Pronounced Enhancement of the Lower Critical Field and Critical Current Deep in the Superconducting State of $PrOs_4Sb_{12}$

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We have observed an unexpected enhancement of the lower critical field $H_{c1}(T)$ and the critical current $I_c(T)$ deep in the superconducting state below $T \approx 0.6$ K ($T/T_c \approx 0.3$) in the filled skutterudite heavy fermion superconductor $PrOs_4Sb_{12}$. From a comparison of the behavior of $H_{c1}(T)$ with that of the heavy fermion superconductors $U_{1-x}Th_xBe_{13}$ and UPt_3, we speculate that the enhancement of $H_{c1}(T)$ and $I_c(T)$ in $PrOs_4Sb_{12}$ reflects a transition into another superconducting phase that occurs below $T/T_c \approx 0.3$. An examination of the literature reveals unexplained anomalies in other physical properties of $PrOs_4Sb_{12}$ near $T/T_c \approx 0.3$ that correlate with the features we have observed in $H_{c1}(T)$ and $I_c(T)$.

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The filled skutterudite compound $PrOs_4Sb_{12}$ has attracted an enormous amount of interest since it was discovered several years ago [1,2]. This compound is the first heavy fermion superconductor based on Pr (all of the others are based on Ce and U), the superconductivity appears to be unconventional, and the pairing of superconducting electrons may be mediated by electric quadrupole fluctuations, rather than magnetic dipole fluctuations that are believed to be responsible for pairing in the other heavy fermion superconductors. A number of experiments have provided evidence for unconventional superconductivity in $PrOs_4Sb_{12}$. Structure in the jumps of both the specific heat [2–4] and thermal expansion [5,6] associated with the superconducting transition suggests that there may be two distinct superconducting phases with superconducting critical temperatures $T_{c1} = 1.85$ K and $T_{c2} = 1.74$ K in zero field. Superconducting penetration depth measurements, extracted from muon spin relaxation (μSR) experiments in a magnetic field of 200 Oe [7], and nuclear quadrupole resonance (NQR) measurements [8] indicate that the superconductivity of $PrOs_4Sb_{12}$ is in the strong coupling regime and has an isotropic energy gap. In contrast, measurements of the angular (ϕ) dependence of the thermal conductivity $\kappa(\phi, H)$ in a magnetic field H [9] have been interpreted as evidence for two distinct superconducting phases, a low field phase with two point nodes and a high field phase with four or six point nodes. The superconducting penetration depth λ, measured in very low field by means of a microwave technique [10], is consistent with point nodes in the energy gap. Muon spin relaxation measurements in zero field reveal that spontaneous magnetic moments develop below T_c, indicative of time reversal symmetry breaking [11]. A high field ordered phase (HFOP), between 4.5 and 16 T and below 1 K, has been inferred from electrical resistivity [2,12,13], specific heat [3,4], thermal expansion [5,6], magnetization [13–15], and magnetostriction [6] measurements. From neutron diffraction measurements at high magnetic fields, the HFOP was identified with antiferroquadrupolar order [16]. This suggests that the unconventional superconductivity in $PrOs_4Sb_{12}$ may occur in the vicinity of a quadrupolar quantum critical point (QCP), similar to the situation with certain Ce and U compounds where superconductivity is found in the vicinity of an antiferromagnetic (AFM) QCP [17]. In this Letter, we report measurements of the lower critical field $H_{c1}(T)$, critical current $I_c(T)$, ac magnetic susceptibility $\chi_{ac}(T)$, and specific heat $C(T)$ in order to obtain more information about the unconventional superconductivity exhibited by this intriguing material. Our measurements indicate that a transition to another superconducting phase, characterized by enhanced $H_{c1}(T)$ and $I_c(T)$, occurs deep within the superconducting state at $T \approx 0.6$ K ($T/T_c \approx 0.3$) in zero field.

