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Crystalline electric field effects in the electrical resistivity of $PrOs_4Sb_{12}$

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Abstract

The temperature T and magnetic field H dependences of the electrical resistivity ρ of the recently discovered heavy-fermion superconductor $PrOs_4Sb_{12}$ have features that are associated with the splitting of the Pr^{3+} Hund's rule multiplet by the crystalline electric field (CEF). These features are apparently due to magnetic exchange and aspherical Coulomb scattering from the thermally populated CEF-split Pr^{3+} energy levels. The $\rho(T)$ data in zero magnetic field can be described well by calculations based on CEF theory for various ratios of magnetic exchange and aspherical Coulomb scattering, and yield CEF parameters that are qualitatively consistent with those previously derived from magnetic susceptibility, specific heat, and inelastic neutron scattering measurements. Calculated $\rho(H)$ isotherms for a Γ_3 ground state qualitatively account for the 'dome-shaped' feature in the measured $\rho(H)$ isotherms.

1. Introduction

The filled skutterudite compound $PrOs_4Sb_{12}$ was recently discovered to be the first Pr-based heavy-fermion superconductor, with a superconducting transition temperature $T_c = 1.85$ K and an effective mass $m^* \approx 50\ m_e$, where m_e is the mass of the free electron [1, 2]. Features observed in the magnetic susceptibility $\chi(T)$, specific heat $C(T)$, and inelastic neutron scattering (INS) [3] all indicate that the Hund's rule $J = 4$ multiplet of the Pr^{3+} ion is split by the crystalline electric field (CEF). An analysis of these data within the context of a cubic CEF using the theory of Lea, Leask, and Wolf (LLW) yielded a Γ_3 nonmagnetic doublet ground state, a Γ_5 triplet first excited state at ~10 K, and higher Γ_4 triplet and Γ_1 singlet excited states at ~130 K and ~313 K, respectively. A 'roll-off' near ~8 K of the electrical resistivity $\rho(T)$ in zero magnetic field was attributed to a decrease in spin- or charge-dependent scattering from the low-lying Γ_5 excited state whose population decreases with decreasing temperature, while features in $\rho(H, T)$ at low temperatures <1.5 K and high fields >4.5 T were identified with a high-field ordered phase (HFOP) of magnetic or quadrupolar character [3, 4].

In a lanthanide compound, the conduction electrons interact with the localized 4f electrons through magnetic exchange and the direct Coulomb interaction. For lanthanide ions whose 4f electrons are hybridized with conduction electrons, the exchange interaction can be negative, which favours screening of the magnetic moments of the 4f electrons by the conduction electron spins. This leads to contributions to the electrical resistivity that increase as $\log T$ with decreasing temperature that are associated with the Kondo effect. Since no Kondo-like contribution has been found in $\rho(T)$, we disregard 4f conduction electron hybridization and treat the 4f electrons in the ionic limit, as a first approximation. When the degeneracy of the Hund's rule multiplet of a lanthanide ion is lifted in a CEF, the change of the resulting lanthanide energy level populations with temperature introduces temperature-dependent features in the electrical resistivity. These features are more subtle than those seen in properties such as magnetic susceptibility and specific heat, but can still be described on the basis of the CEF Hamiltonian of LLW [5].

This paper presents calculations of the electrical resistivity due to magnetic exchange and aspherical Coulomb scattering associated with the CEF splitting of the Pr^{3+} Hund's rule multiplet in $PrOs_4Sb_{12}$. Electrical resistivity $\rho(T)$ data in zero magnetic field are directly fitted with the calculated equations, providing parameters that are used to calculate $\rho(H)$ isotherms. It is shown that a Γ_3 ground state can qualitatively account for the 'dome-shaped' features that have been observed in the measured $\rho(H)$ isotherms.

