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Superconductivity and disorder in $PrOs_4Sb_{12}$

M E McBriarty, P Kumar, G R Stewart and B Andraka

Department of Physics, University of Florida, PO Box 118440, Gainesville,
FL 32611-8440, USA

E-mail: andraka@phys.ufl.edu

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Abstract

The specific heat, and dc and ac magnetic susceptibility are reported for a large single crystal of $PrOs_4Sb_{12}$ and, after grinding, its powder. The physical properties of the crystal are typical of the majority of reported $PrOs_4Sb_{12}$ samples. The room temperature effective paramagnetic moment of the crystal was consistent with the Pr^{3+} ionic configuration and full (or nearly full) occupancy of the Pr sublattice. The crystal showed two distinct anomalies in the specific heat and an overall discontinuity in C/T of approximately 1000 mJ K^{-2} mol^{-1}. The upper transition (at T_{c1}) was characteristically rounded. The anomaly at T_{c2} was very sharp, consistent with a good quality for the crystal. We observed a shoulder in χ' and two peaks in χ'' below T_{c1}. However, there were no signatures in χ' of the lower temperature transition. Grinding to powder size smaller than 50 μm completely suppresses the upper superconducting transition in both the specific heat and magnetic susceptibility. It also strongly reduces $\Delta C/T_c$ at T_{c2}. Stress annealing brings back some of this lost $\Delta C/T_c$ but does not restore the upper temperature transition. Possible explanations of the existence of two superconducting specific heat anomalies for single crystals are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$PrOs_4Sb_{12}$ is the first discovered Pr based heavy fermion superconductor [1] that attracts widespread attention on account of several anomalous properties. These anomalies include a multiplicity of ground states and transitions and unusual signatures of these transitions. Most of the reported samples exhibited two superconducting transitions [2–8] accompanied by huge discontinuities in the specific heat and a slow, sometimes two step-like, drop in the magnetic susceptibility as a function of temperature below T_c. The last feature would lead one to suspect that the appearance of coherence in this system is inhomogeneous, i.e. the flux expulsion takes place in a non-uniform manner. Measson *et al* [6] have reported a decrease in the ratio of the specific heat discontinuities at the upper and lower transitions in a sample that was reduced to a size of 120 μm by polishing, arguing further in support of inhomogeneous ground states. It has been suggested that the upper transition may be associated with Pr deficient regions near a surface.

To understand these anomalies further, we report here results on a single crystal that has been first measured for its properties, such as specific heat, ac and dc magnetic susceptibility, and then, for comparison, ground to dimensions of order of 10–50 μm and measured again. We find unusually strong effects of the grinding on superconducting anomalies as well as the normal state specific heat.

2. Single crystal

The investigated crystal (≈20 mg) had almost perfect cubic shape with all six faces smooth and regular. It was obtained by slow, 1 °C h^{-1}, cooling of $PrOs_4Sb_{20}$ (the 'self-flux' method). Before presenting the superconducting characteristics of the crystal we discuss its magnetic susceptibility measured in a Quantum Design squid magnetometer between 1.8 and 350 K. The measurement was performed using a configuration[1] to minimize holder contribution to the magnetization, which in the case of small single crystals can be larger than the magnetization of the sample itself. The inset to figure 1 shows the susceptibility (χ) in a field of 0.5 T parallel to

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[1] The crystal was placed between two concentric straws of the same length, which was much larger than the length of an individual scan.