The $PrOs_4Sb_{12}$ single crystals studied in this investigation were grown from an Sb flux in a manner described elsewhere [18]. Powder x-ray diffraction studies of crystals grown in this run revealed that the samples are single phase. The residual resistivity (at a temperature right above T_c) of crystals grown in this manner is typically less than 5 $\mu\Omega$ cm. Specific heat measurements were made in a semiadiabatic ^{3}He calorimeter by means of a standard heat pulse technique. The lower critical field H_{c1} was determined from isothermal magnetization curves taken with a custom made SQUID magnetometer. In this arrangement, the detection loop is located in the mixing chamber of a dilution refrigerator, and the sample is stationary and in direct contact with the liquid ^{3}He–^{4}He mixture. The ac magnetic susceptibility was measured in the same arrangement using a mutual inductance bridge with the SQUID as a null detector [19].

Measurements of $C(T)$ and $\chi_{ac}(T)$ were performed on the same $PrOs_4Sb_{12}$ single crystal in the vicinity of the superconducting transition. The $C(T)$ data are shown in Fig. 1 and reveal the "double jump" structure, reminiscent of two distinct superconducting transitions at the critical temperatures $T_{c1} = 1.86$ K (onset) and $T_{c2} = 1.72$ K. It is interesting to note that the jump ΔC_1 at T_{c1} is rather broad, while the jump ΔC_2 at T_{c2} is very sharp. Also shown in Fig. 1 are $\chi_{ac}(T)$ data, taken with a field amplitude $H_{ac} = 1.2$ mOe and a frequency $f = 160$ Hz. From the in-phase component of the susceptibility, 90% of the transition occurs at T_{c1} with the last 10% "foot" extending to T_{c2}. At T_{c2}, the magnitude of χ_{ac} reaches its maximum value observed in the limit $T \rightarrow 0$ K.

The "double jump" feature in $C(T)$, originally reported in Refs. [2,3,5], has been confirmed by several other groups [4,20,21] and seems to be an intrinsic property of $PrOs_4Sb_{12}$. Measurements in a magnetic field indicate that T_{c1} and T_{c2} track each other and lie on curves with similar shapes displaced from one another in the $H - T$ plane [3,4,21]. Since the large diamagnetic change in χ_{ac} occurs at T_{c1} due to induced supercurrents, it is clear that the transition at T_{c1} is associated with superconductivity. The sharp jump in $C(T)$ at T_{c2} suggests that the transition at T_{c2} is also due to superconductivity.

The lower critical field $H_{c1}(T)$ was determined from magnetization (shielding) isotherms; typical examples at different temperatures are shown in Fig. 2. Each magnetization curve was taken after zero-field cooling the sample to the desired temperature. The lower critical field H_{c1} was defined as the first deviation from the shielding slope in the $M(H)$ curve, as illustrated in the inset of Fig. 2. The resultant $H_{c1}(T)$ data are plotted in Fig. 3(a) vs T (inset) and T^2. We observe a pronounced enhancement of H_{c1} below $T \approx 0.6$ K. Similar enhancements of $H_{c1}(T)$ have been observed by various groups [19,22] in $U_{1-x}Th_xBe_{13}$ for x between 0.02 and 0.04 and in UPt_3 [23] below their second (lower) superconducting transition temperatures T_{c2}. We have fitted the H_{c1} vs T^2 data in Fig. 3(a) with two straight lines. Extrapolation of these lines to $T = 0$ yields values of $H_{c1}(0)$ of 31 and 44 Oe from the high temperature ($T > 0.6$ K) and the low temperature ($T < 0.6$ K) data, respectively. Since our crystal was in the shape of a rectangular parallelopiped of $5 \times 0.2 \times 0.3$ mm^3 and the magnetic field was aligned parallel to the largest dimension, we have not introduced demagnetization corrections to the given values of H_{c1}. The sharp kink and enhancement of $H_{c1}(T)$ reported in this Letter are consistent with the positive curvature in $H_{c1}(T)$ deduced from previous magnetization measurements on $PrOs_4Sb_{12}$ [13], although these measurements did not have enough resolution to reveal the sharp kink in $H_{c1}(T)$ at $T \approx 0.6$ K.

