Superconductivity and the high field ordered phase in the heavy fermion compound PrOs$_4$Sb$_{12}$

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Abstract.

Superconductivity is observed in the filled skutterudite compound PrOs$_4$Sb$_{12}$ below a critical temperature temperature $T_c = 1.85$ K and appears to develop out of a nonmagnetic heavy Fermi liquid with an effective mass $m^* \approx 50 m_e$, where $m_e$ is the free electron mass. Features associated with a cubic crystalline electric field are present in magnetic susceptibility, specific heat, electrical resistivity, and inelastic neutron scattering measurements, yielding a Pr$^{3+}$ energy level scheme consisting of a Γ$_3$ nonmagnetic doublet ground state, a low lying Γ$_5$ triplet excited state at $\sim 10$ K, and much higher temperature Γ$_4$ triplet and Γ$_1$ singlet excited states. Measurements also indicate that the superconducting state is unconventional and consists of two distinct superconducting phases. At high fields and low temperatures, an ordered phase of magnetic or quadrupolar origin is observed, suggesting that the superconductivity may occur in the vicinity of a magnetic or quadrupolar quantum critical point.

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1. Introduction

Since the mid 1990’s, several compounds of Pr have been found to exhibit heavy fermion behavior. The crystalline electric field (CEF) ground state of the Pr$^{3+}$ ions in these compounds appears to be a Γ$_3$ nonmagnetic doublet that carries an electric quadrupole moment. It is conceivable that the heavy fermion state in these Pr compounds could originate from the interaction between the Pr$^{3+}$ electric quadrupole moments and the charges of the conduction electrons. This would be the electric analogue of the exchange interaction between the magnetic dipole moments of Ce or U ions and the conduction electron spins that is widely believed to be responsible for the heavy fermion state in most Ce and U heavy fermion compounds. In fact, such a mechanism was proposed by Cox in 1987 [1] to account for the non-Fermi liquid temperature dependences of certain normal state physical properties of the heavy electron superconductor UBe$_{13}$. The Pr
compounds that display heavy fermion behavior include PrInAg$_2$ [2], PrFe$_4$P$_{12}$ [3], and, possibly, PrFe$_4$Sb$_{12}$ [4].

About a year ago, we reported that the compound PrOs$_4$Sb$_{12}$ exhibits superconductivity with a superconducting critical temperature $T_c = 1.85$ K that apparently develops out of a heavy Fermi liquid with a quasiparticle effective mass $m^* \approx 50 m_e$, where $m_e$ is the mass of the free electron [5, 6]. As far as we know, PrOs$_4$Sb$_{12}$ is the first example of a heavy fermion superconductor based on Pr; all of the other known heavy fermion superconductors are compounds of Ce or U. The superconducting state appears to be unconventional in nature and may consist of two distinct superconducting phases [7, 8]. An ordered phase, presumably of magnetic or quadrupolar origin, occurs at high fields $> 4.5$ tesla and low temperatures $< 1.5$ K [7, 9, 10, 11, 12, 13], suggesting that the superconductivity may occur in the vicinity of a magnetic or quadrupolar quantum critical point (QCP). In an effort to obtain information about the interactions that are responsible for the heavy fermion state and superconductivity in PrOs$_4$Sb$_{12}$, we have performed measurements of various normal and superconducting state properties of this compound as a function of temperature, pressure, and magnetic field [5, 6, 7, 9]. Analysis of magnetic susceptibility $\chi(T)$, specific heat $C(T)$, electrical resistivity $\rho(T)$, and inelastic neutron scattering measurements within the context of a cubic crystalline electric field (CEF) yields a Pr$^{3+}$ energy level scheme that consists of a $\Gamma_3$ nonmagnetic doublet ground state that carries an electric quadrupole moment, a low lying $\Gamma_5$ triplet excited state at $\sim 10$ K, and $\Gamma_4$ triplet and $\Gamma_1$ singlet excited states at much higher temperatures ($\sim 130$ K and $\sim 313$ K, respectively) [5, 6, 7, 9]. This scenario suggests that the underlying mechanism for the heavy fermion behavior in PrOs$_4$Sb$_{12}$ may involve the interaction of Pr$^{3+}$ electric quadrupole moments with the charges of the conduction electrons, rather than Pr$^{3+}$ magnetic dipole moments with the spins of the conduction electrons. It also raises the possibility that electric quadrupole fluctuations play a role in the superconductivity of PrOs$_4$Sb$_{12}$. In this paper, we briefly review the current experimental situation regarding the heavy fermion state, the superconducting state, and a high field, low temperature phase that is apparently associated with magnetic or quadrupolar order in PrOs$_4$Sb$_{12}$.