2. Calculation of the electrical resistivity in the crystalline electric field

The effects on electrical resistivity due to magnetic exchange [6, 7] and aspherical Coulomb [8] scattering have been separately considered many times in the past; often one effect was neglected in favour of the other. The present calculations follow the procedure of Fisk and Johnston [9], where it was demonstrated that both contributions are important for describing the temperature dependence of the electrical resistivity for the compound PrB_6 and, in addition, the relevant equations were presented in a form appropriate to the Stevens operator equivalent formulation of the LLW crystal field Hamiltonian [10, 11]. In this notation [7], the total contribution to the electrical resistivity from CEF effects, ρ_{CEF}, is

$$\rho_{\mathrm{CEF}} = \rho_0[r\,\mathrm{Tr}(P\,Q^{\mathrm{M}}) + (1-r)\,\mathrm{Tr}(P\,Q^{\mathrm{A}})], \tag{1}$$

where r is a coefficient representing the ratio of the magnetic exchange term to the aspherical Coulomb scattering term. The temperature-dependent matrix, P_{ij}, is common to both terms:

$$P_{ij} = \frac{\mathrm{e}^{-\beta E_i}}{\sum_k \mathrm{e}^{-\beta E_k}} \frac{\beta(E_i - E_j)}{1 - \mathrm{e}^{-\beta(E_i - E_j)}}, \tag{2}$$

where E_i are the eigenvalues of the CEF eigenstates and $\beta = 1/k_{\mathrm{B}}T$. The Q^{M}_{ij}-matrix represents magnetic exchange scattering, and the Q^{A}_{ij}-matrix is associated with aspherical Coulomb scattering due to the quadrupolar charge distribution of the Pr^{3+} ion. The Q_{ij}-matrices are

$$Q^{\mathrm{M}}_{ij} = |\langle i|J_z|j\rangle|^2 + \tfrac{1}{2}|\langle i|J_+|j\rangle|^2 + \tfrac{1}{2}|\langle i|J_-|j\rangle|^2, \tag{3}$$

$$Q^{\mathrm{A}}_{ij} = \sum_{m=-2}^{+2} |\langle i|y_2^m|j\rangle|^2, \tag{4}$$

where the $|i\rangle$ s are the CEF eigenstates, and the y_2^m s are the operator equivalents of the spherical harmonics for $L = 2$ (i.e., quadrupolar terms), and are given elsewhere [12]. The Q_{ij}-matrices

are also normalized to each other [9], such that

$$\sum_{i,j} Q_{ij}^{\mathrm{M}} = \sum_{i,j} Q_{ij}^{\mathrm{A}} = (2J+1)J(J+1) = 180 \qquad (\text{for } J = 4). \tag{5}$$

Assuming that Matthieson's rule is valid, the electrical resistivity is separated into impurity, phonon, and CEF contributions:

$$\rho = \rho_{\mathrm{imp}} + A\rho_{\mathrm{La}} + \rho_{\mathrm{CEF}} \tag{6}$$

where ρ_{imp} is the impurity scattering term, ρ_{La} is the lattice term of the previously measured isostructural compound without f electrons, $LaOs_4Sb_{12}$ [13], and ρ_{CEF} is given by equation (1). The constant A was used to scale the lattice contributions of $\rho(T)$ of $LaOs_4Sb_{12}$ and $PrOs_4Sb_{12}$ to one another, assuming that they have the same temperature dependence, and to account for uncertainties in the geometrical factor due to the irregular shape of the crystals and/or microcracks in the crystals. For ρ_{CEF}, the energies E_i can be expressed in terms of the parameters x and W in accordance with the LLW formalism, where x is the ratio of the fourth- and sixth-order terms of the angular momentum operators and W is an overall energy scale factor [5]. In the absence of a magnetic field, the eigenstates $|i\rangle$ are the same for all values of x and W for $J = 4$ in a cubic CEF. Additional terms due to tetrahedral symmetry in the crystal field Hamiltonian [14] were not included in this analysis in order to keep the calculations consistent with those previously made for these samples. Equation (6) was fitted to the original data from [2] between 1.9 and 20 K, assuming a Γ_3 doublet ground state, with results shown in figure 1. The best fit to the data yields an impurity scattering term $\rho_{\mathrm{imp}} = 1.67\ \mu\Omega$ cm, a scaling factor for the $LaOs_4Sb_{12}$ lattice $A = 0.21$, a CEF scaling factor $\rho_0 = 0.385\ \mu\Omega$ cm, a CEF scattering mechanism ratio $r = 0.46$, and LLW values of $x = -0.7225$ and $W = -2.97$, which results in the first excited state Γ_5 triplet lying $\sim$5 K above the Γ_3 doublet ground state.

