Low-temperature anomalies in the specific heat of $PrOs_4Sb_{12}$

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The electronic specific heat of $PrOs_4Sb_{12}$ was measured on different single crystals at temperatures down to 40 mK using a relaxation method. All investigated crystals exhibited a broad shoulder in specific heat near 0.4 K. This anomaly seems to be related to that found previously in Sb nuclear quadrupolar resonance study and possibly in lower critical-field and penetration-depth measurements. The onset of the specific-heat anomaly shows no response to magnetic fields as large as 0.2 T. These results imply a modification of superconducting properties (and normal-state properties) rather than appearance of a new superconducting phase at low temperatures. Our measurement detects low-temperature nuclear specific heat, which we suggest might be due to nuclear quadrupolar specific heat of Pr atoms, frozen in off-center positions.

I. INTRODUCTION

The ground state of the first Pr-based heavy-fermion superconductor,[1] $PrOs_4Sb_{12}$, is poorly understood. Different measurements provide conflicting insights into its state below 1 K. The heavy fermion behavior has been established by the specific heat above 1 K. The measured discontinuity[1–6] in C/T at T_c (1.85 K) is 500–700 mJ/K^2 mol, implying the electronic specific-heat coefficient to be of order 500 mJ/K^2 mol. However, the enhancement of cyclotron mass, as measured by the de Haas–van Alphen technique below 400 mK, is small,[7] typical of transition metals. For instance, the cyclotron mass in the isostructural heavy fermion, also Pr-based,[8] material $PrFe_4P_{12}$ is an order of magnitude larger than that in $PrOs_4Sb_{12}$, and consistent with specific-heat values.

There was a suggestion that different temperature regimes of these measurements might be responsible for the discrepancies.[7] Thus, the heavy-fermion behavior in $PrOs_4Sb_{12}$ might be restricted to a temperature window near T_c, which is of order of the lowest crystalline electric field energy[9] of Pr in this compound (8 K). There are no indications of the heavy fermion state above 10 K. Electrical resistivity,[10] one of the characteristic properties of heavy fermions, above 8 K and up to 45 K, has a quadratic variation on temperature, $\rho = \rho_0 + AT^2$, with the coefficient A indicating no or negligible mass enhancement.[2] The limit of $d\rho/dT^2$ at $T=0$, in overcritical fields (>2 T), has a small value, again consistent with an ordinary metal. At intermediate temperatures,[11] for T^2 between 0.2 and 0.6 K^2, ρ is proportional to T^2, with a slope consistent with heavy electrons. At ≈ 0.4–0.5 K, there seems to be a crossover between these variations in the resistivity.

There are several reported and unexplained anomalies in various physical properties at temperatures 0.4–0.7 K, which might be signatures of a phase transition or a crossover behavior. There is a pronounced enhancement[5] of the lower critical magnetic field below 0.6–0.7 K. The London penetration depth[12] rapidly decreases below 0.6 K. The Sb nuclear quadrupole resonance (NQR) spin-lattice relaxation rate (T_1^{-1}) has a minimum[13] at 0.4 K. More recent Sb-NQR study[14] found also anomalous behavior near and below 0.4 K although with a different saturation value of T_1^{-1} at lowest temperatures. Because of these discrepancies, and also lack of any evidence of a corresponding transition in the specific heat, extrinsic origin of these low-temperature anomalies is suspected. Here we report specific-heat results, which provide additional support for the existence of the transition or a crossover behavior in $PrOs_4Sb_{12}$ at ≈ 0.4 K.

II. EXPERIMENTAL AND RESULTS

We have performed low-temperature specific-heat measurements of this compound using the relaxation technique. Most of the previous low-temperature (<1 K) measurements[15–17] were by adiabatic or semiadiabatic methods. It is not clear whether particularly strong discrepancies below 0.6 K, by a factor larger than ten, are due to systematic errors related to the measurement techniques or due to sample variation. Normally, the adiabatic method detects the total specific heat consisting of both electronic and nuclear components at low temperatures. The nuclear component in $PrOs_4Sb_{12}$ in zero field is due to a large nuclear quadrupolar moment of Sb. It grows rapidly with decreasing temperature, eventually dominating the total heat capacity. The nuclear specific heat is expected[13,15] to be tenfold the electronic one at 80 mK. Moreover, this nuclear contribution is weakly coupled with electrons, resulting in both long measurement times and large uncertainty. However, this weak coupling can be advantageous when using the relaxation method of the heat capacity; it may be employed to find the electronic contribution to specific heat directly.

