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Crystalline electric field effects in the filled skutterudite compound $PrOs_4P_{12}$

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Abstract
The filled skutterudite compound $PrOs_4P_{12}$ was synthesized in single-crystal form using a molten metal flux growth technique. Low-temperature magnetization, specific heat, and electrical resistivity measurements showed no indication of a phase transition down to 0.1 K but had features indicative of crystalline electric field (CEF) effects. Analyses of these features in terms of a cubic CEF suggest a Γ_1 singlet or a Γ_3 doublet ground state separated by 30–50 K from a Γ_5 triplet first excited state.

1. Introduction

The filled skutterudites have the chemical formula MT_4X_{12} (M = alkali metal, alkaline-earth, lanthanide, or actinide; T = Fe, Ru, or Os; and X = P, As, or Sb). Current interest in the filled skutterudites is motivated by the wide range of strongly correlated electron behaviour that these compounds exhibit at low temperatures. Among the filled skutterudites, the Pr-based systems, in particular, have attracted a considerable amount of attention in recent years, as a result of the discoveries of heavy fermion superconductivity in $PrOs_4Sb_{12}$ [1, 2], antiferroquadrupolar ordering in $PrFe_4P_{12}$ [3, 4], and a metal–insulator transition in $PrRu_4P_{12}$ [5].

Various measurements performed on the filled skutterudites reveal features that have been interpreted in terms of crystalline electric field (CEF) effects [1, 3, 6–9]. These features range from Schottky anomalies in the specific heat [1] to deviations of the inverse magnetic susceptibility from Curie–Weiss behaviour at temperatures comparable to the CEF splittings between the Pr^{3+} energy levels [6]. In developing an understanding of the various types of phenomena exhibited by the Pr-based filled skutterudite compounds, it is important to determine the Pr^{3+} energy level scheme and how it depends on structure and composition.

For instance, measurements of the physical properties of the filled skutterudite compound $PrOs_4Sb_{12}$, which represents the first Pr-based heavy fermion superconductor, display features that reflect strong CEF effects [1, 8, 9]. A complete picture of the CEF splitting in $PrOs_4Sb_{12}$ may shed light on how the heavy fermion behaviour and unconventional superconductivity occur in this system. This approach can be extended to include a comparison of the physical properties of various Pr-based filled skutterudites and their associated CEF effects, which may lead to a more general understanding of how strongly correlated electron behaviour develops in these compounds. With this in mind, the filled skutterudite compound $PrOs_4P_{12}$ was considered for study. Previous measurements of polycrystalline $PrOs_4P_{12}$ showed no indication of a phase transition down to 1.7 K [5, 10]. In this paper, we present new measurements on single crystals of $PrOs_4P_{12}$ to determine the CEF energy level scheme and to check for magnetic or quadrupolar ordering below 1.7 K.

2. Experimental details

Single crystals of $PrOs_4P_{12}$ were synthesized using a molten tin flux growth technique from a mixture of elemental Pr (3N), Os (3N8), P (5N), and Sn (5N) in a ratio of 1:4:20:50. The elements were sealed in a carbon-coated quartz tube under 150 Torr ultra-high purity Ar. The sealed quartz tube was then placed in a box furnace and heated to 1130 °C for 5 days; this was followed by a slow cooling at 2 °C h^{-1} to 600 °C. The resulting crystals typically had overall dimensions of less than 1 mm.

X-ray powder diffraction measurements were performed using a Rigaku D/MAX B x-ray machine on a powder of ground single crystals. Further x-ray structural refinement was performed on two single crystals with similar dimensions. The x-ray intensity data were collected on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.071\,073$ nm). Orientation matrix and unit cell parameters were derived using the program DENZO [11]. No absorption corrections were necessary because of the rather regular shape and small dimensions of the investigated crystals. The structure was refined with the aid of the SHELXS-97 program [12].