2. Evidence for a heavy fermion state in PrOs$_4$Sb$_{12}$

The first evidence for a heavy fermion state in the filled skutterudite compound PrOs$_4$Sb$_{12}$ emerged from specific heat $C(T)$ measurements on a PrOs$_4$Sb$_{12}$ pressed pellet (formed by pressing a collection of small single crystals in a cylindrical die) at low temperatures. Specific heat data in the form of a plot of $\frac{C}{T}$ vs $T$ between 0.5 K and 10 K for the PrOs$_4$Sb$_{12}$ pressed pellet from Refs. [5] and [6] are shown in Fig. 1. The $C(T)$ data have been corrected for excess Sb derived from the molten Sb flux in which the crystals were grown. The line in the figure represents the expression $C(T) = \gamma T + \beta T^3 + C_{Sch}(T)$, where $\gamma T$ and $\beta T^3$ are electronic and phonon contributions, respectively, and $C_{Sch}(T)$ is a Schottky anomaly for a two level system consisting of a
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Figure 1. Specific heat $C$ divided by temperature $T$, $C/T$, vs $T$ for a PrOs$_4$Sb$_{12}$ pressed pellet. The line represents a fit of the sum of electronic, lattice, and Schottky contributions to the data. Upper inset: $C_e/T$ vs $T$ near $T_c$ for a PrOs$_4$Sb$_{12}$ pressed pellet ($C_e$ is the electronic contribution to $C$). Lower inset: $C/T$ vs $T$ near $T_c$ for PrOs$_4$Sb$_{12}$ single crystals, showing the structure in $\Delta C$ near $T_c$. Data from Refs. [5, 6].

doublet ground state and a triplet excited state at an energy $\Delta$ above the ground state. The best fit of this expression to the data yields the values $\gamma = 607$ mJ/mol K$^2$, $\beta = 3.95$ mJ/mol K$^4$ (corresponding to a Debye temperature $\theta_D = 203$ K), and $\Delta = 7.15$ K. Superimposed on the Schottky anomaly is a feature in the specific heat due to the onset of superconductivity at $T_c = 1.85$ K which is also observed as an abrupt drop in $\rho(T)$ to zero and as a sharp onset of diamagnetism in $\chi(T)$. The feature in $C(T)/T$ due to the superconductivity is also shown in the top inset of Fig. 1 along with an entropy conserving construction from which the ratio of the jump in specific heat $\Delta C/Tc, \Delta C/Tc = 632$ mJ/mol K$^2$, has been estimated. Using the BCS relation $\Delta C/\gamma Tc = 1.43$, we obtain another estimate for $\gamma$ of 440 mJ/mol K$^2$. The value of $\Delta C/T_c$ is larger than that reported in Ref. [6] due to the correction of the $C(T)$ data for the excess Sb (about 30 percent of the total mass). This value is comparable to that inferred from the fit to the $C/T$ vs $T$ data in the normal state above $T_c$, and indicative of heavy fermion behavior. A similar analysis of the $C(T)$ data taken at the University of Karlsruhe on several single crystals of PrOs$_4$Sb$_{12}$ prepared in our laboratory yielded $\gamma = 313$ mJ/mol K$^2$, $\theta_D = 165$ K, $\Delta = 7$ K, and $\Delta C/\gamma T_c \approx 3$, much higher than the BCS value of 1.43 and indicative of strong coupling effects [10]. It is interesting that we also find a large value of $\Delta C/\gamma T_c \approx 3$ in recent $C(T)$ measurements on one single crystal of PrOs$_4$Sb$_{12}$ at UCSD. Although the values of $\gamma$ determined from these experiments vary somewhat, they are all indicative of a heavy electron ground state and an effective mass $m^* \approx 50 m_e$.