When discussing any low-temperature measurements of $PrOs_4Sb_{12}$, it is important to keep in mind that this material shows unexplained yet significant, sample-dependent variation in its superconducting properties. These discrepancies are particularly striking in the specific-heat data near the superconducting transition. A majority of the reported results reveal two superconducting transitions,[2–6,17] a broad peak

with a high-temperature onset at 1.86 K (T_{c1}) and a sharp discontinuity at 1.7 K (T_{c2}). Typically, there are two corresponding structures in ac susceptibility. An incomplete flux repulsion starts at T_{c1}, followed by a step at T_{c2}. There is no consensus as to whether both transitions are intrinsic, i.e., if they correspond to stoichiometric $PrOs_4Sb_{12}$ and take place simultaneously. The broadness of the upper temperature transition argues for the hypothesis that inhomogeneous superconductivity is responsible for T_{c1}. The inhomogeneous scenario is also consistent with the fact that the two specific-heat anomalies are sample dependent. At least two groups have reported the existence of crystals with a single transition[16,18] at T_{c2}. On the other hand, it is puzzling that most of the published values of T_{c1} and T_{c2} agree well if the inhomogeneous model is valid. We report on low-temperature specific-heat measurements of two types of crystals with different specific-heat behavior near T_c.

Single crystals were grown by the Sb-self-flux method. In order to avoid possible formation of multiple crystallographic phases, the temperature window of crystal growth was narrowed to between 870 and 810 °C from the previously used 950–650 °C range. Nevertheless, most of our crystals exhibited two superconducting anomalies in the specific heat; these anomalies were crystal dependent, even within a single batch. Because of the low temperatures of the measurement and anticipated smallness of the measured heat capacity, special attention was paid to mounting samples, to avoid the so-called τ_2 effect.[19] The crystals for very low-temperature investigations (down to 50 mK) were polished to less than 1/2 mm thickness, embedded in silver epoxy and attached to relatively large and smooth sapphire disks of 5 mm diameter. These disks were mounted on a calorimeter, whose main part was another 5 mm sapphire disk, with highly conductive thermal grease.[20] This mounting method was used in the past and no τ_2 effect was observed.

We present results for three crystals, crystal 1 with a mass of 0.8 mg, 2 of 2.2 mg, and 3 of 40 mg. Crystal 3 was investigated at temperatures down to 0.37 K but its specific heat and magnetic susceptibility near and just below T_c were almost identical to those for crystal 1. Therefore, we shall initially focus on the first two crystals. A plot of specific heat divided by temperature versus temperature (C/T versus T) between 1.4 and 2 K is shown in Fig. 1. Crystal 1 (and, likewise, 3) exhibits a typical variation in C/T: a broad anomaly starting at T_{c1} is followed by a discontinuity at T_{c2}. The ac-susceptibility measurements (not shown) reveal a two-step superconducting structure. Crystal 2 (lower panel of Fig. 1) has somewhat unique properties in the context of previously published results. The ac susceptibility has a single step at T_{c1}. Since ac susceptibility reveals diamagnetic shielding behavior, the presence of a single step is not an evidence for a single transition but it is a consistent single transition. C/T is discontinuous at T_{c1}. This is clearly seen in the relaxation heat capacity. Temperature decays (logarithm of change in temperature versus time) over a small temperature interval had an abrupt change in slope at T_{c1}. Thus, the anomaly at T_{c1} is due to a second-order phase transition. However, roundness of C/T below T_{c1} is most likely indicative of still considerable degree of inhomegeneity. It is also interesting to note that the overall discontinuity in C/T, as
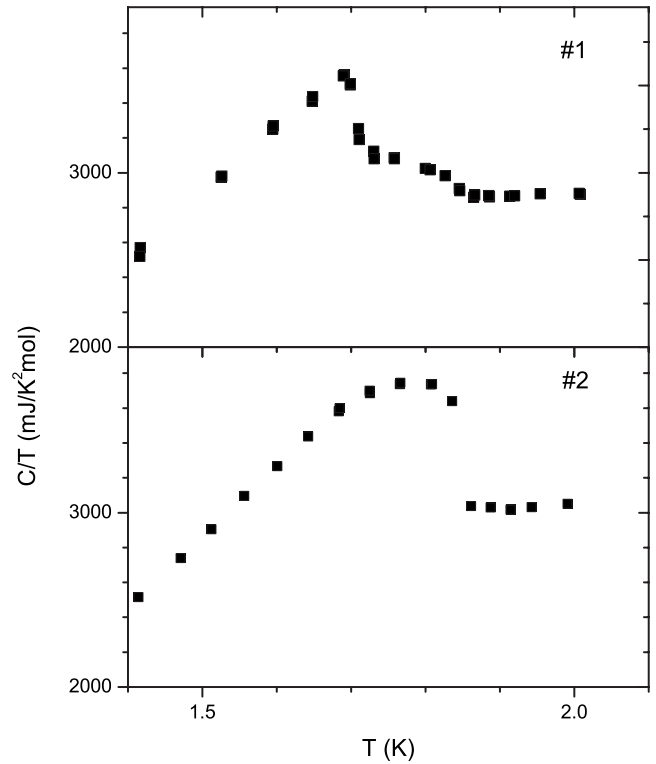