Magnetization measurements were performed using a Quantum Design Magnetic Properties Measurement System (MPMS) in magnetic fields, H, up to 5.5 T for 1.7 K $\leqslant T \leqslant$ 300 K. Electrical resistivity $\rho(H, T)$ measurements were made using a four-probe ac technique for 2 K $\leqslant T \leqslant$ 300 K in fields up to 8 T in a Quantum Design Physical Properties Measurement System (PPMS) with a constant current of 1 mA and for 0.1 K $\leqslant T \leqslant$ 2.6 K in fields up to 8 T using a ^{3}He–^{4}He dilution refrigerator with a constant current of 300 μA. Specific heat $C(T)$ measurements on $PrOs_4P_{12}$ were performed for 0.5 K $\leqslant T \leqslant$ 90 K in a semi-adiabatic ^{3}He calorimeter on a collection of single crystals with a total mass of 80 mg.

3. Results

The x-ray powder diffraction pattern indicates that $PrOs_4P_{12}$ is single phase with no major impurity peaks and a cubic unit cell parameter $a = 8.0751(5)$ Å, in good agreement with a previous measurement, where $a = 8.0710(10)$ Å [13]. The single-crystal structural refinement confirmed that $PrOs_4P_{12}$ possesses a $LaFe_4P_{12}$-type structure (space group $Im\bar{3}$) with two formula units per unit cell, and $a = 8.080(1)$ Å. The crystal structure parameters, from the structural refinement of $PrOs_4P_{12}$, are listed in table 1.

The dc magnetic susceptibility χ_{dc} and inverse dc magnetic susceptibility χ_{dc}^{-1} versus T, measured in a magnetic field of 500 Oe, between 2 and 300 K, are displayed in figure 1. A Curie–Weiss fit to the $\chi_{dc}^{-1}(T)$ data from 100 to 250 K yields an effective moment

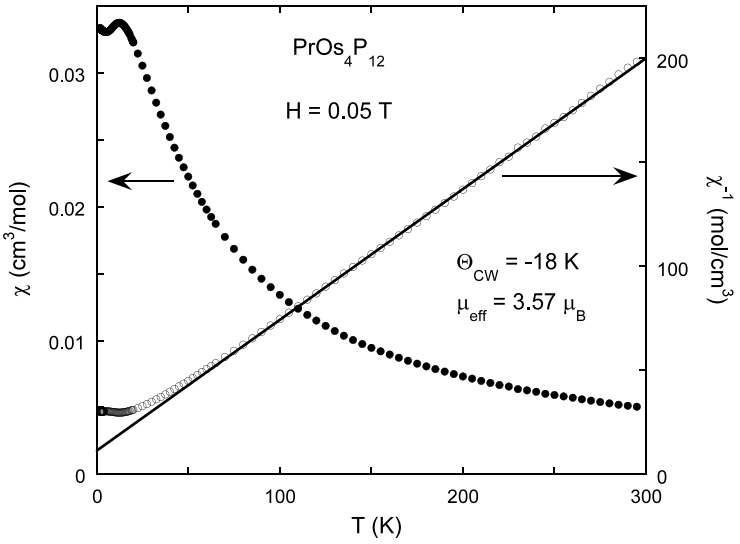

Figure 1. The dc magnetic susceptibility $\chi_{\rm dc}$ (solid circles) and $\chi_{\rm dc}^{-1}$ (open circles) versus temperature T at $H = 0.05$ T for $PrOs_4P_{12}$. The straight line is a Curie–Weiss fit to $\chi_{\rm dc}^{-1}(T)$.

Table 1. Single-crystal structural data for $PrOs_4P_{12}$ ($LaFe_4P_{12}$-type, space group $Im\bar{3}$; No. 204) taken at $T = 296$ K, with a scattering angle range of $2° < 2\theta < 80°$.

