Low-Temperature Specific Heat of the Heavy-Fermion Superconductor $PrOs_4Sb_{12}$

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We report the magnetic field dependence of the specific-heat C of single crystals of the first Pr-based heavy-fermion superconductor $PrOs_4Sb_{12}$. The variation of C at low temperature and the magnetic phase diagram inferred from C, the resistivity and magnetization provide compelling evidence of a doublet ground state. Two distinct superconducting anomalies in C indicate an unconventional superconducting state, where the splitting may arise from a weak lifting of the ground state degeneracy. In combination this identifies $PrOs_4Sb_{12}$ as a strong contender for quadrupolar pairing, i.e., superconductivity that is neither electron-phonon nor magnetically mediated.

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Superconductive pairing that is not mediated by a conventional electron-phonon interaction has been the subject of considerable scientific interest. In recent years, intermetallic compounds have been discovered which, together with the high-T_c cuprates, are prime candidates for magnetically mediated pairing. Surprisingly, however, magnetically mediated pairing has thus far been considered the only serious alternative to electron-phonon mediated pairing, while excitonic and polaronic mechanisms have also been proposed.

Recently heavy-fermion superconductivity was discovered in the filled scutterudite compound $PrOs_4Sb_{12}$ [1] , for which the nonmagnetic ground state appeared best described as a crystalline electric field (CEF) doublet with a low lying triplet first excited state. The doublet ground state in turn suggested that the heavy Fermi liquid is of quadrupolar origin and that, consequently, quadrupolar fluctuations mediate the superconductive pairing. However, a magnetic origin for the heavy Fermi liquid could not be ruled out [1] and recent specific-heat measurements have been reported to be consistent with a singlet CEF ground state, thus questioning our hypothesis of quadrupolar pairing [2]. Settling the question of the ground state of the electron liquid demands definitive establishment of (i) the CEF energy level scheme, (ii) the nature of the superconductivity, and (iii) coupling of the CEF excitations to the conduction electrons. Here, we report specific-heat measurements on high-quality single crystals of $PrOs_4Sb_{12}$ at low temperature T and in high magnetic field B. We show that the magnetic phase diagram as established from the specific heat, resistivity, and magnetization, as well as the observation of a novel high-field ground state, unambiguously identify a nonmagnetic doublet CEF ground state that is intimately linked to the conduction electrons. Moreover, we observe two superconducting transitions giving evidence of two distinct superconducting phases consistent with a weak lifting of the ground state degeneracy [3]. This establishes $PrOs_4Sb_{12}$ as a prime candidate for superconductive pairing mediated by quadrupolar fluctuations.

The first experiments on single crystals of $PrOs_4Sb_{12}$ [1] showed that the electrical resistivity ρ drops monotonically from room temperature to $T_c = 1.85$ K by nearly 2 orders of magnitude with a shoulder at $T \sim 7$ K. The low T bulk properties, notably ρ, C, and magnetic susceptibility χ are dominated by a single energy scale of order several K, with a Curie–Weiss behavior of $\mu_{CW} = 2.97\mu_B$ at high T. These results [1], together with preliminary inelastic neutron scattering [4] and nonlinear susceptibility data [5] are consistent with a doublet ground state, but a singlet ground state could not be ruled out. Superconductivity with an upper critical field $B_{c2}(T \to 0) = 2.5$ T involves heavy quasiparticles with a thermodynamic effective mass $m^*_{td} \approx 50m_e$ as inferred from the jump of C at T_c, the slope of B_{c2} near T_c, and the normal-state electronic specific-heat coefficient γ. Quantum oscillatory studies exhibit a large electron mass renormalization $m^*_{qo} \approx 7.6m_e$ that accounts for $\sim$50% of the zero-field γ [6]. This is supported by nuclear quadrupole resonance (NQR) studies [7] which together with transverse-field muon spin relaxation of the superconducting flux line lattice [8] provide evidence of unconventional superconductivity. Multiple superconducting phases were recently derived from the thermal conductivity [9].