FIG. 1. C/T of two $PrOs_4Sb_{12}$ crystals near T_c.

defined by the difference between the maximal value of C/T in this temperature range (1.4–2 K) and its value at 1.9 K, is identical for both samples (about 700 ± 40 mJ/K^2 mol). The overall C/T discontinuity for all recently measured slowly grown single crystals, using consistent method of extracting data, amounted to the same value, despite different ratios of individual discontinuities at T_{c1} and T_{c2}. These results suggest that the two superconducting transitions are indeed due to two different phases of $PrOs_4Sb_{12}$; they will be named "type 1" with the superconducting transition at T_{c1} and "type 2" with the transition at T_{c2}. These phases have similar C/T discontinuities (at T_{c1} and T_{c2}, respectively) of approximately 700 mJ/K^2 mol, and therefore we expect a similar mass enhancement. We have searched for possible structural differences between crystals 1 and 2 using a microprobe technique. We have obtained a slightly larger Pr-filling fraction for crystal 1 of 0.99 versus 0.98 for crystal 2. However, the differences were within the error bars of 0.02, thus most likely insignificant.

The nuclear heat capacity of Sb in $PrOs_4Sb_{12}$ is important below 1 K. In the past we have proposed the method of measuring heat capacity using relaxation calorimetry for the case of a significant nuclear contribution.[21] In general, the relaxation is nonexponential in time requiring fits to complicated functions. This nonexponential dependence is due to an additional time scale, T_1 (spin-lattice relaxation time), characterizing the coupling between electrons and nuclei. There are two naturally occurring Sb isotopes, ^{121}Sb and ^{123}Sb, which exist in almost equal abundance. NQR measurements indicate that the spin-lattice relaxation times of ^{123}Sb and ^{121}Sb are approximately 100 and 30 s, respectively, at 0.3 K, thus two orders of magnitude larger than the expected relax-
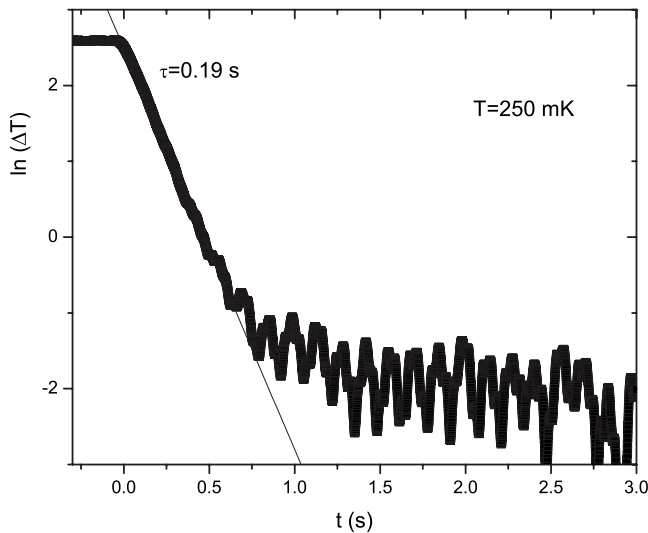
FIG. 2. A typical decay of temperature at low temperatures. The specific heat shown in Fig. 3 was calculated using the time constant τ characterizing the initial decay of temperature.