It is notable that the fit of equation (6) to the zero-field $\rho(T)$ data between T_c and 20 K is excellent (upper inset of figure 1), and the agreement between the fit and the data at high temperatures >50 K is qualitatively good (lower inset of figure 1). Since the magnetic exchange and aspherical Coulomb scattering contributions to the CEF are nearly temperature independent above $\sim$75 K, the discrepancy is most likely due to the $LaOs_4Sb_{12}$ lattice term not being an accurate representation of the $PrOs_4Sb_{12}$ lattice term, which is reasonable considering the anomalous resistivities of other La-based compounds compared to their Y- and Lu-based counterparts without f electrons [15]. Unfortunately, single crystals of these YOs_4Sb_{12} or $LuOs_4Sb_{12}$ compounds, which may provide more accurate MOs_4Sb_{12} filled skutterudite lattice resistivities, are not available. The data were also fitted with the CEF scattering mechanism ratio r fixed at intervals of 0.25, and the results are presented in table 1. All values of r resulted in satisfactory fits of the $\rho(T)$ data at low temperatures, with the value of the splitting between Γ_3 and Γ_5, Δ_{35}, increasing from 3.3 K for $r = 1$ (magnetic exchange scattering only) to 6 K for $r = 0$ (aspherical Coulomb scattering only). The values for $r = 0$ are closer to the values determined from $\chi(T)$, $C(T)$, and INS measurements. It is possible that a better determination of the lattice term could result in a more definitive result for the value of r. While it is unlikely that magnetic exchange scattering is completely unimportant, it does appear that aspherical Coulomb scattering contributes considerably to the electrical resistivity of $PrOs_4Sb_{12}$.

3. The high-field ordered phase in $PrOs_4Sb_{12}$

Measurements of the electrical resistivity, specific heat, and thermal expansion of $PrOs_4Sb_{12}$ at low temperatures <1.5 K and high magnetic fields >4.5 T reveal features that appear to be associated with an ordered phase, one that may be quadrupolar in nature [3, 4, 16–18]. In the

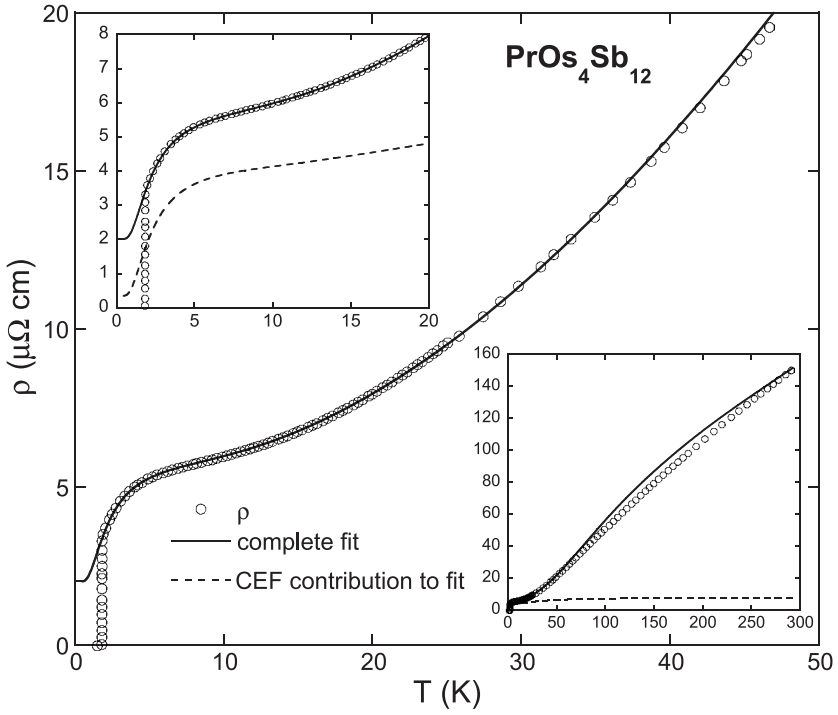

Figure 1. Electrical resistivity ρ versus temperature T between 1 and 50 K for a single crystal of $PrOs_4Sb_{12}$. The solid curve is a fit of the function described in the text (equation (6)), consisting of contributions from the scattering of electrons by impurities, phonons (represented by the scaled phonon contribution to the resistivity of $LaOs_4Sb_{12}$), and magnetic exchange and aspherical Coulomb interactions. Upper inset: ρ versus T between 1 and 20 K for the same single crystal of $PrOs_4Sb_{12}$. The dashed curve is the CEF contribution to the fit represented by the solid curve. Lower inset: $\rho(T)$ for $PrOs_4Sb_{12}$ between 1 and 300 K. The CEF contribution (dashed curve) is nearly negligible at higher temperatures.