$PrOs_4P_{12}$		
Crystal size $60 \times 74 \times 83\ \mu m^3$	Lattice parameter (Å) $a = 8.080(1)$	Density (g cm^{-3}) $\rho = 8.017$
Reflections in refinement $286 \geqslant 4\sigma(F_0)$ of 322	Number of variables = 12 Goodness of fit = 1.068	$R_F^2 = \sum \lvert F_0^2 - F_c^2 \rvert \sum F_0^2$ = 0.0156
Pr in 2a (0, 0, 0); Occupancy = 1.02(2)	Thermal displacements (Å^2) Pr: $U_{11} = U_{22} = U_{33}$ = 0.0079(1)	Interatomic distances (Å) Pr–12 P 3.1091
Os in 8c (1/4, 1/4, 1/4); Occupancy = 1.00(1)	Thermal displacements (Å^2) Os: $U_{11} = U_{22} = U_{33}$ = 0.0004(1)	Interatomic distances (Å) Os–6 P 2.3617
P in 24g (0, y, z); y: 0.143 04(6) z: 0.357 22(6) Occupancy = 1.00(1)	Thermal displacements (Å^2) P: $U_{11} = 0.0017(2)$ $U_{22} = 0.0023(2)$ $U_{33} = 0.0028(2)$	Interatomic distances (Å) P–1 P 2.3073 –1 P 2.3115 –2 Os 2.3617 –1 Pr 3.1091

$\mu_{\rm eff} = 3.57\mu_{\rm B}$/f.u. and a Curie–Weiss temperature $\Theta_{\rm CW} = -18$ K. This value of $\mu_{\rm eff}$ is close to the Pr^{3+} free-ion value of $3.58\mu_{\rm B}$/f.u. as well as the value of $3.63\mu_{\rm B}$/f.u. previously found for polycrystalline $PrOs_4P_{12}$ [5]. At low temperatures, $\chi_{\rm dc}^{-1}(T)$ deviates from a Curie–Weiss law, while $\chi_{\rm dc}(T)$ develops a broad peak centred at 12 K. This peak is much more pronounced than the feature observed in the $\chi(T)$ data for polycrystalline $PrOs_4P_{12}$ and is a strong indication of CEF effects [5], which will be discussed in more detail in section 4.

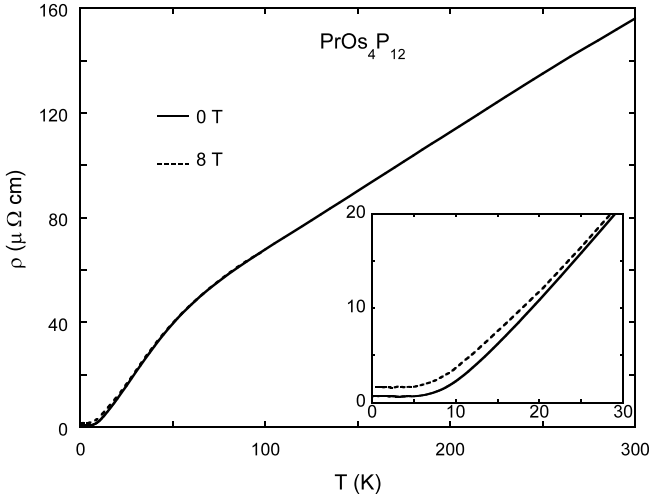

Figure 2. Electrical resistivity ρ versus T for $PrOs_4P_{12}$ at $H = 0$ and 8 T. The inset displays the low-temperature behaviour below 50 K.

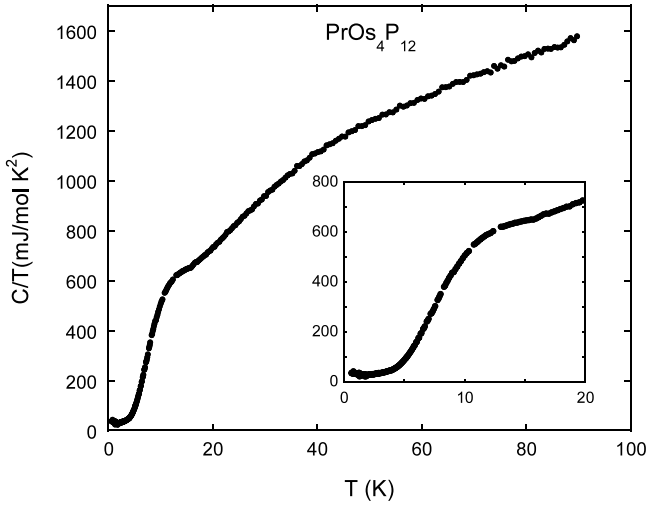

Figure 3. Specific heat C divided by temperature T versus T for $PrOs_4P_{12}$. The inset reveals the low-temperature behaviour of $C(T)/T$ below 20 K.