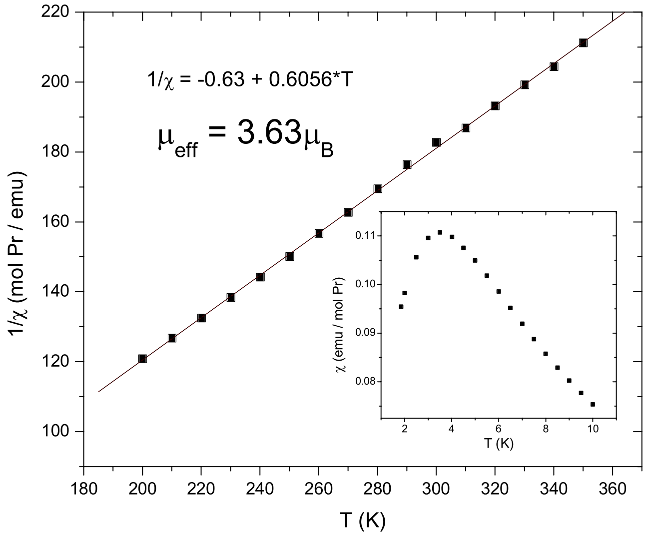

Figure 1. Inverse of magnetic susceptibility versus temperature for the single crystal of $PrOs_4Sb_{12}$. The inset shows low temperature magnetic susceptibility measured in 5 kOe along the (001) direction.

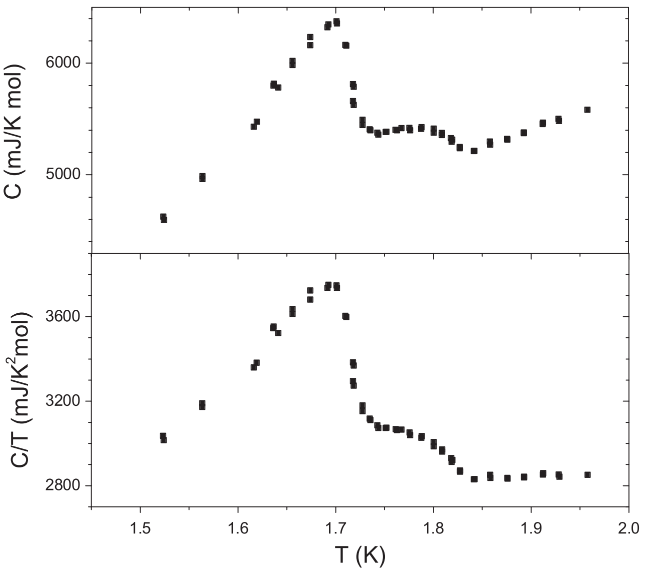

Figure 2. Specific heat (upper panel) and specific heat divided by temperature (lower panel) versus temperature for the single crystal of $PrOs_4Sb_{12}$.

the (001) crystallographic direction. The susceptibility has a low temperature maximum of 112 memu mol^{-1} at 3.5 K. The paramagnetic effective moment, obtained from the straight line fit of $1/\chi$ versus T (temperature) between 200 and 350 K, is 3.63 μ_B/Pr (figure 1). This fit yields a very small, approximately 1 K, positive Curie–Weiss temperature. A similar fit performed for the data between 150 and 300 K yields an effective moment of 3.65 μ_B/Pr and a negative Curie–Weiss temperature of 3 K. The small absolute value of the derived Curie–Weiss temperatures indicates that Pr moments are essentially non-interacting with each other at these high temperatures. These high temperature effective moments are only slightly larger than the theoretical value for free trivalent Pr of 3.58 μ_B. Considering this (weak) variation of the measured moment with fitting range, we might expect that at temperatures much higher than the overall crystal field splitting (210 K) the measured value would be even closer to the theoretical one. At this point we stress that susceptibility measurements on all our single crystals with mass of at least 5 mg resulted in almost identical values of the high temperature effective moment. This is in disagreement with most of the published magnetic susceptibility results [1, 2, 8] by other research groups implying much smaller μ_{eff}, a large concentration of Pr vacancies or inclusions of Sb flux. The susceptibility results suggest that the Pr occupancy of our crystal is close to 1.

