double-step structure in the ac susceptibility is consistent with a macroscopic separation of two superconducting phases. The study of the upper critical field provided an evidence for a correlation between the existence of a positive curvature (or a change of slope) in $H_{c2}$ versus $T$ near $T_c$ and the existence of two superconducting anomalies. The analysis of this curvature in the two-band superconductivity model implies that the upper superconducting transition is due to lighter electrons while heavier electrons contribute to the lower temperature transition. Our results suggest that the ratio of the effective masses of the two bands is about 2. This result is in disagreement with the results of the penetration depth experiment suggesting much different masses of the two bands but is in agreement with similar sizes of the two superconducting anomalies in the specific heat.
REFERENCES


BIOGRAPHICAL SKETCH

Costel Remus Rotundu was born March 3, 1974 in Dingeni, Romania. Raised in Hulub and then Trușești, he went to Botoșani to attend the A. T. Laurian National College, mathematics-physics section, where he graduated from high school in June 1992. He graduated with a Bachelor of Science degree in physics (specializing in theoretical physics) from Romania’s oldest university, Al. I. Cuza University, in June 1997. One year and a half later he graduated from the same university with Masters of Science in physics (specializing in nonlinear theory phenomena). After working 2 years as a research assistant (theorist) at the National Institute of Research and Development for Technical Physics from the same city, he left for the U.S. to continue his graduate studies at University of Florida, where he pursued a Ph. D. degree in experimental condensed matter physics. He worked under Dr. Bohdan Andraka’ supervision in the heavy-fermion area. During his stay at University of Florida he was also appointed as Physics I and II laboratory instructor. After graduation he got a Research Associate position with Dr. Richard Greene, at the Center for Superconductivity Research (CSR) - University of Maryland College Park.