Crystalline electric field contribution to the magnetoresistance of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$

C. R. Rotundu, K. Ingersent, and B. Andraka*

Department of Physics, University of Florida, P. O. Box 118440, Gainesville, Florida 32611-8440, USA

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Resistivity measurements were performed on Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ single crystals at temperatures down to 20 mK and in fields up to 18 T. The results for dilute-Pr samples ($x=0.3$ and 0.67) are consistent with model calculations performed assuming a singlet crystalline-electric-field (CEF) ground state. The residual resistivity of these crystals features a smeared step centered around 9 T, the predicted crossing field for the lowest CEF levels. The CEF contribution to the magnetoresistance has a weaker-than-calculated dependence on the field direction, suggesting that interactions omitted from the CEF model lead to avoided crossing in the effective levels of the Pr$^{3+}$ ion. The dome-shaped magnetoresistance observed for $x=0$ and 0.05 cannot be reproduced by the CEF model, and likely results from fluctuations in the field-induced antiferroquadrupolar phase.

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I. INTRODUCTION

PrOs$_4$Sb$_{12}$, the first discovered Pr-based heavy fermion and superconductor,$^1$ remains a focus of extensive theoretical and experimental investigation. Its significance lies in the fact that the origin of the heavy-fermion behavior is associated with non-Kramers $f$-electron ions, for which the conventional Kondo effect seems unlikely. Our previous specific-heat results in magnetic fields$^2$ established that the crystalline-electric-field (CEF) ground state is a nonmagnetic $\Gamma_1$ singlet. The field dependence of the CEF Schottky anomaly for fields greater than 14 T is clearly inconsistent with the alternative scenario of a nonmagnetic $\Gamma_3$ doublet ground state. This conclusion was independent of whether the exact $T_h$ point-group symmetry or the higher (approximate) $O_h$ symmetry was assumed for the Pr sites.$^3$ The singlet nature of the CEF ground state was subsequently confirmed by inelastic neutron scattering measurements and their analysis within the $T_h$ symmetry scheme.$^4$

Despite the overwhelming evidence in favor of a singlet CEF ground state, there are experimental results for Pr$_{0.3}$Sb$_{12}$ that seem to be better understood in terms of a doublet ground state. For example, the magnetoresistance$^{1,5-7}$ at 1.4 K exhibits a dome-like shape that is consistent with model calculations of the CEF resistivity for a $\Gamma_3$ ground state and inconsistent with similar calculations for a $\Gamma_1$ ground state.$^5$ However, the CEF resistivity is a single-ion property that might be strongly affected in Pr$_{0.3}$Sb$_{12}$ by lattice coherence and by strong quadrupolar and exchange interactions. To probe this possibility, we have performed magnetoresistance measurements on single-crystal Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$, in which lattice translational symmetry is broken and intersite effects should be weaker than in the pure compound. Based on previously published magnetic susceptibility and specific heat results,$^8$ we do not expect significant changes in CEF energies (and eigenstates) of Pr upon doping with La. In addition, we have extended magnetoresistance measurements of the undoped material down to 20 mK.

We find that the magnetoresistance of pure Pr$_{0.3}$Sb$_{12}$ at 20 mK is inconsistent with model calculations for either the $\Gamma_3$ or the $\Gamma_1$ CEF ground state, and conclude that the dome feature most probably results from fluctuations in the field-induced antiferroquadrupolar (AFQ) phase. On dilution of the Pr lattice with La, the dome in the magnetoresistance is replaced by a smeared step that is consistent with the picture of a $\Gamma_1$ singlet CEF ground state but not with a $\Gamma_3$ doublet. The dependence of the $f$-electron contribution to the magnetoresistance on the direction of the magnetic field is smaller than is predicted theoretically based on a CEF model. This discrepancy suggests that interactions omitted from the CEF model lead to avoided crossing in the effective levels of the Pr$^{3+}$ ion.

II. METHODS

Results are presented below for Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ with four different La concentrations: $x=0$, 0.05, 0.3, and 0.67. For $x=0$, 0.05, 0.3, and 0.67, we grew large single crystals (cubes with masses as large as 50 mg) on which accurate magnetic susceptibility measurements were performed up to 300 K in order to extract the room-temperature paramagnetic effective moment. In each case, this moment was within 10% of that expected for Pr$^{3+}$. (For the undoped compound, this finding contradicts a wide range of values reported in literature.) The superconducting transition temperatures $T_c$ of the large single crystals and of smaller resistivity bars, also obtained in the same growths, were checked via ac susceptibility measurements. A good agreement between $T_c$ values of large and small crystals confirmed the stoichiometry assigned to samples used in this study. The residual resistivity ratio (the ratio of the resistance at room temperature to that extrapolated to $T=0$) was $R_{RR}=100$, 50, 180, and 170 for $x=0$, 0.05, 0.3, and 0.7, respectively. The value $R_{RR}=100$ exceeds those reported previously$^{1,7,9}$ for pure Pr$_{0.3}$Sb$_{12}$, indicative of the high quality of our samples. The $x=0.05$ crystal was from the batch for which results were reported in Ref. 8.