Table 1. Parameters resulting from a fit of equation (6) to the data in figure 1. The value of the CEF scattering ratio r was fixed at various values to determine how the other parameters would change. The larger the aspherical Coulomb scattering contribution (smaller r), the closer the value of Δ_{35} to values previously calculated.

r	ρ_{imp} ($\mu\Omega$ cm)	A	ρ_0 ($\mu\Omega$ cm)	x	W (K)	Δ_{35} (K)
0	1.88	0.204	0.373	−0.716	−2.52	5.99
0.25	1.80	0.207	0.378	−0.720	−2.78	5.33
0.5	1.64	0.208	0.387	−0.723	−3.00	4.73
0.75	1.33	0.206	0.406	−0.726	−3.18	3.93
1	0.86	0.200	0.435	−0.728	−3.30	3.33

electrical resistivity, these features are manifested as 'roll-offs' in $\rho(T)$ and large 'domes' in $\rho(H)$ [3, 16, 19]. The 'domes' in $\rho(H)$ are especially intriguing, as it is expected that scattering should be lower in an ordered state. It has been suggested that the crossings of the CEF energy levels in magnetic fields are related to the HFOP [17, 19] and can contribute to the increase of scattering in this region. Recent neutron diffraction experiments have also suggested the existence of an antiferroquadrupolar ordered state that is associated with magnetic field-

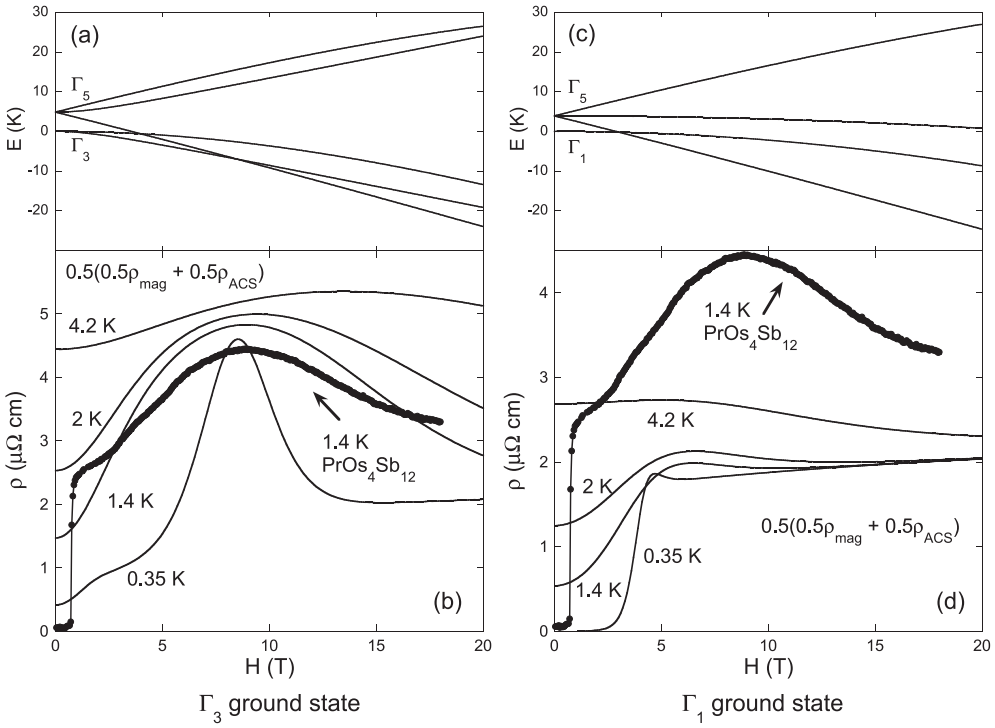

Figure 2. (a) Low-temperature energy level splittings E as a function of magnetic field H for the LLW parameters $x = -0.723$ and $W = -3.00$. (b) Calculated electrical resistivity ρ versus magnetic field H for the energy splittings in (a). It was assumed that magnetic exchange and aspherical Coulomb scattering contributed equally to the CEF resistivity ($r = 0.5$ in equation (1)). The calculated curves were also scaled by $\rho_0 = 0.5$ in order to bring the curves to the same scale as those measured experimentally. For comparison, the solid circles are the measured ρ versus H for $PrOs_4Sb_{12}$ at 1.4 K [16]. (c) E versus H for the LLW parameters $x = 0.508$ and $W = 2.46$. (d) ρ versus H for the energy splittings in (c), and similar constraints as (b).

induced energy level crossings for a Γ_1 ground state [20]. To check this hypothesis for electrical resistivity, ρ was calculated as a function of H in order to qualitatively observe the shape of the CEF contribution to the electrical resistivity.