FIG. 3. Low-temperature electronic specific heat of two PrOs$_4$Sb$_{12}$ crystals. The inset in the upper panel shows the specific heat of crystal 1 up to 2 K.

ation times of electrons at this temperature (≈ 0.2 s). Therefore, one does not expect any nuclear contribution to the measured heat capacity in zero field.

Nevertheless all relaxation curves below 0.7 K showed two different time scales. An exemplary decay is shown in Fig. 2. The initial "fast" decay of temperature, is followed by a "slow" decay. Throughout the rest of the discussion, τ is defined as a time constant corresponding to the initial (fast) part of the decay as illustrated in Fig. 2. τ for crystals 1 and 2 was in the range 0.15–0.4 s, for all temperatures. Time constants characterizing the slow part of decays were 2–5 s. This is an unexpected result suggesting additional degrees of freedom besides electrons and nuclear quadrupoles of Sb contributing to low-temperature specific heat. In superconductors, the nuclear component of heat capacity is rarely seen even using adiabatic (slow) techniques.[22] This is because the nuclear relaxation is due to spin-flip processes involving nuclei and electrons, which is suppressed in superconductors with an energy gap. Nevertheless, the slow temperature decays can be only explained by nuclei. These nuclei nay not be Sb with their large T_1.

Providing there is no the so-called τ_2 effect, the initial rate of a temperature decay always corresponds to electronic heat capacity[21] (we neglect here unimportant at low-temperatures phonons). Only if the spin-lattice relaxation time $T_1=0$, which is unphysical, the initial rate reflects the total heat capacity, i.e., electronic and nuclear. In practice, observation of the decay due to electrons only requires good separation of relevant time scales.

In our measurements, there was always at least an order of magnitude difference between the time constant characterizing the initial part of decays (τ) and time constants describing the tail. We have approximated the electronic specific heat from τ, neglecting the tail (Fig. 2). A similar method was used previously by Collan *et al.*[23] to measure the specific heat of bismuth at temperatures below 0.8 K. This way extracted low-temperature nonnuclear specific heat, the pri-
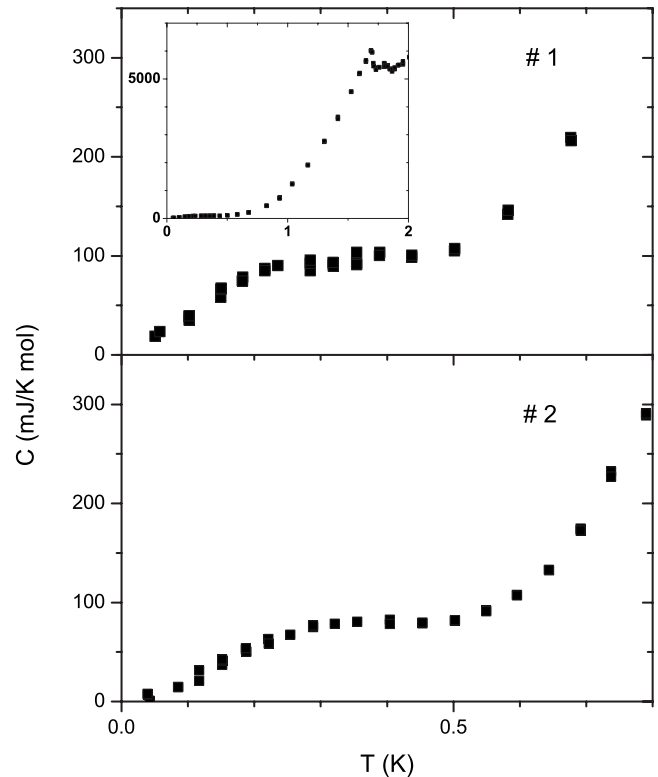
mary focus of this investigation, is shown in Fig. 3. Note that neglecting the tail leads to relatively small systematic errors (of order 1%) of the electronic heat capacity.[24] Nevertheless, there is still significant uncertainty in the data shown in Fig. 3 below 0.6 K due to other contributions, such as addenda and difficulty with measuring short time constants. Specific heat of all components of the addenda, including silver epoxy [H31LV (Ref. 25)] and sapphire, were measured in separate investigations using sufficient amounts of these components. At low temperatures, heat capacity of H31LV is due to Ag and is linear in temperature. Below 0.6 K, addenda amounted to about 35% of the total measured electronic heat capacity for crystal 1. We estimate the absolute error to be smaller than 50% of the measured specific-heat values at all temperatures. The possible error has no significant temperature variation.