Further evidence of heavy fermion superconductivity is provided by the upper critical field $H_{c2}$ vs $T$ curve shown in Fig. 2 [6, 7]. The orbital critical field $H_{c2}(0)$ can
Figure 2. Magnetic field - temperature ($H - T$) phase diagram of a PrOs$_4$Sb$_{12}$ single crystal showing the regions exhibiting superconductivity (SC) and the high field ordered phase (HFOP). The boundary delineating the SC phase is based on measurements of $\rho(H, T)$, while the HFOP phase boundary is based on $\rho(H, T)$, $C(H, T)$, $M(H, T)$, and $\alpha(H, T)$ measurements (see text). The dashed line, derived from a peak in $d\rho/dT$ vs $T$, is a measure of the splitting between the highest and lowest Zeeman levels of the Pr$^{3+}$ $\Gamma_3$ ground and $\Gamma_5$ excited states, respectively (see text for further details). Data from Refs. [6, 7, 9, 10, 11, 26].

be derived from the slope (-19 kOe/K) of the $H_{c2}$ curve near $T_c$ and used to estimate the superconducting coherence length $\xi_0 \approx 116$ Å via the relation $H_{c2}^*(0) = \Phi_0 / 2\pi\xi_0^2$, where $\Phi_0$ is the flux quantum. The Fermi velocity $v_F$ can be obtained from the BCS relation $\xi_0 = 0.18\hbar v_F / k_BT_c$ and used to determine the effective mass $m^*$ by means of the expression $m^* = \hbar v_F / v_F$. Using a simple free electron model to estimate the Fermi wave vector $k_F$, an effective mass $m^* \approx 50 m_e$ is obtained [6, 7]. Calculating $\gamma$ from $m^*$ yields $\gamma \sim 350$ mJ/mol K$^2$, providing further evidence for a heavy fermion state in PrOs$_4$Sb$_{12}$.

Recently, Sugawara et al. [14] performed de Haas-van Alphen effect measurements on PrOs$_4$Sb$_{12}$. They found that the topology of the Fermi surface is close to that of the reference compound LaOs$_4$Sb$_{12}$ and is explained well by band structure calculations. In contrast to the similarity in the Fermi surface topologies of PrOs$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$, the cyclotron effective masses $m^*_c$ of PrOs$_4$Sb$_{12}$ are enhanced up to $\sim 6$ times relative to those of LaOs$_4$Sb$_{12}$. The Sommerfeld coefficient $\gamma$ estimated from the Fermi surface
volume and the value of \( m^* \), assuming a spherical Fermi surface, is \( \sim 150 \text{ mJ/mol K}^2 \), which is two to three times smaller than the value of \( \gamma \) inferred from the normal and superconducting properties of PrOs\(_4\)Sb\(_{12}\). Our studies of LaOs\(_4\)Sb\(_{12}\) single crystals reveal superconductivity with a \( T_c \) of 1 K.