The high-quality single crystals studied here were grown from a Sb flux [10]. The samples have narrow superconducting transitions in both ρ and χ and a low residual resistivity $\rho_0 < 5\ \mu\Omega$ cm. The samples spontaneously crystallized in a cubic shape, where the principal crystallographic axes were confirmed to coincide with faces of the cubes. Powder x-ray diffraction using a careful Rietveld analysis showed that the samples were single phase with a stoichiometric ratio $a_0 = 1$ of Pr atoms per formula unit [11]. De Haas–van Alphen oscillations in single-crystal samples from the same growth provide evidence of long charge-carrier mean free paths [12].

Here we report C of an aggregate of five small single-crystal pieces (~ 10 mg) all showing very well-developed facets. This aggregate displayed the highest C thus far reported, while that of a large single piece (~ 3.55 mg) that served for comparison is reduced by 9%, indicating a small quantity of Sb inclusions. We find that T^* of the peak of the Schottky anomaly and T_c are sample independent. Moreover, we find two distinct superconducting transitions in *all* of our single-crystal samples studied to date, apart from the pressed pellets which were subject to large internal stresses [4].

The specific heat was measured with a quasiadiabatic heat pulse technique in a ^{4}He cryostat down to 1.5 K in magnetic fields up to 14 T [13] and in a dilution refrigerator down to 100 mK in magnetic fields up to 6.65 T [14]. Magnetic fields were applied along the principal cubic axes. We observe quantitative agreement to better than a few per cent in the temperature and field range of overlap between the two experimental setups, which employ different thermometers and sample holders. We note that C of materials with large, weakly coupled nuclear contributions such as $\mathrm{PrOs_4Sb_{12}}$ display quasiadiabatic thermal relaxation times that easily exceed several minutes. Using a very low-noise resistance bridge and automated detection electronics we were able to keep track of these extremely slow relaxation processes. Our results distinctly differ from recent reports [2]. However, our data are consistent with those reported in [2] when evaluating the initial T versus time dependence following a heat pulse, for which nuclear contributions are still decoupled and hence thermal equilibrium in the sample has not yet been reached.

Shown in Fig. 1 is C/T versus T for low B. With decreasing T, C/T exhibits the well-established maximum at $T^* \approx 2.1$ K, decreases again, followed by a very pronounced upturn at the lowest T. The superconducting transition at $T_c \approx 1.85$ K is accompanied by a well-developed anomaly in C consisting of a double jump.

We first focus on the normal state. For $B = 0$ and $T > T_c$ up to 10 K, $C(T)$ is well described as the sum of a Sommerfeld contribution $C_{\mathrm{el}} = \gamma T$ where $\gamma = 313\ \mathrm{mJ/mol\,K^2}$, a phonon contribution $C_p = \beta T^3$, where β corresponds to a Debye temperature $\Theta_D = 165$ K and a Schottky term C_S discussed below. The exponential freezing out of the Pr rattling modes assuming an Einstein spectrum is not accounted for, because $T \ll \Theta_E \approx 55$ K, where Θ_E is estimated following Ref. [15] and room temperature x-ray and neutron data. The slightly reduced value of γ observed here may be related to the higher sample quality and/or the different account of the lattice contribution, which was previously taken as the lattice specific heat of $\mathrm{LaOs_4Sb_{12}}$ ($\Theta_D = 304$ K).

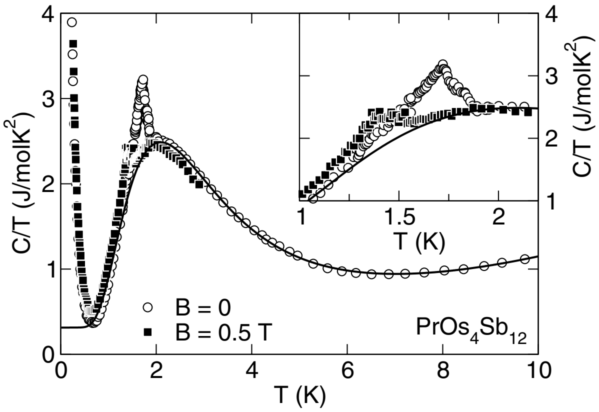

FIG. 1. C/T vs T at $B = 0$ and $B = 0.5$ T for $B \parallel \langle 100 \rangle$. The inset displays C/T near T_c, where the double transition can no longer be resolved at 0.5 T. The line represents a fit composed of a Sommerfeld electronic and Debye lattice contribution plus a Schottky anomaly described in the text.