Shown in figure 2(a) are the energy level splittings as a function of magnetic field ($H \parallel (001)$) for the Γ_3 doublet ground state and Γ_5 triplet first excited state, using the LLW values of x and W derived from the fit to the electrical resistivity of $PrOs_4Sb_{12}$ with the CEF scattering mechanism ratio r chosen to be 0.5. This value of r was used because it is consistent with the value determined by Fisk and Johnston [9] for PrB_6 as well as being a compromise between aspherical Coulomb scattering, which results in a Δ_{35} that is closer to values estimated from other analyses ($\chi(T)$, $C(T)$, INS), and magnetic exchange scattering, which is more universal in lanthanide compounds. The corresponding plot of ρ versus H for various temperatures is shown in figure 2(b). The parameter ρ_0 was chosen such that the calculated $\rho(H)$ curves were on the same scale as those measured experimentally. A dome shape, which sharpens considerably at lower temperatures, can be clearly seen in the graph. A plot of ρ versus H for $PrOs_4Sb_{12}$ at 1.4 K [16] is presented for comparison to the theoretical curves. The maximum of the dome corresponds to the magnetic field at which the ground state changes from one of the Γ_3 states to one of the Γ_5 states. The dome structure can be

understood by taking the limit of the equation for the P_{ij}-terms, equation (2), as the lowest excited state $E_i \to 0$, assuming $E_j = 0$ is the ground state, and the other energy levels are large enough to be ignored in the sum in the denominator. Equation (2) then becomes

$$\lim_{E_i \to 0} P_{ij} \approx \frac{\beta E_i}{2 \sinh \beta E_i} \qquad \text{for } E_j = 0. \tag{7}$$

The shape of this equation as a function of energy is a dome centred on $E_i = 0$ that sharpens considerably as the temperature is lowered. Since E_i is nearly proportional to H (figure 2(a)), domes also appear in $\rho(H)$. These domes are present in both magnetic exchange and aspherical Coulomb scattering, as there are $\Gamma_3 \to \Gamma_5$ transitions in both mechanisms, which unfortunately contributes to the uncertainty in determining the relative importance of the two types of scattering.

Similar to CEF fits to magnetic susceptibility $\chi(T)$, it is also possible to fit $\rho(T)$ for $PrOs_4Sb_{12}$ at low temperatures $T \leqslant 20$ K with an energy level scheme that has a Γ_1 singlet ground state and a Γ_5 triplet first excited state. The fit resulted in similar impurity and lattice fitting parameters to those for a Γ_3 ground state, with LLW values of $x = 0.508$ and $W = 2.46$. The parameters from the zero-temperature fit were used to calculate the energy level splittings as a function of magnetic field, as shown in figure 2(c), with the corresponding plot of ρ versus H shown in figure 2(d). It is immediately apparent that the dome shapes in $\rho(H)$ due to CEF scattering are less pronounced and are not in agreement with the data when the ground state is Γ_1, even though the fits to $\rho(T, H = 0)$ are nearly identical. A qualitative reason for this is that $\Gamma_1 \to \Gamma_5$ transitions only occur in aspherical Coulomb scattering, and the energy levels cross at a much lower field than for the Γ_3 ground state situation.

4. Summary

Features in the electrical resistivity of $PrOs_4Sb_{12}$ can be explained in terms of effects arising from the temperature- and magnetic field-dependent populations of CEF energy levels. Fits to the $\rho(T)$ data were accomplished by a combination of magnetic exchange and aspherical Coulomb scattering in the context of a Γ_3 ground state. The parameters resulting from this fit were used to calculate isotherms of $\rho(H)$ that qualitatively agree well with isotherms previously measured. While it was possible to fit the $\rho(T)$ data well with a Pr^{3+} energy level scheme with a Γ_1 ground state, when $\rho(H)$ isotherms were calculated using CEF parameters for this case, they were not in good agreement with the measured $\rho(H)$ isotherms. It is evident that the HFOP that is also observed in high-field measurements of $C(T)$ and $\alpha(T)$ is closely related to the ground state crossover in the energy level–magnetic field phase diagram.

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