High Magnetic Field Phase Diagram of $PrOs_4Sb_{12}$

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The magnetic phase diagram of $PrOs_4Sb_{12}$ has been investigated by specific heat measurements between 8 and 32 T. A new Schottky anomaly, due to excitations between two lowest crystalline-electric-field (CEF) singlets, has been found for both $H \parallel (100)$ and $H \parallel (110)$ above the field where the field-induced ordered phase (FIOP) is suppressed. The constructed $H - T$ phase diagram shows weak magnetic anisotropy and implies a crossing of the two CEF levels at about 8–9 T for both field directions. These results provide an unambiguous evidence for the Γ_1 singlet being the CEF ground state and suggest the level crossing (involving lowest CEF levels) as the driving mechanism of FIOP.

A recent discovery of superconductivity [1] in $PrOs_4Sb_{12}$ is an important milestone in the field of strongly correlated electrons for a number of reasons. First, a large discontinuity in the specific heat at the superconducting transition temperature T_c unambiguously establishes that Pr-based materials can support heavy fermion (hf) states. Second, proposed crystalline electric field (CEF) schemes suggest nonmagnetic ground states and exclude a conventional Kondo effect, believed to be the source of hf behavior in Ce- and U-based metals. The only other serious microscopic mechanism considered as the origin of the hf behavior is a controversial quadrupolar Kondo effect [2]. Finally, two superconducting transitions observed [3] in this compound imply an anisotropic order parameter. Therefore, $PrOs_4Sb_{12}$ is a candidate for a novel mechanism of superconducting pairing that is due to neither phonons nor magnetic interactions.

Correct interpretations of these new exciting phenomena hinge crucially on the proper accounting for the CEF configuration of Pr. The consensus is that the nonmagnetic (non-Kramers) Γ_3 doublet is the ground state and Γ_5 is the first excited triplet, although available experimental data do not rule out the possibility of the Γ_1 singlet as the ground state. For instance, Frederick and Maple [4] have demonstrated that a model with a doublet ground state describes more closely the electrical resistivity and magnetoresistance than a similar model with a singlet ground state. This conclusion, however, relies on a difficult task of separating several mechanisms contributing to the electron scattering. Specific heat in zero and small magnetic fields, on the other hand, was used to argue for either of the two possible CEF configurations. In particular, the zero-field Schottky-like anomaly at 3.1 K can be related to the Γ_3-Γ_5 model, assuming these two levels are split by 7.5 K, or Γ_1-Γ_5 model with the splitting of 8.4 K. Inelastic neutron scattering measurements [5] yield the

lowest-energy peak at 8 K. Entropy changes in small fields and as a function of temperature were also used to argue for either of the models [1,3,5,6]. The difficulty with interpreting these low-temperature, low field results is related to strong hybridization of 4f and conduction electrons, as evident from the large electronic specific heat coefficient and the size of the discontinuity in the specific heat (C) at T_c. Therefore, we have performed specific heat measurements in high magnetic fields, in which a coupling between conduction and f electrons is expected to be suppressed, to get insight into the CEF configuration of Pr in $PrOs_4Sb_{12}$.