Displayed in figure 2 are electrical resistivity $\rho(T)$ data for a $PrOs_4P_{12}$ single crystal with a residual resistivity ratio ∼180 between 0.1 and 300 K at $H = 0$ and 8 T. In zero field, $\rho(T)$ displays a linear decrease from 300 to 75 K, followed by a rapid downturn that approaches a constant value of 0.65 $\mu\Omega$ cm below 5.5 K. Except for a small positive magnetoresistance below 30 K, the behaviour of $\rho(T)$ does not change in applied fields up to 8 T. The specific heat C divided by temperature T versus T data for $PrOs_4P_{12}$ from 0.6 to ∼80 K are shown in figure 3. The only clear feature is a Schottky-like shoulder centred around 13 K (inset to figure 3), which gives further evidence for CEF effects in $PrOs_4P_{12}$. The $C(T)/T$ data below the shoulder decrease to a value of ∼32 mJ mol^{-1} K^{-2}.

4. Discussion

The T-dependences of χ_{dc}, ρ, and C/T of $PrOs_4P_{12}$ reveal features that indicate the presence of strong CEF effects. These features can be fitted by expressions that depend on the CEF splitting scheme and provide more information about the Pr^{3+} ion ground and excited states

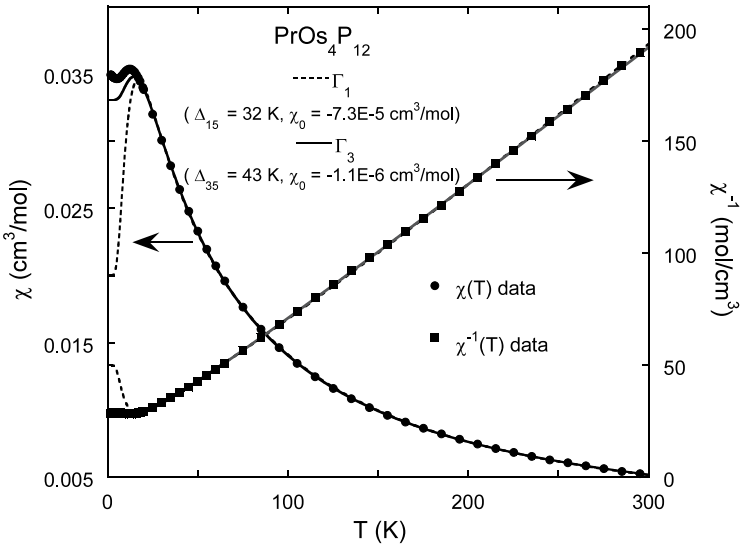

Figure 4. Fits of $\chi_{dc}(T)$ (solid circles) and $\chi_{dc}^{-1}(T)$ (solid squares) by CEF models with a Pr^{3+} Γ_1 (dashed line) and Γ_3 (solid line) ground state. See the text for explanation of the parameters indicated in the figure.

and their splittings in $PrOs_4P_{12}$. For simplicity, the CEF calculations were made for cubic O_h symmetry which, in zero field, closely approximate those made for the actual tetrahedral T_h symmetry of $PrOs_4P_{12}$. The Pr^{3+} ninefold degenerate $J = 4$ Hund's rule ground state multiplet splits in a cubic CEF into a Γ_1 singlet, a Γ_3 doublet, and Γ_4 and Γ_5 triplets. The CEF variables used to make the fits are those developed by Lea, Leask, and Wolf (LLW), where X_{LLW} is the ratio of the fourth- and sixth-order terms of the angular momentum operators and W is an overall energy scale [14]. The lack of magnetic order above 0.1 K, as well as 2 K magnetization M versus H measurements (not shown) that indicate a magnetization of only $0.3\mu_B$/f.u. by 5 T, imply a nonmagnetic ground state for the Pr^{3+} ions in $PrOs_4P_{12}$. Given a nonmagnetic ground state, the CEF fits will be performed for the cases of both Γ_1 singlet and Γ_3 doublet nonmagnetic ground states.

