Pronounced enhancement of the lower critical field and critical current deep in the superconducting state of PrOs$_4$Sb$_{12}$

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We have observed an unexpected enhancement of the lower critical field $H_c(1)$ 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$_4$Sb$_{12}$. From a comparison of the behavior of $H_c(1)$ with that of the heavy fermion superconductors U$_{1-x}$Th$_x$Be$_{13}$ and UPt$_3$, we speculate that the enhancement of $H_c(1)$ and $I_c(T)$ in PrOs$_4$Sb$_{12}$ 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$_4$Sb$_{12}$ near $T/T_c \approx 0.3$ that correlate with the features we have observed in $H_c(1)$ and $I_c(T)$.

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The filled skutterudite compound PrOs$_4$Sb$_{12}$ 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$_4$Sb$_{12}$. Structure in the jumps of both the specific heat [3, 4, 5] and thermal expansion [6, 7, 8], associated with the superconducting transition suggests that there may be two distinct superconducting phases with superconducting critical temperatures $T_{c1} \sim 1.85$ K and $T_{c2} \sim 1.74$ K in zero field. Superconducting penetration depth measurements, extracted from muon spin relaxation ($\mu$SR) experiments in a magnetic field of 200 Oe [9], and nuclear quadrupole resonance (NQR) measurements [10] indicate that the superconductivity of PrOs$_4$Sb$_{12}$ is in the strong coupling regime and has an isotropic energy gap. In contrast, measurements of the angular ($\phi$) dependence of the thermal conductivity $\kappa(\phi, H)$ in a magnetic field $H$ [11, 12] 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 $\lambda$, measured in very low field by means of a microwave technique [13], 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 [14]. A high field ordered phase (HFOP), between 4.5 T and 16 T and below 1 K, has been inferred from electrical resistivity [2, 12, 13], specific heat [3, 4], thermal expansion [3, 6], magnetization [13, 14, 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$_4$Sb$_{12}$ 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 $H_c(1)$, 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 $H_c(1)$ 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$_4$Sb$_{12}$ 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 $\mu\Omega\text{cm}$. Specific heat measurements were made in a semi-adiabatic $^3$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$_4$Sb$_{12}$ 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 $\Delta C_1$ at $T_{c1}$ is rather broad, while the jump $\Delta C_2$ 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 $\chi_{ac}$ reaches its maximum value observed in the limit $T \to 0$ K.

The “double jump” feature in $C(T)$, originally reported in references [2, 3, 4], has been confirmed by several other groups [21] and seems to be an intrinsic property of PrOs$_4$Sb$_{12}$. 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 $\chi_{ac}$ 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. 2 as $H$ (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 in U$_{1-x}$Th$_x$Be$_{13}$ [22] for Th concentrations $x$ between 2% and 4% 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. 2 with two straight lines. Extrapolation of these lines to $T = 0$ K yields a value of $H_{c1}(0)$ of 31 Oe for the high temperature ($T > 0.6$ K) superconducting phase and 45 Oe for the low temperature ($T < 0.6$ K) superconducting phase. Since our crystal was in the shape of a rectangular parallelepiped 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$_4$Sb$_{12}$ [3], 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. 2(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, $M_{\text{rem}}$ is proportional to the critical current $I_c$. Coincident with the enhancement of $H_{c1}(T)$ 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.

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 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$_4$Sb$_{12}$ single crystal within the limits of detectability. Furthermore, although $H_{c1}(T)$ of pure Os is $\sim 1.4$ times larger than that of PrOs$_4$Sb$_{12}$ below $T_{c3}$, 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$_4$Sb$_{12}$. 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. 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 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. 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 $\approx 0.05$ K. On the other hand, recent microwave surface impedance measurements on PrOs$_4$Sb$_{12}$ down to 1.2 K have been interpreted in terms of Josephson-coupled two-band superconductivity, implying two order parameters of the same symmetry. 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$_4$Sb$_{12}$ 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 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 three 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 mea-

![FIG. 3: (a) Lower critical field $H_{c1}$ vs $T^2$ for the PrOs$_4$Sb$_{12}$ single crystal. The inset shows the same data plotted as $H_{c1}$ vs $T$. (b) Remanent magnetization $M_{\text{rem}}$ vs $T$ for the PrOs$_4$Sb$_{12}$ single crystal. $M_{\text{rem}}(T)$ is proportional to the critical current $I_c(T)$.](image-url)
The exponential dependence of $1/T_1$ implies that the superconducting energy gap is isotropic; interestingly, $\mu$SR measurements of the penetration depth $\lambda$ in a magnetic field of 200 Oe also yield evidence for an isotropic energy gap. In contrast, the $\kappa(\phi, H)$ data of Izawa et al. indicate that there are point nodes in the energy gap. However, the abrupt levelling off of $1/T_1$ at $T \approx 0.6$ K following its exponential decrease suggest 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$_4$Sb$_{12}$ by Chia et al. 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 K 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$_4$Sb$_{12}$ was made using a high resolution scanning tunneling microscope (STM) by Suderow et al. 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 $\Delta$ 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 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, consistent with an isotropic gap was performed for $T \geq 0.6$ K, while the penetration depth analysis, 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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