The Schottky term, C_S, exceeds $C_{\mathrm{el}} + C_p$ by a large margin up to 10 K. It arises from a splitting of the Pr^{3+} $J = 4$ Hund's rule multiplet into a singlet (Γ_1), a doublet (Γ_3), and two triplets (Γ_4 and Γ_5) in the tetrahedral T_h symmetry of the CEF [16]. Up to 10 K it is well approximated as $C_S = d_{gs} d_{fs} a_0 R (\Delta/T)^2 e^{-\Delta/T} / (d_{gs} + d_{fs} e^{-\Delta/T})^2$, where R is the gas constant and d_{gs} and d_{fs} are the degeneracy of ground state and first excited state, respectively. Consistency with the magnetic susceptibility [1] suggests three combinations of ground state with first excited state as most likely: (i) singlet-triplet, (ii) doublet-triplet, and (iii) triplet-doublet. In each case Δ is unambiguously determined by T^* of the Schottky anomaly and thus does not represent a free fit parameter. *This in turn leaves a_0 as the only adjustable parameter.* For case (i) $a_0 \rightarrow 0.5$, implying a Pr filling ratio of only 50% in contradiction to the x-ray analysis. Moreover, the shape of the fitted curve, which for clarity is not shown, does not track the experimental data points. In contrast, for case (ii) shown in Fig. 1 we find $\Delta = 7$ K and $a_0 \approx 0.99$ corresponding to the expected stoichiometry. Case (iii) only converges for $\Delta = -7$ K and $a_0 \approx 0.99$, i.e., case (ii). Our single-crystal study hence unambigously identifies a doublet CEF ground state and settles the key issue [1].

We next consider the consistency of the doublet ground state with the anomaly at T_c, which exhibits a double transition as shown in Figs. 1 and 2. Here the jump at the higher T coincides with the ρ and χ transition temperature. A double transition is also observed in the thermal expansion of the single crystals [17]. In fact, a double transition of identical size and transition temperature has been observed in *all* of our single-crystal samples studied to date, i.e., more than ten, apart from the pressed pellet [1,4]. The absence of a double transition in the pressed pellets suggests a high sensitivity to internal stresses,

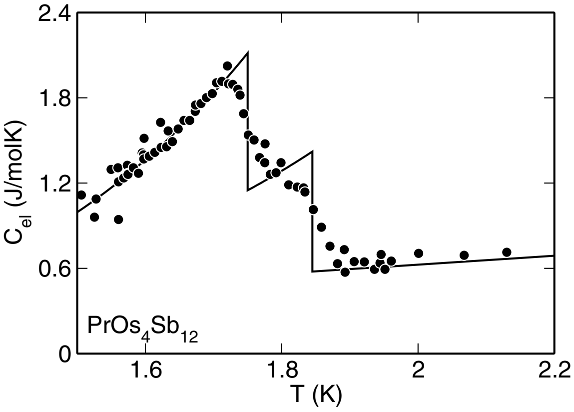

FIG. 2. Electronic contribution to the specific heat $C_{\rm el}$ vs T after subtraction of the lattice and Schottky term. The solid curve shows an entropy conserving construction for the determination of $T_{c1} = 1.75$ K and $T_{c2} = 1.85$ K, respectively.

possibly present in samples studied by other groups [2], which nevertheless recently reported multiple superconducting phases [9]. It has been shown that the pairing symmetry related to a doublet ground state results in two superconducting transitions when the degeneracy is slightly lifted [3], e.g., by a tiny Jahn-Teller distortion. Such a Jahn–Teller distortion may also be relevant to the high-field phase presented below.