3. Normal state of PrOs\(_4\)Sb\(_{12}\)

The \( \chi(T) \) data for PrOs\(_4\)Sb\(_{12}\) exhibit a peak at \( \sim 3 \text{ K} \) and saturate to a value of \( \sim 0.11 \text{ cm}^3/\text{mol} \) as \( T \to 0 \), indicative of a nonmagnetic ground state. At temperatures above \( \sim 5 \text{ K} \), \( \chi(T) \) is strongly T-dependent, as expected for well defined Pr\(^{3+} \) magnetic moments. In the analysis of the \( \chi(T) \) data, interactions between Pr\(^{3+} \) ions and hybridization of the Pr 4f and conduction electron states were neglected, while the degeneracy of the Hund’s rule multiplet of the Pr\(^{3+} \) ions was assumed to be lifted by a cubic crystalline electric field (CEF) and to have a nonmagnetic ground state. According to Lea, Leask, and Wolf (LLW) \[15\], in a cubic CEF, the Pr\(^{3+} \)J = 4 Hund’s rule multiplet splits into a \( \Gamma_1 \) singlet, a \( \Gamma_3 \) nonmagnetic doublet that carries an electric quadrupole moment, and \( \Gamma_4 \) and \( \Gamma_5 \) triplets. It was assumed that the nonmagnetic ground state of the Pr\(^{3+} \) ions corresponds to either a \( \Gamma_1 \) singlet or a \( \Gamma_3 \) nonmagnetic doublet \[6\]. Although reasonable fits to the \( \chi(T) \) data could be obtained for both \( \Gamma_1 \) and \( \Gamma_3 \) ground states, the most satisfactory fit was obtained for a \( \Gamma_3 \) nonmagnetic doublet ground state with a \( \Gamma_5 \) first excited triplet state at 11 K and \( \Gamma_4 \) and \( \Gamma_1 \) excited states at 130 K and 313 K, respectively. Inelastic neutron scattering measurements on PrOs\(_4\)Sb\(_{12}\) \[7\] reveal peaks in the INS spectrum at 0.71 meV (8.2 K) and 11.5 meV (133 K) that appear to be associated with transitions between the \( \Gamma_3 \) ground state and the \( \Gamma_5 \) first and \( \Gamma_4 \) second excited states, respectively, that are in good agreement with the Pr\(^{3+} \) CEF energy level scheme determined from the analysis of the \( \chi(T) \) data. As noted above, the Schottky anomaly in the \( C(T) \) data on PrOs\(_4\)Sb\(_{12}\) taken at UCSD and at the University of Karlsruhe \[10\] can be described well by a two level system consisting of a doublet ground state and a low lying triplet excited state with a splitting of \( \sim 7 \text{ K} \), a value that is comparable to the values deduced from the \( \chi(T) \) and INS data.

While a magnetic \( \Gamma_5 \) Pr\(^{3+} \) ground state (\( \Gamma_4 \) is not a possible ground state for a cubic system in the LLW formulation) could also produce a nonmagnetic heavy fermion ground state via an antiferromagnetic exchange interaction (Kondo effect), the behavior of \( \rho(T) \) of PrOs\(_4\)Sb\(_{12}\) in the normal state does not resemble the behavior of \( \rho(T) \) expected for this scenario. For a typical magnetically-induced heavy fermion compound, \( \rho(T) \) often increases with decreasing temperature due to Kondo scattering, reaches a maximum, and then decreases rapidly with decreasing temperature as the highly correlated heavy fermion state forms below the coherence temperature. At low temperatures, \( \rho(T) \) typically varies as \( AT^2 \) with a prefactor \( A \approx 10^{-5} \text{ [}\mu\Omega \text{ cm K}^2(\text{mJ/mol})^{-2}] \) \( \gamma^2 \) that is consistent with the Kadowaki-Woods relation \[16\]. In contrast, \( \rho(T) \) of PrOs\(_4\)Sb\(_{12}\) \[5\] exhibits typical metallic behavior with negative curvature at higher temperatures and a pronounced ‘roll off’ below \( \sim 8 \text{ K} \) before it vanishes abruptly when the compound...
Superconductivity and the high field ordered phase in PrOs$_4$Sb$_{12}$ becomes superconducting. The ‘roll off’ in $\rho(T)$ is consistent with a decrease in charge or spin dependent scattering of conduction electrons by the Pr$^{3+}$ ions due to the decrease in population of the low lying first excited state ($\Gamma_5$) as the temperature is lowered. The ‘roll off’ below $\sim 8$ K and the negative curvature at higher temperatures in $\rho(T)$ can be described reasonably well by calculations based on magnetic and aspherical Coulomb scattering of conduction electrons by the Pr$^{3+}$ ions with a low lying $\Gamma_5$ excited state separated from the $\Gamma_3$ ground state by $\sim 6$ K and excited $\Gamma_4$ triplet and $\Gamma_1$ singlet states at much higher energies comparable to those found from the analysis of the $\chi(T)$ and INS measurements \[17\]. The $\rho(T)$ data can be described by a temperature dependence of the form $AT^2$ between $\sim 8$ K and 45 K, but with a prefactor $A \approx 0.009 \mu\Omega$ cm/K$^2$ that is nearly two orders of magnitude smaller than that expected from the Kadowaki-Woods relation ($A \approx 1.2 \mu\Omega$ cm/K$^2$ for $\gamma \approx 350$ mJ/mol K$^2$) \[16\]. Interestingly, $\rho(T)$ is consistent with $T^2$ behavior with a value $A \approx 1 \mu\Omega$ cm/K$^2$ in fields of $\sim 5$ tesla \[9\] in the high field ordered phase discussed in Section 5. The zero-field temperature dependence of $\rho(T)$ is similar to that observed for the compound PrInAg$_2$, which also has a low value of the coefficient $A$, an enormous $\gamma$ of $\sim 6.5$ J/mol K$^2$, and a $\Gamma_3$ nonmagnetic doublet ground state \[2\]. Another possible source of the enhanced effective mass in PrOs$_4$Sb$_{12}$ may involve excitations from the ground state to the the low lying first excited state in the Pr$^{3+}$ CEF energy level scheme \[18\].

