Heavy fermion superconductivity in the filled skutterudite compound PrOs$_4$Sb$_{12}$

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Abstract

The filled skutterudite compound PrOs$_4$Sb$_{12}$ has been found to exhibit superconductivity with a critical temperature $T_c = 1.85$ K that develops out of a heavy Fermi liquid with an effective mass $m^* \approx 50 m_e$. 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$_{12}$ is briefly reviewed herein.

Key words: superconductivity; heavy fermion; f-electron material; filled skutterudite

1. Introduction

About a year ago, we reported that the compound PrOs$_4$Sb$_{12}$ exhibits heavy fermion superconductivity below a critical temperature $T_c = 1.85$ K [1,2]. The heavy fermion state is characterized by an effective mass $m^* \approx 50 m_e$, where $m_e$ is the free electron mass. To our knowledge, this is the first heavy fermion superconductor based on Pr; all of the other known heavy fermion superconductors (about 20) are compounds of Ce or U. In an effort to obtain information about the interactions that are responsible for the heavy fermion state and the superconductivity of PrOs$_4$Sb$_{12}$, we have performed measurements of certain normal and superconducting state properties of this compound as a function of temperature, pressure, and magnetic field [1,2,3,4]. An analysis of magnetic susceptibility $\chi(T)$, specific heat $C(T)$, and inelastic neutron scattering INS measurements on PrOs$_4$Sb$_{12}$ within the context of a cubic crystalline electric field (CEF) yielded a Pr$^{3+}$ energy level scheme with 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 above the ground state, and $\Gamma_4$ triplet and $\Gamma_1$ singlet excited states at much higher energies ($\sim 130$ K and $\sim 313$ K, respectively). This scenario suggests that the underlying mechanism of the heavy fermion behavior in PrOs$_4$Sb$_{12}$ may involve electric quadrupole fluctuations, rather than magnetic dipole fluctuations. It also raises the possibility that electric quadrupole fluctuations play a role in the superconductivity of PrOs$_4$Sb$_{12}$. In magnetic fields greater than 4.5 T and at temperatures below 1.5 K, we have also found evidence for the existence of a region in which there is magnetic or quadrupolar order [3,4]. This suggests that the superconducting phase may occur in the vicinity of a magnetic or quadrupolar quantum critical point (QCP).

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

The first evidence that the superconductivity of the filled skutterudite compound PrOs$_4$Sb$_{12}$ develops out of a heavy Fermi liquid emerged from measurements of the temperature dependence of the specific heat $C(T)$. Specific heat data from Refs. [1] and [2] in the form of a plot of $C/T$ vs $T$ between 0.5 K and 10 K for a PrOs$_4$Sb$_{12}$ pressed pellet (formed by pressing a collec-
Further evidence of heavy fermion superconductivity is provided by the upper critical field $H_{c2}$ vs $T$ curve shown in Fig. 2 [2,3]. The slope of the $H_{c2}$ curve near $T_c$ can be used to determine the orbital critical field $H_{c2}(0) = \Phi_0/2\pi\xi_{\ast}^2$, where $\Phi_0$ is the flux quantum, and, in turn, the superconducting coherence length $\xi_0$ yielding the value $\xi_0 \approx 116$. The BCS relation $\xi_0 = 0.18h\nu_F/k_BT_c$ can be used to estimate the Fermi velocity $\nu_F$ and, in turn, the effective mass $m^*$ by means of the relation $m^* = h\nu_F/\nu_F$. Using a simple free electron model to estimate the Fermi wave vector $k_F$, an effective mass $m^* \approx 50 m_0$ has been obtained [2,3]. Calculating $\gamma$ from $m^*$ yields $\gamma \sim 350$ mJ/mol K$^2$, providing further evidence for heavy fermion superconductivity in PrOs$_4$Sb$_{12}$.

3. Nature of the superconducting state

Several features in the superconducting properties of PrOs$_4$Sb$_{12}$ indicate that the superconductivity of this compound is unconventional in nature. First, $C(T)$ follows a power law $T$-dependence, $C_s(T) \sim T^{-2.5}$ after the Schottky anomaly and $\beta T^3$ lattice contributions have been subtracted from the $C(T)$ data. Second, there is a ‘double-step’ structure in the jump in $C(T)$ near $T_c$ in single crystals (lower inset of Fig. 1) that suggests that there are two distinct superconducting phases with different $T_c$'s: $T_{c1} \approx 1.70$ K and $T_{c2} \approx 1.85$ K [3,5]. This structure is not evident in the $C(T)$ data near $T_c$ 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, it is not clear whether these
two apparent jumps in $C(T)$ are associated with two distinct superconducting phases or 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, UPt₃ and U₁₋ₓThₓBe₁₃ (0.1 ≤ x ≤ 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 [6], which, from the Ehrenfest relation, reveal that $T_{c1}$ and $T_{c2}$ have considerably different pressure dependencies, suggesting that they are associated with two distinct superconducting phases.

Recent transverse field $μ$SR [7] and Sb-NQR measurements [8] on PrOs₄Sb₁₂ 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. Recently, the superconducting gap structure of PrOs₄Sb₁₂ was investigated by means of thermal conductivity measurements in magnetic fields rotated relative to the crystallographic axes by Izawa et al. [9]. These measurements reveal two regions in the $H - T$ plane, a low field region in which $Δ(k)$ has two point nodes, and a high field region where $Δ(k)$ 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 phase and the normal phase, $H_{c2}(T)$, converges with $T_{c1}$ as $H \rightarrow 0$. Clearly, more research will be required to further elucidate the nature of the superconducting state in PrOs₄Sb₁₂.