In Fig. 3(b), we show values of the remanent magnetization M_{rem} obtained by cycling the zero-field-cooled crystal up to the field corresponding to the critical state (full penetration of vortices in the sample), removing the magnetic field, and recording the number of expelled vortices with a digital flux counter as the crystal is heated to $T \gg T_c$. In this case, M_{rem} is proportional to the critical current I_c. Coincident with the enhancement of H_{c1} at $T = 0.6$ K, we observe a dramatic increase in I_c below the same temperature, indicating that the superconducting phase below $T \approx 0.6$ K has substantially stronger pinning. By comparison with UPt_3 and thoriated UBe_{13}, one is tempted to identify the temperature $T = 0.6$ K below which $H_{c1}(T)$ and $I_c(T)$ are enhanced with a third superconducting transition at a critical temperature $T_{c3} \approx 0.6$ K.

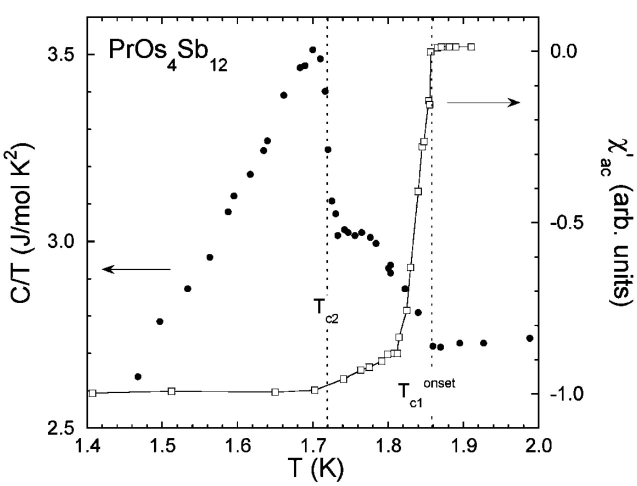

FIG. 1. Specific heat C divided by temperature T (closed circles, left scale) and ac magnetic susceptibility χ_{ac} (open squares, right scale) vs T for the single crystal of $PrOs_4Sb_{12}$ studied in this work. The value $\chi_{ac} = -1$ has been taken based on the values of χ_{ac} for $T \rightarrow 0$.

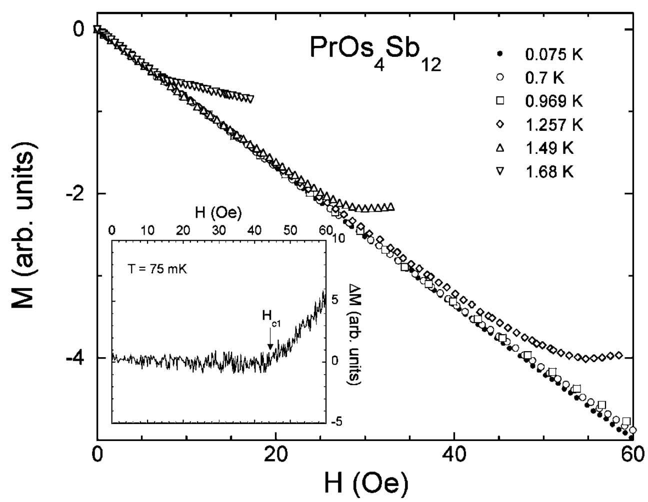

FIG. 2. Isothermal magnetization $M(H)$ curves taken after zero-field cooling at different temperatures for the same single crystal of $PrOs_4Sb_{12}$ upon which the $C(T)$ and $\chi_{ac}(T)$ data shown in Fig. 1 were taken. The inset shows the deviation in the $M(H)$ curve at H_{c1}.