The crystal used in our investigation was from the same batch of high quality samples for which a host of other measurements were reported [6,7]. The specific heat study to 14 T was performed in a superconducting magnet. The measurements above 14 T were carried out in a resistive Bitter magnet. The calorimetry employed the relaxation method, in which a small sample of about 1.5 mg was used to optimize measuring conditions. Figures 1 and 2 show specific heat in fields ranging from 10 to 32 T. The field was applied along the nominal (100) direction. Our estimate of the probable error in the sample alignment is about 5°. All the data presented are after subtracting the phonon background approximated by a Debye temperature (Θ_D) of 165 K (after Vollmer *et al.* [3]). This value of Θ_D is quite controversial. In fact, Bauer *et al.* [1], Aoki *et al.* [6], and Maple *et al.* [5] suggested Θ_D to be 304, 320, and 259 K, respectively. Changing Θ_D to 320 K does not alter the main conclusions of our study, but has some quantitative impact on the results, as discussed further. A relatively high low-temperature limit was chosen to avoid complications associated with a nuclear contribution of Pr. This nuclear contribution is strongly enhanced by coupling with orbital moments of f electrons [8]. The specific heat, at temperatures where the nuclear degrees of freedom
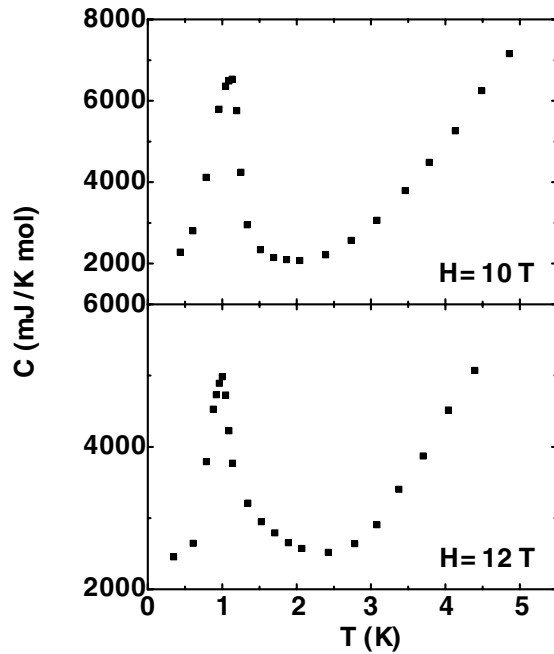
FIG. 1. Specific heat of $PrOs_4Sb_{12}$ in 10 and 12 T in the vicinity of the FIOP transition. The magnetic field was applied along the (100) direction. Phonon contribution was subtracted assuming $\Theta_D = 165$ K.

dominate, is difficult to measure by a conventional relaxation method because of an additional time scale(s) entering the experiment, the nuclear spin-lattice relaxation time T_1 [9]. Strongly nonexponential temperature decays observed at the lowest temperatures (e.g., below 0.5 K in the field of 10 T and below 1.5 K in the field of 32 T) indicate the importance of nuclear degrees of freedom and cannot be analyzed using the so-called τ_2 correction. Therefore, these lowest temperature points carry large uncertainty and are not analyzed in detail.

Figure 1 shows the low-temperature specific heat for 10 and 12 T. Pronounced peaks in the vicinity of 1 K correspond to a transition to a field-induced ordered phase (FIOP), which was first observed by Aoki *et al.* [6] for fields larger than 4 T also applied along the (100) direction. The highest field used in this latter study was 8 T. This long range order was confirmed by other investigations, including the specific heat of Vollmer *et al.* [3] and magnetization study of Tayama *et al.* [10]. It has been proposed that the order parameter corresponding to FIOP is antiferroquadrupolar type. This type of order is consistent with large anomalies in the specific heat and a very small value of the ordered (antiferromagnetic) moment (about $0.025\mu_B$ at 0.25 K and 8 T) [11]. Combining our results with those of Aoki *et al.* [6] and Vollmer *et al.* [3] shows that the transition temperature (T_n) identified as a position of the peak in the specific heat (C) reaches a maximum value somewhere near 9 T. Similarly, $C(T_n)$ has a nonmonotonic field dependence, attaining the highest value between 8 and 10 T. Notice a large reduction of $C(T_n)$ and small but clearly discernible decrease of T_n
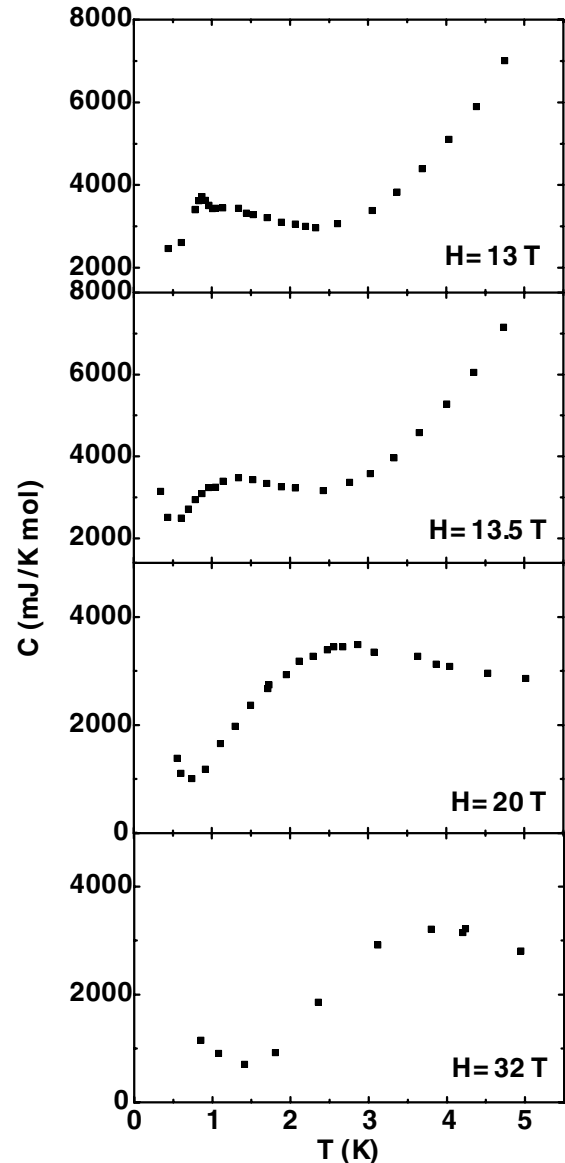
FIG. 2. Specific heat of $PrOs_4Sb_{12}$ in magnetic fields 13, 13.5, 20, and 32 T applied parallel to (100), after phonon subtraction. Notice the appearance of a shoulder at about 1.2–1.3 K at 13 T and the disappearance of the FIOP transition at 13.5 T. The low temperature tails are due to nuclear contribution of Pr.