The specific heat data between 1.45 and 2 K are shown in figure 2. Our crystal exhibits a clear separation of the anomalies in the specific heat (upper panel). The onset of the first superconducting transition is at ≈1.85 K (T_{c1}). C has a broad maximum near 1.79 K. The onset of the second transition is at ≈1.74 K (T_{c2}) and C (C/T) has a maximum at 1.7 K. As opposed to the upper transition, the anomaly corresponding to T_{c2} is very sharp suggesting good quality of the crystal. During our measurement the specific heat was averaged over at least 2% of T (e.g., over ≈40 mK at 1.8 K). Thus, if not for this averaging procedure (necessary to avoid large scattering) we would expect this transition to be even sharper. This variation of the specific heat near the superconducting transitions is typical of the majority of single crystals studied and reported. C/T reaches a maximum near 1.7 K. The overall $\Delta C/T$, i.e., the difference between C/T at 1.7 and 1.85 K is approximately 1000 mJ K^{-2} mol^{-1}, among the largest ever reported. Application of the conservation of entropy construction (which is not straightforward and carries large uncertainty in the case of two close transitions) would probably increase this value. The height of the first anomaly in C/T is roughly 1/2 of the anomaly at T_{c2}. Thus, both transitions are clearly bulk-type. In the inhomogeneous scenario, they would imply large and comparable fractions of the crystal undergoing superconducting transitions at two different temperatures.

The ac susceptibility measurement performed on the same crystal is shown in figure 3. The upper panel is the real part of the ac susceptibility (χ'), the lower panel is the imaginary part (χ''). The temperature variation of the real part of the susceptibility in a typical superconductor is step-like due to a transition from a full penetration of the ac field at higher temperatures to a perfect screening of this field below T_c. The imaginary part is due to dissipation associated with flux motion. The onset of the superconducting transition is approximately at 1.85 K according to χ'. This corresponds well to the onset of the bulk transition in either C or C/T shown in figure 2. χ' versus T exhibits a shoulder near 1.8 K. Such a shoulder could be due to a superposition of two steps related to two superconducting transitions. However, this possible lower temperature step takes place near 1.8 K, thus at a temperature higher than the onset of the lower superconducting transition in C. A similar shoulder at 1.8 K (and an additional step at lower temperatures) can be seen for one of the crystals (n1b) reported in [7]. According to our χ' data, the transition

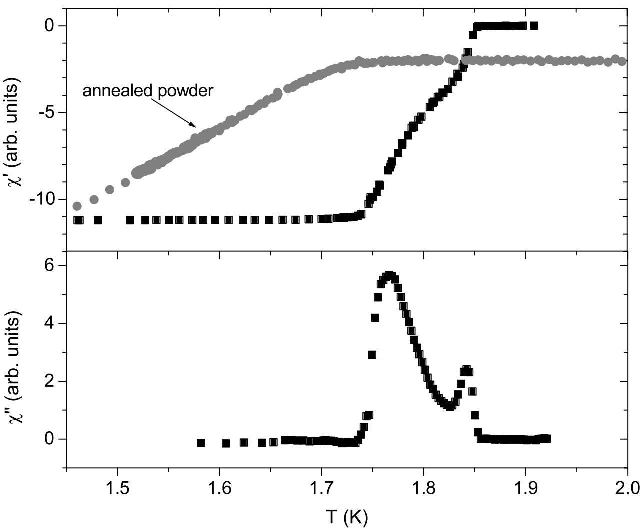

Figure 3. Real (upper panel) and imaginary (lower panel) parts of the ac susceptibility (263 Hz) for the single crystal of $PrOs_4Sb_{12}$. The upper panel shows also χ' versus T for the 24 h annealed powder. See text for details.

is essentially complete at 1.73 K, which is approximately the onset of the lower superconducting transition in C (C/T). Therefore, we have examined the dissipative part of the ac susceptibility. Interestingly, our crystal showed two peaks in χ'', at 1.84 and 1.77 K. Again, there is no structure in χ'' below 1.73 K, corresponding to the lower superconducting transition in the specific heat.