Since the systematic error depends on the size of the crystal, we have looked for possible discrepancies between crystals with different masses. Both crystals, 1 and 2 (lower panel of Fig. 3) measured down to 40 mK exhibit a shoulder or a broad maximum in the specific heat near 0.4 K. This structure is very weak compared to the Schottky or superconducting anomaly (inset to Fig. 3). The entropy associated with this structure is somewhere between 100–400 mJ/K mol. The large uncertainty is due to the aforementioned uncertainty in the low-temperature specific heat but also because of an unknown temperature variation in the specific heat in the superconducting state. Such a small value of entropy might suggest extrinsic (impurity phase) origin of the
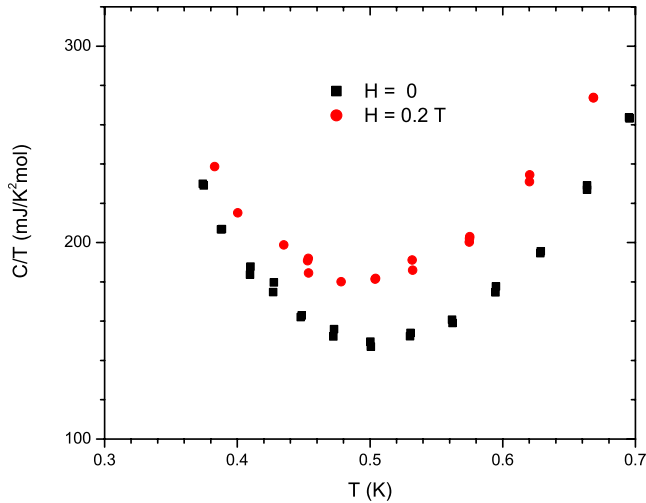
FIG. 4. (Color online) C/T versus T for crystal 3 in $H=0$ and 0.2 T.

feature. However, the total entropy of a superconductor deep in the superconducting state is small.

In Fig. 4 we present C/T for crystal 3 (40 mg) between 0.37 and 0.7 K, measured in a different calorimeter than crystals 1 and 2. In this case, the measured temperature-decay-time constants were much larger, $\tau \approx 7$ s at the lowest temperature, thus comparable to both T_1 of ^{121}Sb and the time constant of the slow component seen for crystals 1 and 2. As opposed to small crystals, relaxations were exponential in time down to the lowest temperature. Therefore, we expect the specific-heat values shown in Fig. 4 to include also a fraction of hyperfine contribution (at least due to ^{121}Sb and unknown nuclear component). We have also modeled thermal relaxations assuming a hyperfine contribution and fairly large range of T_1/τ values, where τ is the time constant of the decay without hyperfine contribution. The theoretical decays are quasiexponential, described by a time constant in the range of τ and $\tau + c_N/\kappa$, where c_N is the hyperfine heat capacity and κ is the weak link conductance. The quadrupolar nuclear specific heat depends on the product of the quadrupolar moment and electric field gradient at the nucleus. This product was measured directly by Sb NQR.[13] Accordingly, the total quadrupolar nuclear specific heat of both isotopes of Sb can be expressed as $C_N = A/T^2$, where $A \approx 0.84$ mJ K/mol. The measured rise of C/T by approximately 80 mJ/K^2 mol between 0.5 and 0.37 K is eightfold that expected from the nuclear contribution of both nuclei of Sb and, as argued above, cannot be explained by systematical errors of the measurement technique.