between 10 and 12 T. It is interesting to note a relatively large discrepancy for C at T_n between all three reports for overlapping fields. This discrepancy is probably due to the anisotropic response of the specific heat in magnetic fields near T_n, discussed below, and some misalignment of the sample with respect to the (100) direction. An increase of the field from 12 to 13 T (Fig. 2) results in a small reduction of T_n and large suppression of $C(T_n)$. Moreover, a shoulder appears on the high temperature side of the FIOP anomaly. The specific heat value at this shoulder is about 3400 mJ/K mol. This shoulder evolves into a broad maximum for a slightly higher field of 13.5 T. Again, the value of C at the maximum is between 3400 and 3500 mJ/K mol. In this field, we no longer detect a

signature corresponding to FIOP. Thus, our results strongly imply a disappearance of FIOP before T_n reaches 0. A similarly broad peak exists at all fields studied up to at least 32 T. The temperature of this broad maximum increases with the field strength (Fig. 2).

The magnitude of the maximum, in fields of 13 T and larger, is essentially field independent and ranges from 3300 to 3500 mJ/K mol. These values are within about 10% of the maximum value for a Schottky anomaly of a two level system with identical degeneracies [12]. The uncertainty of our specific heat measurements in these fields (and at temperatures where nuclear contribution is small) is about 10%. In addition, there is the aforementioned uncertainty associated with a subtraction of the phonon term. Increasing the Debye temperature from 165 K, used in our subtraction, to the other extremal value proposed, 320 K, raises the estimate of the electronic part of C by about 290 mJ/K mol at 3.5 K. Thus, the extracted values at the maximum are well within the realistic error bar of the theoretical 3650 mJ/K mol. Since the 32 T field is large enough to significantly split any degenerate levels, the observed Schottky anomaly has to represent excitations between two singlets. The temperature of the maximum, T_m, is related to the energy separation of the two levels δ, $T_m = 0.417\delta$. An extrapolation of T_m to $T = 0$ (Fig. 3) determines the field at which the two levels cross. Our best estimate of this crossing field, using the lowest fields, is between 8 and 9 T.