To our knowledge, there were no other reports of two peaks in χ'' in $PrOs_4Sb_{12}$. However, the measurement by Drobnik *et al* [9] hints at two structures in χ'' versus T at 1.78 and 1.83 K (inset to figure 2 of [9]). The two-peak effect in χ'' has been previously observed in some (high temperature) granular superconductors [10, 11]. In particular, both χ' and χ'' are highly reminiscent of these properties for granular $YBa_2Cu_3O_{7-x}$ measured in zero dc field [11]. In both materials the temperatures of the peaks in χ'' correspond to the steepest decrease in χ'. In the granular superconductivity scenario, the higher temperature peak would be due to losses associated with London field penetration (intrinsic peak) while the lower temperature peak would be due to losses associated with flux penetrating the grain boundaries (intergranular or coupling peak). Another single crystal of $PrOs_4Sb_{12}$ (also approximately 20 mg), showing a two-peak effect in the ac susceptibility, was investigated as a function of frequency between 86 and 3000 Hz. No change in temperatures of these two peaks was detected. In the case of aforementioned $YBa_2Cu_3O_{7-x}$ no frequency variation was observed for the upper temperature peak, while the lower temperature peak increased with the increase of temperature. Thus, the granular superconductivity explanation for $PrOs_4Sb_{12}$ is somewhat unlikely but cannot be discarded either. The χ'' peaks in granular superconductors are much more sensitive to the strength of the superimposed dc magnetic field. Therefore, a new study of χ'' as a function of the strength of magnetic field, between 0 and 0.1 T is needed.

The separation of these two peaks in the ac susceptibility is 70 ± 10 mK, smaller than the difference of T_{c1} and T_{c2} defined by the onset of the anomalies in the specific heat. It is interesting that we do not observe a step in χ' associated with the very sharp peak in C/T at T_{c2}. Recall that the crystal investigated by Cichorek *et al* [4] also did not show any signature of the lower superconducting transition in the ac susceptibility. Obviously, this can be explained by the shielding effect of the regions becoming superconducting at higher temperature, i.e., at T_{c1}. The results of Measson *et al* [6] suggest that the material near the surface of formed single crystals might have a larger T_c than the interior of the crystal.

3. Powder

In order to break the connectivity of possibly higher T_c material near the surface of the crystal, we powdered our $PrOs_4Sb_{12}$ crystal. The powdering was done in an agate mortar to avoid any magnetic contamination. This powder was examined under a optical microscope. Most of the grains were smaller than 50 μm across, with a typical size of 10–20 μm. Thus, these grains are larger by a factor of 1000 than the superconducting coherence length (170 Å) [1]. Most of this powder was subsequently pressed into a 1/8 inch pellet. A very small amount of the (unpressed) powder was mixed with GE varnish and attached to a copper screw for the ac susceptibility measurement. For comparison, we have also powdered the $LaOs_4Sb_{12}$ crystal using identical procedure to that for $PrOs_4Sb_{12}$. This powder was also pressed into a 1/8 inch pellet.

We have observed small effects of the powdering on the dc magnetic susceptibility of $PrOs_4Sb_{12}$. The low temperature maximum shifts by about 0.5 K (not shown) to a lower temperature and becomes somewhat more rounded. The susceptibility values below 10 K were comparable to those for the crystal. We have not attempted to extract the high temperature effective moment, since a powder holder, with a relatively large magnetization at room temperature, was used.

There is a profound effect of grinding on the specific heat of both superconducting and normal states of $PrOs_4Sb_{12}$. We discuss the normal state, i.e., above 1.85 K, specific heat first. In figure 4 we compare the f-electron C/T (obtained by subtracting normal electrons and phonons contributions using the data for crystalline $LaOs_4Sb_{12}$ [5]), between 0.4 and 4 K, of the powder and a crystal. Identical phonon contribution was assumed for the crystal and powder, which was justified by measurements on powdered $LaOs_4Sb_{12}$, discussed below. (Since the original crystal that was powdered was investigated to 2 K only, the figure shows data for another similar crystal.) C/T at 1.95 K (just above T_{c1}) is reduced from over 2800 mJ K^{-2} mol^{-1} for the crystal to 2070 mJ K^{-2} mol^{-1} for the powder. This observation agrees with the results of Measson *et al* [6], who have found a direct correlation between the quality of samples, as measured by the residual resistivity ratio (RRR), and C/T values just above T_c. The specific heat above T_c is believed to be due to the CEF Schottky anomaly, modified by hybridization effects. The CEF scheme has been established by various experimental