The resistivity was measured by a conventional four-probe technique. Almost all measurements were performed directly in the liquid mixing chamber of a dilution refrigerator. Sample $x=0.67$ was measured to 0.35 K only in vacuum using a $^3$He refrigerator. In each case, special care was taken to avoid self-heating effects by comparing the sample resistance at several different current levels. The estimated uncertainty in the determination of the absolute value of the resis-
tivity was 30% due to the unfavorable geometry of the crystals. Within this uncertainty, the resistivity at room temperature was the same in all cases. In the plots below, we have scaled the resistivity of each sample to a zero-field room-temperature value of 300 $\mu\Omega$ cm, in the range reported previously. It is important to emphasize that this scaling procedure is in no way essential for the conclusions of the paper, which are based on the temperature and field dependence of the resistivity of a given sample.

We calculated the CEF contribution $\rho_{\text{CEF}}$ to the electrical resistivity via the method applied by Fisk and Johnston $^{10}$ to the resistivity of Pr$_3$B$_6$ and by Frederick and Maple $^5$ to the magnetoresistance of PrOs$_4$Sb$_{12}$. This method focuses on a single Pr ion, neglects intersite effects, and takes no account of the direction of the current relative to the crystal axes or to the magnetic field. Our calculations started with one or other of two forms for $\hat{H}_0$, the CEF Hamiltonian for Pr$^{3+}$ in zero magnetic field: that (corresponding in the $O_h$-symmetry notation of Ref. 11 to $W=-2.97$ K and $x=-0.7225$) deduced $^5$ by fitting the temperature dependence of the zero-field resistivity of PrOs$_4$Sb$_{12}$ or the Hamiltonian (described in the $T_h$-symmetry notation of Ref. 3 by $W=3.0877$ K, $x=0.45991$, and $y=0.10503$) determined from elastic $^{12}$ and inelastic $^6$ neutron scattering. Henceforth, we refer to these cases as the “doublet” and “singlet” CEF scheme, respectively, according to the ground-state degeneracy of $\hat{H}_0$.

The CEF states in a magnetic field $\mathbf{H}$ were obtained by diagonalizing the Hamiltonian $\hat{H}_0+g\mu_B\mathbf{H}\cdot\mathbf{J}$, where $g=4/5$ is the Landé $g$ factor for Pr$^{3+}$ and $\mathbf{J}$ is the $f$-electron angular momentum operator. The CEF resistivity is completely determined by these CEF states, the temperature $T$, and two constants $\rho_{\text{ex}}$ and $\rho_{\text{A}}$, which parametrize, respectively, the overall strengths of magnetic exchange and the aspherical Coulomb interaction between the $4f$ and conduction electrons. Following Ref. 5, we took $\rho_{\text{ex}}=\rho_{\text{A}}=0.25$ $\mu\Omega$ cm. However, our conclusions are insensitive to the particular choice of constants.

III. RESULTS AND DISCUSSION

Figure 1 shows the resistivity of undoped PrOs$_4$Sb$_{12}$ for three representative fields, with both current and magnetic field oriented along the (001) direction. The results are similar to those reported by other groups. $^{1,13}$ Below 200–300 mK the resistivity saturates but has a strong field variation. The residual resistivity $\rho_0$ can be obtained using the previously noted $^{1,13}$ temperature variation at fixed field $\rho(T)=\rho_0+B\theta$ with $n\geq 2$. Within the precision of our measurement, there is no difference between $\rho_0$ obtained in this manner and $\rho(T=20$ mK).

This residual resistivity (or resistivity at 20 mK), when plotted against magnetic field (Fig. 2), has a dome shape centered around 9–10 T. Such a dome-shaped magnetoresistance has been reported previously at the somewhat higher temperatures of 1.4 K (Ref. 5) and 0.36 K (Ref. 7). Two explanations for this dome have been considered: field-induced long-range antiferroquadrupolar (AFQ) order, and crossing of the lowest CEF levels. It is striking that $\rho_0(H)$ rises sharply at the AFQ boundaries, indicated by arrows in Fig. 2, and peaks around 10 T, where the AFQ transition temperature is highest. However, Frederick and Maple have shown (see Fig. 2 of Ref. 5) that the width, peak position, and height of the dome in the magnetoresistance of PrOs$_4$Sb$_{12}$ at 1.4 K are reproduced quite well by the single-ion CEF resistivity computed within the doublet scheme. (By contrast, $\rho_{\text{CEF}}$ for the singlet scheme shows a steplike increase in the vicinity of the crossing field at which the lowest $T_h$ $^4G^0_4$ level falls in energy below the $^1G_1$ singlet.)