4. Nature of the nonmagnetic heavy fermion state

Magnetic susceptibility $χ(T)$ measurements on PrOs₄Sb₁₂ indicate that it has a nonmagnetic ground state. According to Lec, Leask, and Wolf [10], in a cubic CEF, the Pr⁴⁺ $J = 4$ Hund’s rule multiplet splits into a $Γ_1$ singlet, a $Γ_3$ nonmagnetic doublet that carries an electric quadrupole moment, and $Γ_4$ and $Γ_5$ triplets. In order to analyze the $χ(T)$ data, it was assumed that the Pr⁴⁺ ions are, to first approximation, noninteracting and the nonmagnetic ground state corresponds to either a $Γ_1$ singlet or $Γ_3$ nonmagnetic doublet ground state [2]. Although reasonable fits to the $χ(T)$ data could be obtained for both $Γ_1$ and $Γ_3$ ground states, the most satisfactory fit was obtained for a $Γ_3$ nonmagnetic doublet ground state with a $Γ_3$ first excited triplet state at 11 K and $Γ_4$ and $Γ_1$ second and third excited states at 130 K and 313 K, respectively. Inelastic neutron scattering measurements on PrOs₄Sb₁₂ reveal transitions at 0.71 meV (8.2 K) and 11.5 meV (133 K) that appear to be associated with transitions between the $Γ_3$ ground state and the $Γ_3$ first and $Γ_4$ second excited states, respectively, that are in good agreement with the Pr⁴⁺ CEF energy level scheme determined from the analysis of the $χ(T)$ data. As noted above, the Schottky anomaly in the $χ(T)$ data on PrOs₄Sb₁₂ taken at UCSD and at the University of Karlsruhe [5] 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 ~ 7 K, a value that is comparable to the values deduced from the $χ(T)$ and INS data. However, a $Γ_1$ ground state cannot, at this point, be completely excluded.

While a magnetic $Γ_4$ or $Γ_3$ Pr⁴⁺ ground state could produce a nonmagnetic heavy fermion ground state via an antiferromagnetic exchange interaction (Kondo effect), the behavior of $ρ(T)$ of PrOs₄Sb₁₂ in the normal state does not resemble the behavior of $ρ(T)$ expected for this scenario. For a typical magnetically induced heavy fermion compound, $ρ(T)$ 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, $ρ(T)$ varies as $AT^2$ with a prefactor $A \approx 10^{-5} \ [μΩ \ cm K^2 (mJ/mol)^{-2}] \ γ^2$ that is consistent with the Kadowaki-Woods relation [11]. In contrast, PrOs₄Sb₁₂ has a very typical metallic resistivity with negative curvature at higher temperatures and a pronounced ‘roll off’ below ~ 8 K before it vanishes abruptly when the compound becomes superconducting. The ‘roll off’ in $ρ(T)$ appears to be due to a decrease in charge or spin dependent scattering from the low lying Pr⁴⁺ CEF energy level due to the decrease in population of this level as the temperature is lowered. The $ρ(T)$ data can be described by a temperature dependence of the form $AT^2$ between ~ 8 K and 45 K, but with a prefactor $A \approx 0.009 \ [μΩ \ cm K^2]$ that is nearly two orders of magnitude smaller than that expected from the Kadowaki-Woods relation which yields $A \approx 1.2 \ [μΩ \ cm K^2]$ for $γ \approx 350 \ [mJ/mol K^2]$ [11]. Interestingly, $ρ(T)$ is consistent with $T^2$ behavior with a value $A \approx 1 \ [μΩ \ cm K^2]$ in fields of ~ 5 T in the high field ordered phase discussed in section 5.) However, the temperature dependence of $ρ(T)$ is similar to that observed for the compound PrInAg₂ which has an enormous $γ$ of ~ 6.5 J/mol K² and a $Γ_3$ nonmagnetic doublet ground state [12]. The compounds PrOs₄Sb₁₂,
PrInAg, and another Pr-based skutterudite, PrFe$_4$P$_{12}$ [13], may belong to a new class of heavy fermion compounds in which the heavy fermion state is produced by electric quadrupole fluctuations. In contrast, magnetic dipole fluctuations are widely believed to be responsible for the heavy fermion state in most Ce and U heavy fermion compounds (with the possible exception of certain U compounds such as UBe$_{13}$). 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 [14].

5. High field ordered phase

Evidence for a high field ordered phase was first derived from magneto-resistance measurements in the temperature range 80 mK $\leq T \leq 2$ K and magnetic fields up to 9 tesla [3,15]. The $H - T$ phase diagram, showing the superconducting region and the high field ordered phase is shown in Fig. 2. The line that intersects the high field ordered state represents the inflection point of the 'roll-off' in $\rho(T)$ at low temperatures and is a measure of the splitting between the Pr$^{3+}$ ground and the first excited states which decreases with field. The high field ordered phase has also been observed by means of large peaks in the specific heat at $T \leq 2 K$ and temperatures $\leq 1.5 K$.

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 $T_c = 1.85$ with two distinct superconducting phases, and a high field phase, presumably associated with magnetic or electric 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 and 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 and unconventional superconductivity will constitute a significant challenge for theoretical description [18].

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