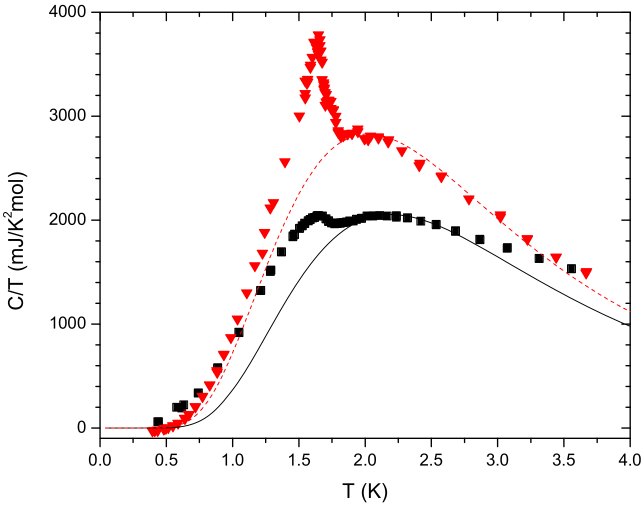

Figure 4. f-electron specific heat of a single crystal (triangles) and powdered (squares) $PrOs_4Sb_{12}$ between 0.4 and 4 K. Non-f-electron contributions were accounted for using the normal state specific heat data of $LaOs_4Sb_{12}$. The solid line represents a Schottky specific heat, corresponding to the system with a singlet ground state separated from the excited doublet by 7.8 K, multiplied by 0.59. The dash line represents a Schottky specific heat, corresponding to the system with a singlet ground state separated from the excited doublet by 7.2 K, multiplied by 0.75.

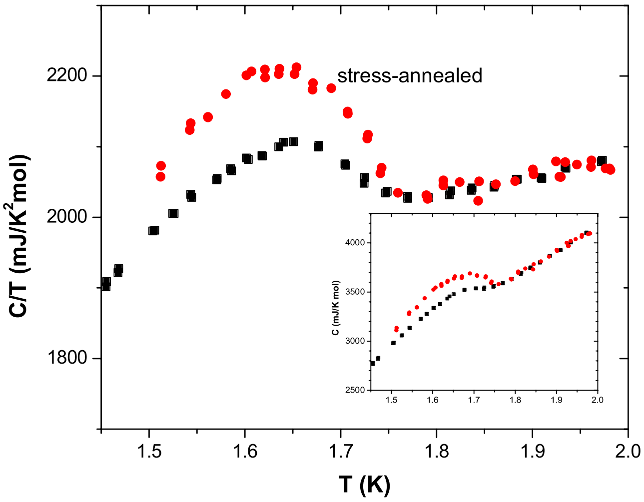

Figure 5. Specific heat divided by temperature versus temperature for the unannealed (squares) and stress-annealed (circles) powder of $PrOs_4Sb_{12}$. The inset shows the specific heat for the powder of $PrOs_4Sb_{12}$.

techniques, including inelastic neutron scattering [14]. C/T values at 2.2 K for the crystal and powder are lower than that expected for the Schottky maximum by ≈25 and 41%, respectively. Furthermore, this experimental maximum for the powder is considerably wider than that for the theoretical Schottky anomaly multiplied by a factor of 0.59 (in order to match C/T values at the maximum).

There is only a single superconducting specific heat anomaly in the powdered material of $PrOs_4Sb_{12}$ (figure 5). The onset of the broad transition is at approximately 1.75 K, thus coincides with the onset (and T_{c2}) of the lower temperature transition in the crystal. $\Delta C/T$ obtained by the conservation of entropy construction is 140 mJ K^{-2} mol^{-1} (as compared to 1000 mJ K^{-2} mol^{-1} for the crystal). We do not observe any signature corresponding to T_{c1}. The ac susceptibility measurement performed on loose powder did not find any signature of the upper temperature transition either, besides a broad transition with an onset at T_{c2}.

The pressed pellet of $PrOs_4Sb_{12}$ was subsequently annealed at 600 °C, initially for 24 h, then for an additional week, and then for 4 weeks more. Specific heat measurements were performed after each annealing. The results of the 24 h annealing are presented in figure 5 (dots). This annealing restored part of the specific heat anomaly at T_{c2}, lost during the powdering of the crystal. $\Delta C/T$ obtained by the conservation of entropy construction increased to ≈300 mJ K^{-2} mol^{-1}. Additional annealing for a week did not change specific heat. Annealing for a month resulted in some small but noticeable reduction of the anomaly with respect to that for the 24 h annealing. Most likely, this long-time annealing results in appreciable loss of Sb affecting the size of the specific heat anomaly at T_{c2}.