The transition temperatures and sizes of the jumps of the superconducting double transition may be determined from an equal-entropy construction given as $C_{\rm el}$ after subtraction of the phonon and Schottky contributions. This is illustrated by the line shown in Fig. 2, where $T_{c1} = 1.75$ K and $T_{c2} = 1.85$ K. The ratio $\Delta C_{\rm sc}/\gamma T_c \approx 3$, where $\Delta C_{\rm sc}$ is the total height of both superconducting jumps taken together, exceeds the weak-coupling BCS value $\Delta C_{\rm sc}/\gamma T_c = 1.43$ and implies strong-coupling superconductivity consistent with pairing of heavy electrons. The superconducting double transition is, moreover, reminiscent of the only other stoichiometric metal exhibiting this type of behavior, UPt$_3$, which displays a complex superconducting phase diagram as a function of magnetic field [18] and pressure [19]. We find that the splitting of the double transition in PrOs$_4$Sb$_{12}$ is independent of field up to 0.4 T and may no longer be resolved in 0.5 T, making more measurements necessary to establish its fate in magnetic field in further detail.

We finally turn to $C(T)$ at high B shown in Fig. 3(a). The Schottky anomaly is strongly suppressed in magnetic field while a strong increase of C develops for $T \rightarrow 0$. The low-T increase is consistent with the splitting of the Γ_3 doublet ground state in a magnetic field and additional contributions from hyperfine-enhanced Zeeman splitting of the Pr nuclear levels. C at low-T exceeds that reported in Ref. [2] by a large margin and does not support a Pr-singlet ground state as reported in [2]. For $B > 4.5$ T, the specific heat develops a pronounced maximum that shifts from $T = 0.7$ K for $B = 5$ T to $T = 1$ K for $B = 6.65$ T and sharpens considerably. This indicates a transition to a new thermodynamic ground state. A change of ground state is also underscored by two distinctly different crossing points common to the $C(T)$ curves [20] at $T_< = 1.4$ K for $B < 4$ T [Fig. 3(b)] and $T_> = 1.15$ K for $B > 4$ K [Fig. 3(c)].

The calculation of the generalized Zeeman splitting of the lowest CEF levels strongly suggests that the high-field phase is driven by a level crossing of the Γ_3 doublet and Γ_5 triplet. For this calculation, we consider a conventional Zeeman term $H_Z = J\mu_B g_J$, where g_J is the Lande g factor, and express the crystal-field potential $\langle V \rangle$ of the T_h point group [16] using the Steven's operator equivalent [21]. The crystal-field potential in this form depends on three parameters, W, a scaling factor, x, the level spacing and y, the mixing of the Γ_4 and Γ_5 triplets that distinguishes the T_h from the O_h point symmetry. For a point-charge model $y \ll 0.1$ [16,22], while for a more realistic charge distribution no estimate of y is possible at present. Therefore, we first compute the Zeeman splitting for the O_h symmetry (Fig. 4), i.e., $y = 0$, where $x = 0.6$ and W is taken from Ref. [10]. The first level crossing at $B \sim 4$ T corresponds roughly to the onset of the high-field phase at $\sim$5 T, suggesting a possible change of ground state. For finite y, tabulated values of the wave functions at $x = 0.6$