Two studies of the nonlinear magnetic susceptibility have been performed in an attempt to determine the CEF ground state of the Pr$^{3+}$ ion in PrOs$_4$Sb$_{12}$ \[12, 19\]. The nonlinear susceptibility $\chi_3$ is the coefficient of the $H^3$ term in the expansion of the magnetization $M$ in a series of odd powers of $H$; i.e., $M \approx \chi_1 H + (\chi_3/6)H^3$, where $\chi_1$ is the ordinary linear susceptibility. In an ionic situation, $\chi_3$ is isotropic and varies as $T^{-3}$ for a magnetic ground state, whereas $\chi_3$ is anisotropic and diverges at low temperatures for $H \parallel [100]$ and approaches a constant for $H \parallel [111]$ for a non-Kramers $\Gamma_3$ doublet ground state \[20\]. This type of study was previously employed in an attempt to determine the ground state of U in the compound UBe$_{13}$ \[21\]. In both studies of PrOs$_4$Sb$_{12}$, $\chi_3(T)$ was found to behave similarly for $H \parallel [100]$ and $H \parallel [111]$, exhibiting a minimum near 4 K followed by a maximum near 1 K and a negative divergence with decreasing temperature. Calculations based on the quadrupolar Anderson-Hamiltonian described the $\chi_3(T)$ data reasonably well for $H \parallel [100]$, but not very well for $H \parallel [111]$. It was concluded that the data were qualitatively consistent with a $\Gamma_3$ ground state, given the limitations of the experiment and the complexity of the theory. The $\chi_3(T)$ studies are difficult to interpret because of the curvature of $M(H)$ and the complications that arise at lower temperatures $T \leq T_c$ and lower fields $H \leq H_{c2}$ due to the superconductivity and at temperatures $T \leq 2$ K and higher fields $H \geq 4.5$ tesla by the onset of the high field ordered phase, discussed in Section 5.
4. Superconducting state of PrOs$_4$Sb$_{12}$