We find that neither CEF scheme accounts satisfactorily for the magnetoresistance measured at 20 mK (Fig. 2), which shows a dome of similar width to that at 1.4 K. Irrespective of the CEF scheme, $\rho_{\text{CEF}}$ for fields oriented along the (001) direction (square symbols in Fig. 3) is discontinuous at the crossing field and essentially flat at higher fields. Although the sharp features in $\rho_{\text{CEF}}$ might be smeared somewhat in experiments, the departures from the measured $\rho_0$ are so large as to suggest that the low-temperature magnetoresistance of PrOs$_4$Sb$_{12}$ is dominated by effects beyond those considered in the single-ion CEF model.

![Image 329x110 to 545x264](image1)

![Image 329x561 to 545x734](image2)

![Image 329x763 to 545x938](image3)
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We now turn to the effects of La doping. Figure 4 shows the magnetoresistance of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ at 20, 310, and 660 mK. Similarly to Pr$_8$Sb$_{12}$, there is a negligible temperature variation of the resistivity below 300 mK in fields above-critical for superconductivity (as evidenced by the overlap of the 20-mK and 310-mK isotherms). However, the shape of the dome for $x=0.05$ is much less symmetric about the peak field than its $x=0$ counterpart. Between 2 and 10 T, $\rho(T=20\text{ mK})$ for the doped sample increases by over 80%, compared to a 25% increase for the undoped material, whereas the resistivity drop above 10 T is greater in percentage terms for $x=0$.

The magnetoresistance becomes qualitatively different at higher La doping. Figure 5 shows the 20-mK magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ for fields along (001), (011), and (010); in each case, the current passed along the (001) direction. All three isotherms exhibit a pronounced but wide step, centered near 9–10 T, superimposed on a linear background. In the investigated field range this $x=0.3$ material exhibits

FIG. 3. Theoretical CEF resistivity at 20 mK vs magnetic field calculated within the singlet (upper panel) and doublet (lower panel) CEF schemes, for fields along (001) (■) and (011) (△).

FIG. 4. (Color online) Longitudinal magnetoresistance of Pr$_{0.95}$La$_{0.05}$Os$_4$Sb$_{12}$ at 20, 310, and 660 mK, for current and field along the (001) direction.

FIG. 5. (Color online) Magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ at 20 mK for three different orientations of the magnetic field. The current direction was (001). The inset shows the nearly isotropic contribution obtained by subtracting a linear (in $H$) background from each isotherm.

neither the dome structure characteristic of $x=0$ and 0.05 nor the sharp peak predicted by our CEF calculations for the doublet ground state (lower panel of Fig. 3), although the latter narrow feature might be difficult to observe experimentally. For each curve, $\rho$ versus $H$ is approximately linear above 13 T. The resistivity of the non-$f$-electron analog LaOs$_4$Sb$_{12}$, measured at 0.36 K, has a quite large and approximately linear field dependence. Furthermore, the directional dependence of the magnetoresistance of LaOs$_4$Sb$_{12}$—$d\rho/dH$ being larger along (011) than along (001)—is in agreement with the trend of the linear background in Fig. 5. It thus seems that the differences between the high-field slopes of $\rho(H)$ in Fig. 5 can be attributed primarily to non-$f$-electron contributions to the magnetoresistance. Subtracting such linear parts results in very similar curves (inset to Fig. 5) for all three field directions. We conclude that the $f$-electron magnetoresistance in this moderately doped material is nearly isotropic.

Compared to the cases $x=0$ and 0.05, the low-temperature magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ for fields along (001) is much closer to that given by the CEF model. The 20-mK measurements (Fig. 5) are more consistent with the singlet CEF scheme than with the doublet scheme, in that the latter predicts a sharp peak that is absent in the data. A second and stronger argument in favor of the singlet scheme is provided by the near isotropy of the $f$-electron magnetoresistance noted in the previous paragraph. Figure 3 plots the CEF resistivity for fields along (001) and (011). The doublet scheme (lower panel in Fig. 3) predicts a highly anisotropic $\rho_{\text{CEF}}$ stemming from the fact that the lowest two CEF levels cross at 8.5 T along (001), but instead diverge along (011). In the singlet CEF scheme (upper panel in Fig. 3), the anisotropy is much smaller because the lowest CEF levels cross at 8.6 T along (001), while along the (011) direction they anticross at 8.3 T with a minimum gap of only 0.7 K. Unlike the doublet
The step along the distance inferred for dilute-Pr alloys and that calculated in the distance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ along magnetoresistance extracted from Fig. 5.