These results can be used to infer new information pertaining to a plausible crystal field configuration of Pr. Pr can be modeled by the following single-site Hamiltonian [11]:

$$\mathcal{H} = \mathcal{H}_{CEF} - g_J\mu_B \mathbf{J} \cdot \mathbf{H} - J\langle \mathbf{J'}\rangle \cdot \mathbf{J} - \sum_i Q_i \langle O_i'\rangle O_i,$$

(1)

where $\mathcal{H}_{CEF}$, $\mathbf{J}$, and O_i represent the CEF Hamiltonian for the cubic T_h symmetry, the total angular momentum, and the ith quadrupole moment (see Ref. [11] for detailed definition). Note that the conventionally used $\mathcal{H}_{CEF}$ [1] with the O_h symmetry [13] is only approximate because it ignores the tetrahedral symmetry of Sb ions [14]. This latter CEF Hamiltonian describes the Zeeman effect roughly but cannot account for the neutron diffraction results in the FIOP region [11]. In particular, the lower T_h symmetry is needed to explain the appearance of a small antiferromagnetic moment along the (010) direction, and not along (100), when the field is applied parallel to the (001) direction. [Directions (100) and (010) are not equivalent.] Using the CEF parameters proposed by Kohgi [11] for the Γ_1-Γ_5 CEF configuration, T_m (with $Q_i = 0$) and the O_{yz}-type quadrupolar ordering temperature T_n are calculated [15]. Note that this model consistently reproduces the inelastic neutron data [5], characteristic maxima appearing in the magnetic susceptibility [1,6], and the zero-field specific heat [1,3,6]. The results of our calculations are presented in the inset of Fig. 3.
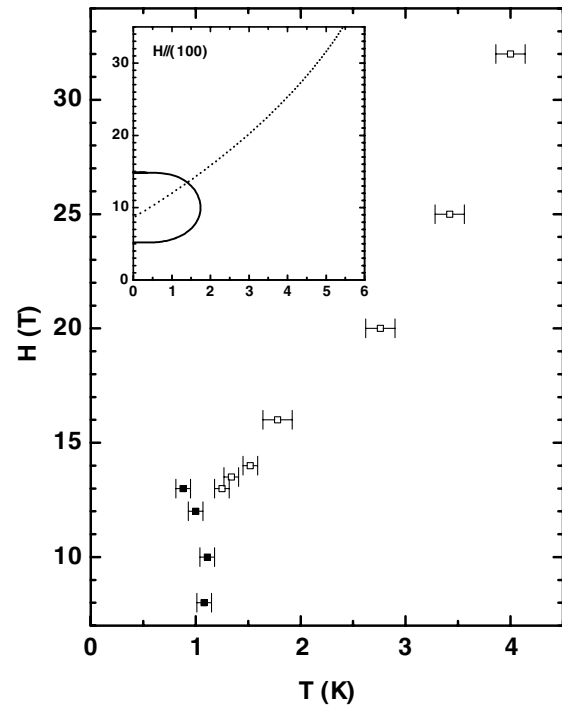
FIG. 3. Magnetic field phase diagram of $PrOs_4Sb_{12}$ for the field parallel to (100). Filled squares represent the FIOP transition. Open squares correspond to the Schottky anomaly. The inset shows a model calculation of the H versus T phase diagram assuming the singlet as the ground state. The solid line represents the FIOP boundary; the dashed line corresponds to a maximum in C ($T_m = 0.417\delta$; δ is the energy separation between the lowest CEF levels). The model Hamiltonian and CEF parameters are identical to those of Ref. [10].

The measured phase diagram (Fig. 3) and the theoretical one expected for the Γ_1-Γ_5 model (inset of Fig. 3) are strikingly similar. In particular, in both diagrams, the crossing field is very close to the one at which the transition temperature of FIOP becomes maximum. Some overestimation of T_n can be attributed to the mean-field nature of the calculations. On the other hand, there is less defined correlation between these two fields in the alternative Γ_3-Γ_5 model. Instead, it has been argued for this latter model that FIOP is related to the crossing of the upper Γ_3 and lower Γ_5 levels [3]. Thus, the observed correlation between the two characteristic fields constitutes our first argument for the Γ_1 singlet being the lowest CEF level.