The annealed for a week pellet was also reexamined by ac susceptibility. χ' versus T is shown in the upper panel of figure 3. The data were obtained on a slow cooling of the powder. The onset of the superconducting transition is at T_{c2} and the transition is broad. χ' starts to saturate somewhere between 0.4 and 0.5 K. There is no indication of superconductivity at T_{c1}.

Interestingly, specific heat measurements, up to 2 K, on a $LaOs_4Sb_{12}$ crystal and a pellet pressed from its powder yielded essentially identical results. Powdering did not affect T_c nor C/T values in the normal state. The specific heat discontinuity at T_c for the powder was as sharp as for the crystal. There was only a slight (15%) reduction of the value of ΔC at T_c for the pressed pellet.

4. Discussion

One of the most interesting observations for the single crystal is an apparent disconnection between various characteristics of the specific heat and ac susceptibility. The specific heat exhibits a very sharp peak at T_{c2}, suggesting a high quality of the crystal, but a rounded anomaly at T_{c1}. The consensus is that the higher temperature feature is related to inhomogeneous superconductivity [6, 7, 13, 15], due to a distribution of T_cs. This distribution can be the result of varying Pr stoichiometry. However, χ'' has a very sharp peak in low excitation fields at a specific temperature of 1.84 K (this temperature does not seem to be crystal-dependent either) suggesting a lack of a significant distribution of T_{c1}. χ' has a shoulder at 1.8 K, i.e. at too high temperature to be associated with the lower temperature superconducting transition. The temperature variation of χ' is very similar to the change of the penetration depth near T_c measured by Chia *et al* [12]. Obviously, the two properties are closely related. The penetration depth also has a shoulder at 1.8 K, which is at a significantly higher temperature than T_{c2}. The origin of this shoulder in both properties, confirmed by us on other large crystals by ac susceptibility and seen in other published results [7], is unknown.

Summarizing, we report several new characteristics of superconductivity in $PrOs_4Sb_{12}$. Both superconducting anomalies are very sensitive to structural defects produced by grinding. Furthermore, the anomaly at T_{c1} is clearly more sensitive to defects than the anomaly at T_{c2}. Contrary to this behavior, $LaOs_4Sb_{12}$, a non-f-analogue of $PrOs_4Sb_{12}$, shows negligible response to similar defects. Thus, this strong sensitivity to structural imperfections might be a new signature of unconventional superconductivity in $PrOs_4Sb_{12}$. The imaginary part of the ac susceptibility for all investigated crystals shows two peaks, somewhat reminiscent of χ'' of granular superconductors. However, lack of detectable frequency dependence of the temperatures of these peaks is inconsistent with granular superconductivity and this explanation has to be discarded at least for now.

The origin of multiple superconducting transitions in $PrOs_4Sb_{12}$ remains an important puzzle. Nevertheless, this study allows us to comment on possible explanations suggested by previous investigations. First, it is unlikely that the anomaly at T_{c1} is due to a minority phase. Powdering has the advantage over polishing or slicing that does not discard any material. Thus, if the secondary phase was present in the crystal it should also exist in the powdered sample. Second, the results disagree with the possibility of the anomaly at T_{c1} due to Pr vacancies. Again, powdering is not likely to improve the quality of material and reduce the concentration of vacancies. Third, the anomaly at T_{c1} does not seem to be related to any kind of defects near the surface. Powdering strongly increases the ratio of surface to volume and thus would rather promote such defects.

Finally, one should be aware that there are significant differences between presented results and earlier data obtained on a pressed pellet [2, 16]. Maple *et al* performed measurements on a pellet formed by pressing a collection of single crystals with a wide range of sizes. Thus, the presence of larger crystals in the pellet and less material damage can account for the higher temperature onset of superconductivity and smaller suppression of the low temperature specific heat (with respect to a single crystal) in these previous reports.

Acknowledgments

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