A number of features in the superconducting properties of PrOs$_4$Sb$_{12}$ indicate that the superconductivity of this compound is unconventional in nature. One of these features is the ‘double-step’ structure in the jump in $C(T)$ near $T_c$ in single crystals (lower inset of Fig. 1) that suggests two distinct superconducting phases with different $T_c$'s: $T_{c1} \approx 1.85$ K and $T_{c2} \approx 1.70$ K. This structure is not evident in the $C(T)$ data taken on the pressed pellet of PrOs$_4$Sb$_{12}$ shown in the upper inset of Fig. 1 possibly due to strains in the single crystals out of which the pressed pellet is comprised that broaden the transitions at $T_{c1}$ and $T_{c2}$ so that they overlap and become indistinguishable. However, at this point, we are unable to eliminate the possibility that the two apparent jumps in $C(T)$ are due to sample inhomogeneity. It is noteworthy that all of the single crystal specimens prepared in our laboratory and investigated by our group and our collaborators exhibit this ‘double-step’ structure. Multiple superconducting transitions, apparently associated with distinct superconducting phases, have previously been observed in two other heavy fermion superconductors, UPt$_3$ and U$_{1-x}$Th$_x$Be$_{13}$ ($0.1 \leq x \leq 0.35$). Measurements of the specific heat in magnetic fields reveal that the two superconducting features shift downward in temperature at nearly the same rate with increasing field, consistent with the smooth temperature dependence of the $H_{c2}(T)$ curve. These two transitions have also been observed in thermal expansion measurements, which, from the Ehrenfest relation, reveal that $T_{c1}$ and $T_{c2}$ have different pressure dependences, suggesting that they are associated with two distinct superconducting phases. Another feature is the power law $T$-dependence of $C_s(T)$, $C_s(T) \sim T^{2.5}$, after the Schottky anomaly and $\beta T^3$ lattice contributions have been subtracted from the $C(T)$ data. (As reported in Ref. 7, $C_s(T)$ follows a power law with $C_s(T) \sim T^{3.9}$ when the Schottky anomaly is not subtracted.) However, this dependence can only be established from $T_c$ down to $\sim 0.4 T_c$, since it is not possible to reliably correct the $C(T)$ data at lower temperatures for an enormous nuclear Schottky anomaly. Power law $T$-dependences of the superconducting properties are generally attributed to nodes in the superconducting energy gap at points or lines on the Fermi surface. Among three recent experiments on PrOs$_4$Sb$_{12}$, described below, two yield evidence for an isotropic energy gap, while another provides evidence for two distinct superconducting phases in the H-T plane with different numbers of point nodes in the energy gap.

Recent transverse field $\mu$SR and Sb-NQR measurements on PrOs$_4$Sb$_{12}$ are consistent with an isotropic energy gap. Along with the specific heat, these measurements indicate strong coupling superconductivity. These findings suggest an s-wave, or, perhaps, a Balian-Werthamer p-wave order parameter. On the other hand, the superconducting gap structure of PrOs$_4$Sb$_{12}$ was investigated by means of thermal conductivity measurements in magnetic fields rotated relative to the crystallographic axes by Izawa et al. These measurements reveal two regions in the $H - T$ plane, a low field region in which $\Delta(k)$ has two point nodes, and a high field region where $\Delta(k)$
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![Graph](image)

**Figure 3.** Upper critical field $H_{c2}$ vs $T$ for LaOs$_4$Sb$_{12}$, based on resistance $R$ vs temperature $T$ data shown in the inset.

**Table 1.** Superconducting critical temperature $T_c$ of LnT$_4$X$_{12}$ compounds for Ln = La, Pr; T = Fe, Ru, Os; and X = P, As, Sb. The $T_c$ values listed are in K and have been derived from references [4, 25, 28, 30, 31, 32, 33, 34, 35]. The symbols † and ‡ indicate that superconductivity has not been observed in those compounds above 2 K and 0.35 K, respectively.

|       | LaT$_4$X$_{12}$ | PrT$_4$X$_{12}$ |
|-------|-----------------|-----------------|
| Fe    | 4.1              | ‡               |
| Ru    | 7.2†             | 10.3‡           |
| Os    | 1.8              | 3.2            |
| ?     | 1.8†             | 2.4            |
| P     | 1.8              | ‡               |
| As    | †                | 1.0             |
| Sb    | ?                | †               |

has six point nodes. The line lying between the low and high field superconducting phases may be associated with the transition at $T_{c2}$, whereas the line between the high field superconducting phase and the normal phase, $H_{c2}(T)$, converges with $T_{c1}$ as $H \to 0$. Clearly, more research will be required to further elucidate the nature of the superconductivity in PrOs$_4$Sb$_{12}$.