Figure 4 shows the CEF fits to the $\chi_{dc}(T)$ and $\chi_{dc}^{-1}(T)$ data from 2 to 300 K assuming Γ_1 singlet and Γ_3 doublet nonmagnetic ground states, respectively. A constant contribution χ_0 to the magnetic susceptibility was also included to improve the quality of the fits. One possible source for this constant term is a Landau diamagnetic contribution due to atomic core electrons, estimated to be -8.4×10^{-4} cm^3 mol^{-1} in the case of $LaFe_4P_{12}$ [15]. The best fit with a Γ_1 singlet ground state was found for $X_{LLW} = 0.46$ and $W = 4.07$, which results in an energy level splitting of 32 K between the Γ_1 singlet ground state and the Γ_5 triplet first excited state. The low-temperature behaviour of the $\chi_{dc}(T)$ data is not accurately reproduced by the CEF fit, similarly to the case of $PrOs_4Sb_{12}$, which was determined to possess a nonmagnetic Γ_1 singlet ground state [16]. For the case of a nonmagnetic Γ_3 doublet ground state, the best fit was found for $X_{LLW} = -0.69$ and $W = -8$, resulting in an energy level splitting of 43 K between the Γ_3 ground state and the Γ_5 first excited state. Below ~15 K, the fit assuming a Γ_3 ground state deviates from the $\chi(T)$ data, but not as significantly as the fit assuming a Γ_1 ground state. The diamagnetic contribution to the CEF fits ranged from -1×10^{-6} cm^3 mol^{-1} for the Γ_3 ground state fit to -7.3×10^{-5} cm^3 mol^{-1} for the Γ_1 ground state fit; varying these values did not significantly affect the two CEF energy level schemes.

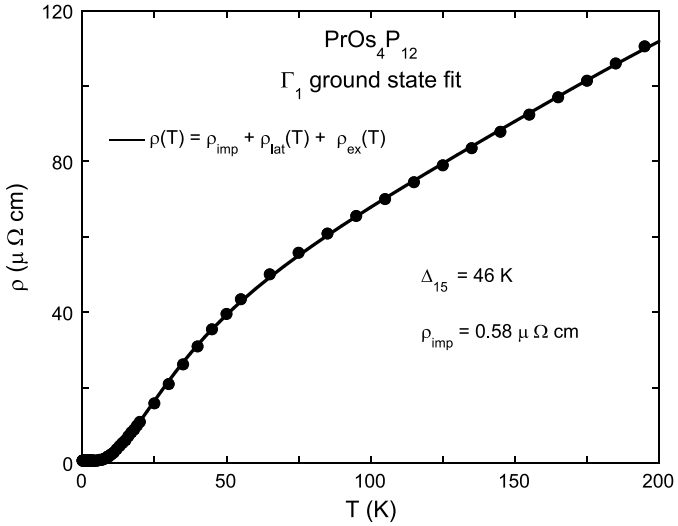

Figure 5. Fit to an expression based on a CEF model to the $\rho(T)$ data using equation (1) assuming a Pr^{3+} Γ_1 ground state. See the text for explanation of the parameters indicated in the figure.