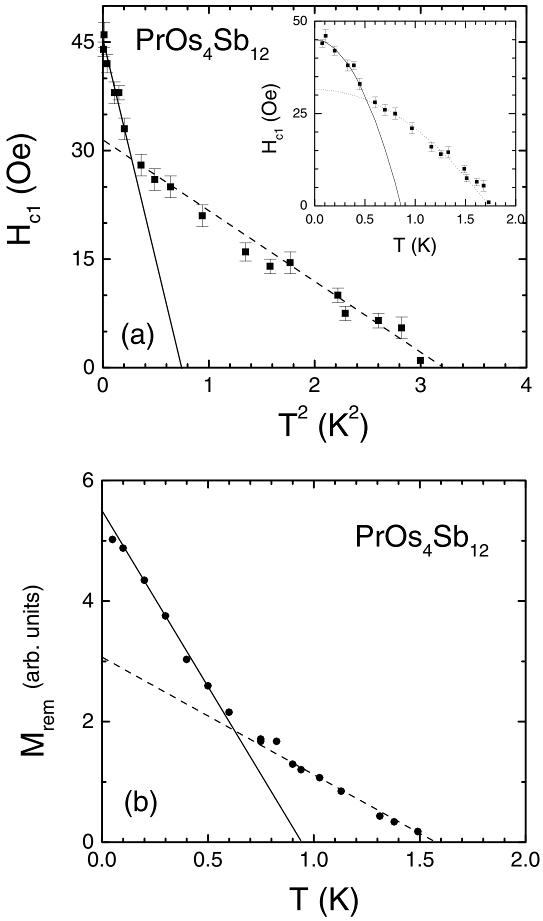

FIG. 3. (a) Lower critical field H_{c1} vs T^2 for the $PrOs_4Sb_{12}$ single crystal. The inset shows the same data plotted as H_{c1} vs T. (b) Remanent magnetization M_{rem} vs T for the $PrOs_4Sb_{12}$ single crystal. $M_{rem}(T)$ is proportional to the critical current $I_c(T)$.

One might ask whether inclusions of free Os in the single crystal could be responsible for the enhancement of $H_{c1}(T)$ and $I_c(T)$ below $T_{c3} \approx 0.6$ K, since the T_c of pure Os of 0.66 K [24] is close to the value of T_{c3}. However, it seems very unlikely that these features in $H_{c1}(T)$ and $I_c(T)$ are due to free Os since x-ray diffraction and electron microprobe studies do not give any indication of the presence of free Os in the $PrOs_4Sb_{12}$ single crystal within the limits of detectability. Furthermore, although $H_{c1}(T)$ of pure Os is about 1.4 times larger than that of $PrOs_4Sb_{12}$ below T_{c3} [24], it would not be detected in measurements of $M(H)$ shielding isotherms. In this case, the first deviation of $M(H)$ from linear Meissner behavior, corresponding to the first vortex penetration, would occur at the lowest H_{c1}, namely, that of $PrOs_4Sb_{12}$. Also, inclusions of free Os would not be expected to increase the pinning of vortices, and, in turn, $I_c(T)$, when they become superconducting.

The second critical temperature T_{c2} inferred from the structure in $C(T)$ (see Fig. 1) does not seem to be associated with the critical temperature T^* separating two superconducting phases, a low field phase with two point nodes in the energy gap and a high field phase with four or six point nodes in the energy gap, inferred from the $\kappa(\phi, H)$ measurements in a magnetic field [9]. The transition between these two superconducting phases with different order parameter symmetries has not been observed in any other physical properties to date.

Zero-field muon spin relaxation measurements reveal the spontaneous appearance of magnetic moments below T_{c1}, indicative of the breaking of time reversal symmetry in the superconducting state. This suggests that the superconducting phases below T_{c1} and T_{c2} are "nonunitary" spin triplet (odd parity) superconducting states, which have nonvanishing spin moments [11]. One possibility is that the two superconducting phases have different order parameter symmetries, as occurs in UPt_3. This material has two superconducting jumps in the specific heat in zero field separated by ≈ 0.05 K. On the other hand, recent microwave surface impedance measurements on $PrOs_4Sb_{12}$ down to 1.2 K have been interpreted in terms of Josephson-coupled two-band superconductivity, implying two order parameters of the same symmetry [25]. It is clear that the superconducting phases associated with T_{c1} and T_{c2} are not well understood and that further research is needed to elucidate their nature.