It is noteworthy that the reference compound without 4f electrons, LaOs$_4$Sb$_{12}$, is also superconducting, but with $T_c \approx 1$ K, considerably smaller than that of PrOs$_4$Sb$_{12}$. This suggests that the pairing interaction is enhanced by the presence of the Pr 4f electrons, possibly through the interaction of the Pr$^{3+}$ electric quadrupole moments with the conduction electrons. In contrast, the values of $T_c$ of the other PrT$_4$X$_{12}$ filled skutterudites are smaller than their La-based counterparts. The values of $T_c$ in K for MT$_4$X$_{12}$ compounds with M = La or Pr are listed in Table I. A plot of the upper critical field $H_{c2}$ vs $T$ for LaOs$_4$Sb$_{12}$ and the resistive $R(T)$ transition curves upon which it is based are shown in Fig. 3.
Figure 4. (a) and (b): Electrical resistivity $\rho$ vs temperature $T$ at various magnetic fields $H$ up to 18 tesla (T) for a PrOs$_4$Sb$_{12}$ single crystal. (c) $\rho$ vs $H$ at various temperatures between 0.35 K and 4.2 K. The rapid drop in $\rho$ to zero for $H < 2.5$ T is due to the superconducting transition, while the shoulder in $\rho(T)$ at $\sim 1$ K above 4.5 T and the kinks in $\rho(H)$ (indicated at $H_1^*$ and $H_2^*$) below 1.7 K are due to a field induced phase (high field ordered phase - HFOP). After Refs. [9, 26].

5. High field ordered phase in PrOs$_4$Sb$_{12}$

Evidence for a high field ordered phase was first derived from magnetoresistance measurements in the temperature range $80 \text{ mK} \leq T \leq 2 \text{ K}$ and magnetic fields up to 10 tesla [7, 9]. Recently, the magnetoresistance measurements have been extended up to 18 tesla for $0.35 \text{ K} \leq T \leq 2 \text{ K}$ [26]. The $H - T$ phase diagram, depicting the superconducting region and the high field ordered phase, is shown in Fig. 2. The line that intersects the high field ordered phase represents the inflection point of the ‘roll-off’ in $\rho(T)$ for $H < 4.5$ tesla at low temperatures and is a measure of the splitting between the Pr$^{3+}$ ground state and the first excited state, which decreases with field (see Fig. 4). The high field ordered phase has also been observed by means of large peaks in the specific heat [10, 13] and thermal expansion [11] and kinks in magnetization vs magnetic field curves [12, 26] in magnetic fields $> 4.5$ tesla and temperatures $< 1.5$ K.

Shown in Fig. 4(a) and (b) are $\rho(T)$ data for various magnetic fields up to 18 tesla for PrOs$_4$Sb$_{12}$, which reveal drops in $\rho(T)$ due to the superconductivity for $H \leq 2.2$ tesla and features in $\rho(T)$ associated with the onset of the high field ordered phase for $H \geq 4.5$ tesla. Isotherms of electrical resistivity $\rho$ vs $H$ at various temperatures $0.35 \text{ K} \leq T \leq 4.2 \text{ K}$ and fields $0 \leq H \leq 18 \text{ tesla}$ are shown in Fig. 4(c). The fields denoting the boundaries of the high field ordered phase, $H_1^*$ and $H_2^*$, are indicated in the figure.
6. Summary

Experiments on the filled skutterudite compound PrOs$_4$Sb$_{12}$ have revealed a number of extraordinary phenomena: a heavy fermion state characterized by an effective mass $m^* \approx 50 m_e$, unconventional superconductivity below $T_c = 1.85$ K with two distinct superconducting phases, and a high field ordered phase, presumably associated with magnetic or quadrupolar order. Analysis of $\chi(T)$, $C(T)$, $\rho(T)$, and INS data indicate that Pr$^{3+}$ has a nonmagnetic $\Gamma_3$ doublet ground state that carries an electric quadrupole moment, a low lying $\Gamma_5$ triplet excited state at $\sim 10$ K, and $\Gamma_4$ triplet and $\Gamma_1$ singlet excited states at much higher energies. This suggests that the interaction between the quadrupole moments of the Pr$^{3+}$ ions and the charges of the conduction electrons, as well as the excitations between the $\Gamma_3$ ground state and $\Gamma_5$ low lying excited state, may play an important role in generating the heavy fermion state and superconductivity in this compound. The heavy fermion state, unconventional superconductivity, and high field ordered phase observed in PrOs$_4$Sb$_{12}$ and reviewed herein present a significant challenge for theoretical description [27, 36, 37, 38, 39].

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