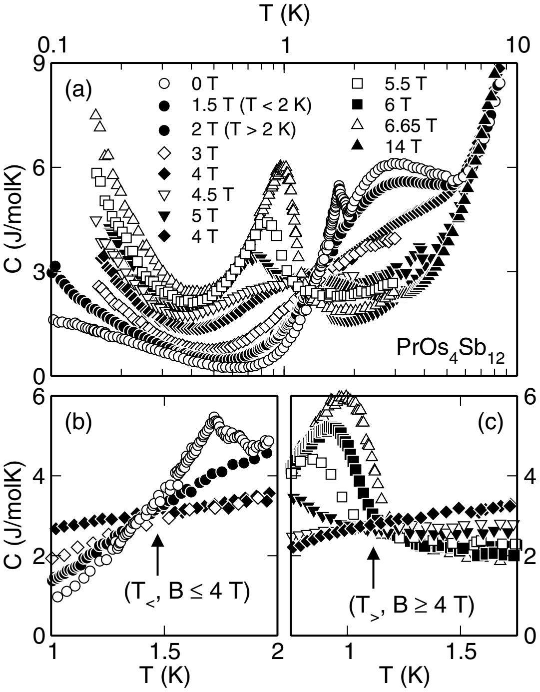

FIG. 3. Specific heat C vs T for $B \parallel \langle 100 \rangle$ up to 14 T. (a) The high T Schottky anomaly is rapidly suppressed up to 14 T. A pronounced anomaly, indicating an ordered state stabilized at high B, is resolved at low T. (b) and (c) Crossing points common to all $C(T)$ curves at $T_< = 1.4$ K for $B < 4$ T and $T_> = 1.15$ K for $B > 4$ T highlight a field induced phase.

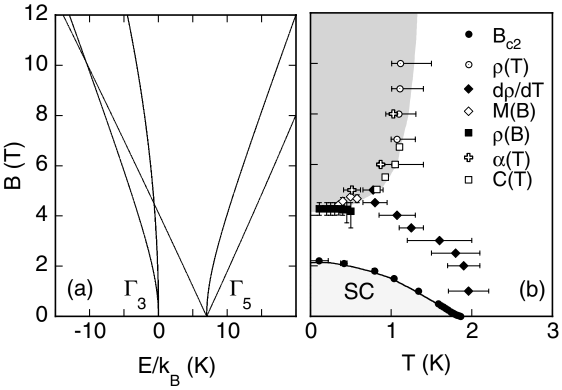

FIG. 4. (a) Zeeman splitting of the Γ_3 doublet and Γ_5 triplet CEF levels used for fitting the zero field specific heat. The doublet and triplet cross at ~4T and ~10T, suggesting a stabilization of a different ground state in this regime. (b) Magnetic phase diagram deduced from the specific heat C (this work), magnetization M [4], resistivity ρ [11], and thermal expansion α [17]. The high field phase is clearly driven by the level crossing due to the Zeeman splitting.

and $y = 0.2$ [16] show that the crossing point is shifted to 10 T, i.e., higher fields. The apparent agreement of the experimental crossing point with octahedral symmetry may be attributed to a weak mixing of the triplets in the T_h point symmetry. A full quantitative calculation of C at high field is not feasible even for the point-charge model, due to complications associated with the hybridization of the f electrons with the conduction electrons and a high sensitivity to small shifts of the energy levels at low temperatures.

The Zeeman splitting of the CEF at high fields makes the high-field phase reminiscent of the quadrupolar order observed in $PrPb_3$ [23] and $PrFe_4P_{12}$ [24], both of which have CEF doublet ground states. For $PrPb_3$, the ordering temperature T_{QO} is shifted to higher values in magnetic field, before it collapses to zero above ~7 T [14]. This is in qualitative agreement with the increase of the onset of the high-field phase in $PrOs_4Sb_{12}$ and recent high-field susceptibility experiments which detect another field-induced phase transition at 13.8 T [6] that may correspond with the second crossing point, which is at ~10.5 T for the O_h symmetry as shown in Fig. 4 and would be shifted to higher field for finite y.

Finally, the interplay of the CEF excitations with the conduction electrons is readily evident from kinks in resistivity ρ and magnetization M at low fields and maxima in M [4], $d\rho/dT$ [11], and thermal expansion α [17]. When combining these features with the sharp anomaly in the specific heat, a unified phase diagram shown in Fig. 4(b) may be constructed that also agrees with features of the magnetization. At low fields the phase diagram tracks the lowest Γ_5 level, hence identifying the dominant energy scale of a few K at $B = 0$ seen in the resistivity, susceptibility, and specific heat. Thus, the CEF sensitively affects the properties of the conduction electrons, even at high magnetic fields.

In conclusion, we have examined C of single crystalline $PrOs_4Sb_{12}$ at low T and high B. The account of the zero-field Schottky anomaly, the superconducting double transition, and the magnetic phase diagram, for which we report a novel high-field phase, strongly indicate a doublet ground state for $B = 0$. When taken together, this establishes $PrOs_4Sb_{12}$ as a strong contender for quadrupolar superconductive pairing, i.e., neither electron-phonon nor magnetically mediated pairing.

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