Other physical properties of $PrOs_4Sb_{12}$ have been reported that exhibit anomalous behavior in the superconducting state in the vicinity of 0.6 K ($T/T_c \approx 0.3$), where a transition to a third superconducting phase appears to occur. Sb nuclear quadrupole resonance measurements [8] reveal that the inverse nuclear spin lattice relaxation time $1/T_1$ does not exhibit a coherence peak near T_c, decreases exponentially with decreasing temperature by over 3 orders of magnitude, and then abruptly levels off below $T \approx 0.6$ K. The absence of a coherence peak near T_c is also found in other Ce and U heavy fermion superconductors. However, the exponential decrease in $1/T_1$ with decreasing T is in marked contrast to the T^3 variation of $1/T_1$ at low temperatures generally observed in Ce and U heavy fermion superconductors, as expected for line nodes in the energy gap. This experiment also yields a large value of the energy gap $2\Delta/k_B T_c \approx 5.2$ indicative of strong coupling, consistent with the large value $\Delta C/\gamma T_c \approx 3$ determined from specific heat measurements [3]. The exponential dependence of $1/T_1$ implies that the superconducting energy gap is isotropic; interestingly, μSR measurements of the penetration depth λ in a magnetic field of 200 Oe also yield evidence for an isotropic energy gap [7]. In contrast, the $\kappa(\phi, H)$ data of Izawa *et al.* [9] and the $\lambda(T)$ data of Chia *et al.* [10] indicate that there are point nodes in the energy gap. However, the abrupt leveling off of $1/T_1$ at $T \approx 0.6$ K following its exponential decrease suggests a transition to a superconducting phase below 0.6 K with states in the energy gap.

The measurements of $\lambda(T)$ on a single crystal of $PrOs_4Sb_{12}$ by Chia *et al.* [10] also exhibit a feature in the vicinity of $T = 0.6$ K. In this study, a small upturn in $\Delta\lambda$ was observed at $T = 0.62$ K in the three directions a, b, and c, at which the ac field was applied. The measured drop in $\Delta\lambda$ at $T = 0.62$ K from the high temperature values, although rather small, clearly points to an increase in the superfluid density for $T < 0.6$ K. The $\lambda(T)$ data were then fitted by the authors from 0.1 to 0.55 K with power laws of the form $\Delta\lambda(T) = A + BT^n$ with $n \approx 2$, suggesting the presence of low lying excitations in this temperature range, incompatible with an isotropic superconducting gap.

A direct measurement of the superconducting energy gap of $PrOs_4Sb_{12}$ was made using a high resolution scanning tunneling microscope by Suderow *et al.* [26]. Measurements on parts of the sample yielded a superconducting density of states with a well-defined energy gap and no low energy excitations. A plot of the energy gap Δ vs T has an overall shape that is consistent with the BCS theory, but with a small feature near 0.6 K that could be associated with the anomalies we have observed at the same temperature in $H_{c1}(T)$ and $I_c(T)$. Furthermore, measurements on other parts of the sample revealed spectra with a finite density of states at the Fermi level in the superconducting gap. It is possible that the superconducting phase that appears to form below $T/T_c \approx 0.3$ is an inhomogeneous phase consisting of regions with a full gap and regions with states in the gap.

In summary, we have observed an unexpected enhancement of $H_{c1}(T)$ and $I_c(T)$ below $T/T_c \approx 0.3$ in the new filled skutterudite heavy fermion superconductor $PrOs_4Sb_{12}$. From a comparison of the behavior of $H_{c1}(T)$ with that of the heavy fermion superconductors $U_{1-x}Th_xBe_{13}$ and UPt_3, we speculate that the enhancements of $H_{c1}(T)$ and $I_c(T)$ in $PrOs_4Sb_{12}$ reflect a transition into another superconducting phase at $T_{c3} \approx 0.6$ K. An examination of the literature revealed unexplained anomalies in other physical properties around $T \approx 0.6$ K. These anomalies should be investigated further in light of the new observations reported in this Letter. Surprisingly, there is no evidence of a jump in the specific heat around $T \approx 0.6$ K [2–4], even in recent more detailed measurements [27]. One reason could be that the transition at T_{c3} is of first order, like the one between the A and B phases of superfluid ^{3}He, or of a higher order than second. A small feature in $C(T)$ could also be obscured by the nuclear Schottky contribution which increases rapidly with decreasing temperature at low temperatures below ~0.6 K. Finally, the discrepancy between different experiments on single crystals at $H = 0$, concerning the nature of the superconducting gap, can be reconciled if the temperature interval covered in the analysis is taken into account. Indeed, the NQR analysis [8], consistent with an isotropic gap was performed for $T \geq 0.6$ K, while the penetration depth analysis [10], consistent with nodes in the gap, was done for $T < 0.55$ K. In view of the enhancement of H_{c1} and I_c below T_{c3} reported here, it seems plausible that the nature of the gap function changes at T_{c3}.

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