CEF scheme, the singlet scheme does a reasonable job of reproducing the measured (011) magnetoresistance. However, it underestimates the width of the step for fields along (001) and still overestimates the anisotropy in the $f$-electron magnetoresistance for the same temperature and field direction for the singlet and doublet CEF ground states.

Figure 6 shows that at the higher temperature of 310 mK, there is much better agreement between the magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ along (001) and $\rho_{\text{CEF}}$ calculated within the singlet CEF scheme. At this temperature, the thermal smearing of the step in $\rho_{\text{CEF}}$ matches quite well the width of the rise in the measured magnetoresistance. The results of similar calculations for the doublet scheme are in gross disagreement with the measurement. (The noise in our low-field magnetoresistance data, which is particularly prominent in Fig. 6, arises from flux jumps in the Nb$_2$Sn magnet during field sweeps.)

The character of the magnetoresistance seems to be little changed by further La dilution. The longitudinal magnetoresistance for x=0.67 was investigated down to 0.35 K and in fields to 14 T. The magnetoresistance at the lowest temperature (Fig. 7) exhibits essentially identical magnetic field dependence to that for x=0.3.

The main difference between the $f$-electron magnetoresistance inferred for dilute-Pr alloys and that calculated in the singlet CEF scheme relates to the low-temperature width of the step along the (001) field direction. The CEF model predicts an almost discontinuous jump of the magnetoresistance at 20 mK at the level-crossing field, while the rise in the measured magnetoresistance of Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ takes place over 3–4 T. Since there is better agreement between the measured and theoretical magnetoresistance along the (011) direction, where level anticrossing is expected, we speculate that interactions omitted from the CEF model mix the lowest levels, preventing any crossing even along high-symmetry field directions and thereby producing isotropic magnetoresistance. These interactions are most likely nonlocal. We note, however, that a mean-field treatment of intersite magnetic and quadrupolar interactions between Pr ions did not find avoided crossing.$^{7,12}$

Figure 6 shows that the measured midpoint field for the magnetoresistance rise in Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ is about 1 T higher than is predicted based on the CEF level scheme determined for pure PrOs$_4$Sb$_{12}$, perhaps pointing to a small shift in the CEF levels upon doping with La. (This suggests that inhomogeneity in the local La concentration might broaden the theoretically predicted magnetoresistance step, in line with our findings for Pr$_{0.7}$La$_{0.3}$Os$_4$Sb$_{12}$ at 20 mK.) By contrast, the similarity between the magnetoresistance steps observed for x=0.3 and 0.67 (and the field value of the midpoint) suggests that there is little further evolution of the CEF energies over this doping range. A weak dependence of CEF levels on La doping is in agreement with our specific-heat measurements of the Schottky anomaly in lightly doped alloys,$^{14}$ and is also supported by the nearly invariant temperature of the maximum in the magnetic susceptibility.$^8$

The contrast between the resistivity versus field curves for the x=0 and x=0.3 samples is striking. The obvious differences between these two compositions are the presence of a field-induced ordered phase for the pure material and the absence of translational symmetry in the diluted case. Our previous specific heat measurements$^{14}$ indicate that the field-induced ordered (AFQ) phase disappears somewhere near x =0.2. Since the model for the CEF resistivity is single site in character, it seems likely that the dome-shaped magnetoresistance observed for x=0 and 0.05 is associated with the presence of long-range order in these materials, perhaps through enhanced scattering of conduction electrons caused by fluctuations in the AFQ order parameter.

In summary, we have shown that a simple CEF model accounts quite well for the $f$-electron contribution to the magnetoresistance of Pr$_{1-x}$La$_x$Os$_4$Sb$_{12}$ with x=0.3 and 0.67. The weak dependence of this contribution on field direction is consistent with the existence of a singlet CEF in zero magnetic field, with avoided level crossing in applied fields. At the lowest temperatures, the magnetoresistance for x=0 and x=0.05 is inconsistent with the results of CEF model calculations. This discrepancy is attributed to the long-range order present in the pure and lightly doped materials.
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*Electronic address: andraka@phys.ufl.edu