More conclusive arguments regarding the CEF configuration can be obtained from the study of the anisotropy of the Zeeman effect. The Zeeman effect is expected to be strongly anisotropic for the Γ_3 doublet and almost isotropic for the Γ_1 singlet [10], for the range of CEF parameters that are consistent with the susceptibility [1]. In particular, there is no crossing involving the lowest CEF levels when the field is applied along the (110) direction in the Γ_3-Γ_5 model. We emphasize that this prediction is quite general; it does not depend on whether one uses the CEF Hamiltonians and parameters proposed
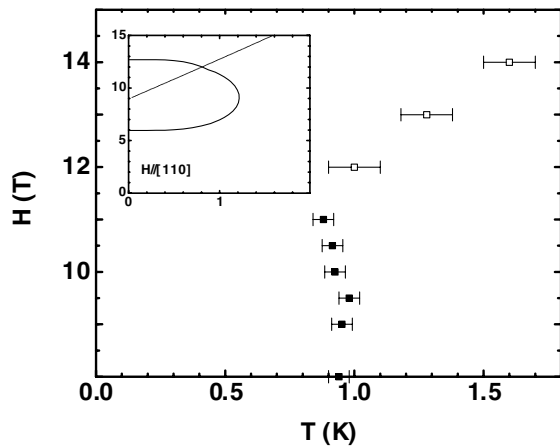
FIG. 4. Magnetic field phase diagram of $PrOs_4Sb_{12}$ for H parallel to (110). For the definition of symbols, see Fig. 3.

by Bauer *et al.* [1] or Kohgi *et al.* [11]. Figure 4 shows the measured high field phase diagram for this field direction. For this direction, we observe a decrease of T_n values with respect to the (100) direction for the corresponding fields, consistent with the previous magnetization measurements [10]. On the other hand, within the uncertainty of the measurement, there is no change in the position of the Schottky anomaly at 13 and 14 T, as expected for the Γ_1 CEF ground state and inconsistent with the Γ_3 scenario. Moreover, for the (110) orientation, we clearly observe the Schottky anomaly already at 12 T. This lower field limit for the Schottky maximum is probably due to competition between the two types of anomalies, discussed below, and lower values of T_n for the (110) direction. A straight line fit for the three T_m points results in the crossing field value of 8.5 ± 0.5 T. This value agrees with our estimate for the (100) direction.

Existence of the crossing field for the (110) direction provides an unambiguous evidence for the Γ_1-Γ_5 model, in fact the strongest evidence until now. We stress that a small misalignment of the sample with respect to the field in either of the measurements cannot explain essentially identical crossing fields for both directions. In fact, the measured difference in T_n values for (100) and (110) directions provides an additional check of the alignment. Similarly to the (100) direction, there seems to be a close correlation between the crossing field and the field corresponding to T_n maximum.

Figures 3 and 4 imply a strong competition between the field-induced order and Schottky peak. The FIOP transition in the specific heat abruptly disappears before T_n reaches zero. Precise magnetization [10] and de Haas van Alphen measurements [7], on the other hand, were able to map T_n as a function of the magnetic field all the way to $T_n \approx 0$. This apparent contradiction can be explained by a very small entropy available for the FIOP transition above 13 and 12 T for fields parallel to the (100) and (110) directions, respectively. Specific heat, being a bulk

measurement, can be less sensitive than magnetization techniques in this situation. A strong competition is to be expected in the Γ_1-Γ_5 scenario. The ground state pseudo-doublet formed at the level crossing carries both magnetic and quadrupolar moments. Since a quadrupolar moment operator does not commute with a dipolar one, the quadrupolar interactions leading to FIOP compete with the magnetic Zeeman effect.

In summary, we find evidence for the level crossing occurring around 8–9 T. This field value is very close to the field at which both T_n and $C(T_n)$ become maximum, suggesting that the crossing of the lowest CEF levels is the driving mechanism of FIOP. In fields above 10 T, there is a strong competition between FIOP and the Schottky peak. Our high field specific heat results provide compelling arguments for the Γ_1 singlet being the CEF ground state of Pr in this system. These results call for a new model of electronic mass enhancement, instead of the ordinary quadrupolar Kondo effect, which has been discussed mainly in the context of the Γ_3 non-Kramers doublet ground state.

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