Crystalline electric field fits were also performed for the zero-field electrical resistivity data (figure 5) using the expression

$$\rho(T) = \rho_{\text{imp}}(T) + \rho_{\text{lat}}(T) + \rho_{\text{ex}}(T), \tag{1}$$

where ρ_{imp} is the residual resistivity due to scattering of electrons by impurities and defects, ρ_{lat} is the lattice contribution associated with scattering of electrons by phonons, and ρ_{ex} is the term due to s–f exchange scattering of electrons from the Pr^{3+} 4f energy levels in a cubic CEF [17]. Since the addition of an aspherical Coulomb scattering term did not improve the quality of the fits to the $\rho(T)$ data for $PrOs_4P_{12}$, this contribution was not included in the analysis. Identical fits to the $\rho(T)$ data could be obtained using equation (1) and assuming either a nonmagnetic Γ_1 singlet ground state (shown in figure 5) or a nonmagnetic Γ_3 doublet ground state. In both fits, the contribution $\rho_{\text{lat}}(T)$ was estimated from the $\rho_{\text{lat}}(T)$ data of $LaOs_4P_{12}$ below 200 K scaled by ∼0.25 [18]. The formula for the contribution ρ_{ex} was also scaled in both cases by ∼2.8. Figure 5 features the Γ_1 ground state fitted with $\rho_{\text{imp}} = 0.58\ \mu\Omega$ cm, where ρ_{ex} is best described by a CEF splitting of 46 K ($X_{\text{LLW}} = 0.38$ and $W = 2.7$) between the Γ_1 singlet ground state and the Γ_5 triplet first excited state. A fit similar to that shown in figure 5 was also found for a Γ_3 ground state with $\rho_{\text{imp}} = 0.67\ \mu\Omega$ cm and ρ_{ex} best described by a CEF splitting of 55 K ($X_{\text{LLW}} = -0.64$ and $W = -5.2$) between the Γ_3 doublet ground state and the Γ_5 triplet first excited state.

Further evidence for a splitting of ∼30–50 K between the Pr^{3+} Γ_1 or Γ_3 nonmagnetic ground state and Γ_5 triplet first excited state for $PrOs_4P_{12}$ was found through fits to a Schottky-like anomaly in the $C(T)/T$ data. In figure 6, the Schottky-like anomaly centred around 13 K was fitted from 2 to 15 K by the equation

$$C(T)/T = C_{\text{e}}(T)/T + C_{\text{lat}}(T)/T + AC_{\text{Sch}}(T)/T, \tag{2}$$

which includes an electronic, lattice, and two-level Schottky contributions with the following forms: $C_{\text{e}}(T) = \gamma T$, $C_{\text{lat}}(T) = \beta T^3$, and $C_{\text{Sch}}(T) = R(\delta/T)^2(g_a/g_b)[1 + (g_a/g_b)\exp(-\delta/T)]^{-2}\exp(-\delta/T)$, where $g_a(g_b)$ is the degeneracy of the ground state (first excited state), δ is the energy level splitting, and A is a scaling factor. The best fit shown in

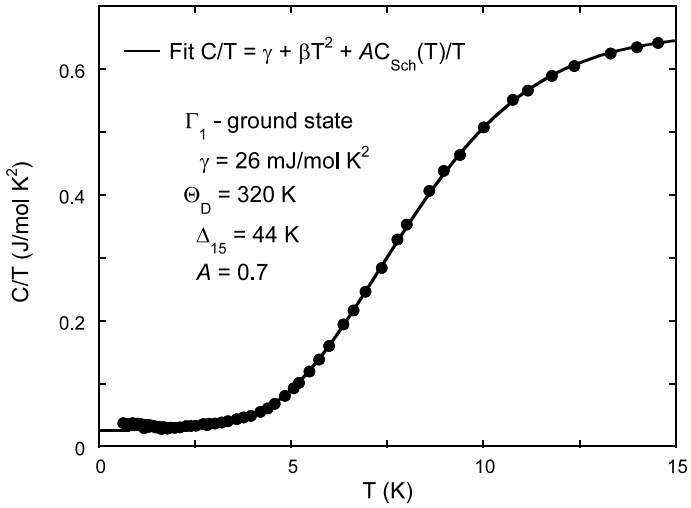

Figure 6. A fit using equation (2) to the $C(T)/T$ data assuming a Pr^{3+} Γ_1 ground state. See the text for explanation of the parameters indicated in the figure.