We have observed anomalous thermal relaxation (the slow component in Fig. 2) for other previously investigated crystals of PrOs$_4$Sb$_{12}$ below 0.5 K. On the other hand we were not able to detect any nuclear component in relaxation curves of LaOs$_4$Sb$_{12}$ crystals, in agreement with large T_1's and small nuclear-heat capacity. The size of LaOs$_4$Sb$_{12}$ crystals used in our measurements ranged from less than 1–40 mg. The Sb-NQR spectrum[26] in LaOs$_4$Sb$_{12}$ is almost identical to that of PrOs$_4$Sb$_{12}$, implying similar hyperfine specific heat in both compounds. Furthermore, since T_1's of Sb in LaOs$_4$Sb$_{12}$ at

temperatures 0.2–1 K are significantly shorter[13] than those for the Pr compound, one should detect the nuclear-heat capacity in the La rather than in the Pr compound. Finally, we stress that the rise of C between 0.6 and 0.4 K and then falloff below 0.3 K cannot be explained by the temperature variation in the coupling between Sb nuclei and electrons (T_1). T_1^{-1} has a shallow minimum at 0.4 K, thus the coupling is the weakest at this temperature.[13] The broad maximum or a shoulder in the specific heat near 0.4 K seems to be an intrinsic electronic property of PrOs$_4$Sb$_{12}$ material.

To further probe the origin of this broad maximum in C, additional measurements were performed under a magnetic field. Such measurements in the case of PrOs$_4$Sb$_{12}$ are difficult to interpret, however. Magnetic fields split and shift low energy-excited crystal-field levels, induce a large nuclear specific heat in Pr, and suppress superconductivity. All these effects, particularly the last two, dominate the specific heat of PrOs$_4$Sb$_{12}$ at fields as low as 1 T. Therefore, in Fig. 4 we present the heat-capacity data for a small field of 0.2 T. These data suggest that the maximum at 0.4 K is rather weakly affected by small or moderate magnetic fields.

This weak low-temperature specific-heat maximum shows up in both predominantly type 1 and type 2 crystals of PrOs$_4$Sb$_{12}$. Figure 4 suggests that the onset of the anomaly occurs at 0.5 K. However, it might actually be happening at a significantly higher temperature, somewhere near 0.7 K. This may be tested by subtracting out the superconducting background and Schottky peak corresponding to crystalline electric field (CEF) excitations of Pr. However, the temperature variation in either of these contributions is unknown. The CEF ground state of isolated Pr ions is a singlet[9] and therefore the formation of a heavy-fermion state requires participation of the excited (triplet) CEF states and modification of the single-to-triplet Schottky anomaly. Interestingly, the specific heat between 0.8 and 1.6 K of all investigated crystals could be well described by the formula $C = A \exp(-B/T)$, with B and C varying slightly from sample to sample. Such a temperature variation is typical of BCS superconductors. The average value of the B coefficient was 4.3 K, or 2.4 T_c, where $T_c = 1.8$ K.

We do not know the origin of the relatively fast nuclear component of the specific heat below 0.6 K. As discussed, it cannot be due to Sb in PrOs$_4$Sb$_{12}$. It could be related to free Sb trapped in the crystals. However, this scenario seems unlikely considering lack of such a component in LaOs$_4$Sb$_{12}$ crystals, at least down to 0.35 K. Structural investigations of our crystals do not find any excess of Sb. Finally, the quadrupolar specific heat of free Sb is small,[27] much smaller than measured C below 0.5 K, shown in Fig. 4. The striking differences between the Pr and La compounds suggest that Pr is most likely responsible for this anomalous behavior. Pr nucleus has small quadrupolar moment[28] and therefore large electric field gradient is required. One does not expect such a large electric field gradient in an essentially cubic site of Pr. However, Pr atoms in PrOs$_4$Sb$_{12}$ are known for their strong rattling in oversized host cages. This rattling is absent at very low temperatures, however Pr atoms can be frozen in off-center positions, with large electric field gradient.[29]

In summary, specific-heat measurements suggest the existence of a low-temperature anomaly, possibly related to pre-

viously found anomalies in the penetration depth, lower critical field, and spin-lattice relaxation times. Thus, unusual physical properties near T_c might not reflect the ground state of $PrOs_4Sb_{12}$. We also detect a slow component in the specific heat, most probably due to hyperfine interactions, which is not present in $LaOs_4Sb_{12}$ and whose origin is unknown. However, it is not due to quadrupolar nuclear moments of Sb.

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