figure 6 for a Γ_1 singlet ground state and a Γ_5 triplet first excited state results in an electronic specific heat coefficient $\gamma \approx 26$ mJ mol^{-1} K^{-2}, a Debye temperature $\Theta_D \sim 320$ K, and a Schottky contribution scaled by $A = 0.7$, with an energy splitting of 44 K between the ground state and first excited state. The scaling of the Schottky anomaly required to achieve an accurate fit for a Γ_1 singlet ground state ($A = 0.7$) could be a result of significant hybridization of the localized 4f and itinerant electron states. This transfer of entropy from the localized f electrons to the conduction electrons has been observed previously in the heavy fermion superconductor $PrOs_4Sb_{12}$ [1]. A fit identical to that shown in figure 6 was also obtained in the case of a Γ_3 doublet ground state and a Γ_5 triplet first excited state; the resulting best fit has an electronic specific heat coefficient $\gamma \approx 27$ mJ mol^{-1} K^{-2}, a Debye temperature $\Theta_D \sim 354$ K, and a Schottky contribution scaled by $A = 1.4$, with an energy splitting of 43 K between the ground state and first excited state. There is no clear explanation for the large scaling parameter $A = 1.4$ required for the best Γ_3 ground state fit to the $C(T)$ data, and this may be an indication that the Γ_1 CEF scheme is more appropriate. The values of the electronic specific heat coefficient are close to that found for $LaOs_4P_{12}$ (21.6 mJ mol^{-1} K^{-2}) and less than the value of 56.5 mJ mol^{-1} K^{-2} found for polycrystalline $PrOs_4P_{12}$ [10]. The Debye temperature is larger than the value determined from a previous measurement of the specific heat of polycrystalline $PrOs_4P_{12}$ which yielded $\Theta_D = 285$ K [10]. One possible source for the discrepancy between the values of γ for polycrystalline and single-crystal $PrOs_4P_{12}$ is tin inclusions in the single crystals, which would result in an overestimate of the $PrOs_4P_{12}$ mass, although no indication of a tin superconducting transition at 3.72 K was observed in $C(T)$ measurements.

After performing the various CEF fits to the magnetic susceptibility, electrical resistivity, and specific heat data, we have concluded that there are two possible CEF schemes for $PrOs_4P_{12}$. Our CEF splitting schemes assuming a Γ_1 ground state are in agreement with CEF fits by Matsuhira *et al* using tetrahedral symmetry T_h, which yielded a splitting of ∼48 K between a nonmagnetic Γ_1 singlet ground state and the triplet first excited state for polycrystalline $PrOs_4P_{12}$ [10]. A potential nonmagnetic Γ_3 doublet ground state was discounted by Matsuhira *et al*, who performed $C(T)$ measurements in an applied magnetic field and looked

for an additional Schottky contribution to $C(T)$ due to Zeeman splitting of the Γ_3 doublet ground state [10]. These $C(T)$ measurements, in fields up to 5 T, revealed no significant change in $C(T)$ down to 1.8 K [10]. In order to confirm the proposed CEF splitting scenario, further experiments, such as inelastic neutron scattering in high fields, are required.

5. Summary

Measurements on $PrOs_4P_{12}$ single crystals do not show any indication of a phase transition even at temperatures as low as 0.1 K. This is in marked contrast to the wide variety of phase transitions that occur at low temperatures in other Pr-based filled skutterudites that include conventional BCS superconductivity, unconventional superconductivity, heavy fermion behaviour, non-Fermi liquid behaviour, magnetic order, quadrupolar order, and metal–insulator transitions. Features found in the temperature dependences of the magnetic susceptibility, electrical resistivity, and specific heat can be interpreted in terms of crystalline electric field effects. CEF fits to these various features indicate a Γ_1 or Γ_3 nonmagnetic ground state separated by 30–50 K from a Γ_5 first excited state, although previous work suggests that the Γ_3 ground state CEF splitting scheme is a less likely scenario.

Acknowledgments

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