Crystal Field Potential of $PrOs_4Sb_{12}$: Consequences for Superconductivity

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The results of inelastic neutron scattering provide a solution for the crystal field level scheme in $PrOs_4Sb_{12}$, in which the ground state in the cubic crystal field potential of T_h symmetry is a Γ_1 singlet. The conduction electron mass enhancement is consistent with inelastic exchange scattering, and we propose that inelastic quadrupolar, or aspherical Coulomb, scattering is responsible for enhancing the superconducting transition temperature. $PrOs_4Sb_{12}$ appears to be the first compound in which aspherical Coulomb scattering is strong enough to overcome magnetic pair breaking and *increase* T_c.

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Praseodymium filled skutterudite compounds, with general formula PrT_4M_{12}, where T is one of the transition metals Fe, Ru, or Os, and M is a pnictogen (P, As, or Sb), show a remarkable variety of interesting physical phenomena, including metal-insulator transitions [1], quadrupolar heavy fermion behavior [2,3], and superconductivity [4]. In particular, $PrOs_4Sb_{12}$ has attracted attention as a heavy fermion superconductor, in which quadrupolar fluctuations may play an important role in the pairing mechanism [5]. This proposal is based on two key observations: (i) there is a significant f-electron-induced mass enhancement of the conduction electrons, observed in specific heat, upper critical field [5,6], and de Haas–van Alphen measurements [7], and (ii) the magnetic susceptibility indicates that the crystal field ground state is nonmagnetic [5].

A knowledge of the crystal field ground state is essential to understanding the role of the f electrons in the superconductivity. In analyzing the magnetic susceptibility and specific heat, Bauer *et al.* considered two possible crystal field models [5]. In cubic symmetry, the Pr^{3+} ion splits into a singlet (Γ_1), a nonmagnetic doublet (Γ_3), and two magnetic triplets (Γ_4 and Γ_5). Crystal field models with either the Γ_1 singlet or Γ_3 doublet as ground state were both broadly consistent with the data; in both cases, the Γ_5 triplet was the lowest excited level estimated to be at less than 1 meV in energy. A Γ_3 non-Kramers doublet ground state is of particular interest, as it provides the necessary conditions for quadrupolar Kondo fluctuations to be responsible for the heavy fermion behavior [8], and is favored by analyses of the entropy [9,10]. However, the alternative Γ_1 singlet ground state has also been proposed following experiments that have explored the crossover to a field-induced ordered phase [11–13], so this important question remains unresolved.

Inelastic neutron scattering is the most direct method of determining the crystal field potential and level scheme of metallic rare earth systems. In this report, we present the results of a comprehensive set of measurements of crystal field transitions in $PrOs_4Sb_{12}$ as a function of temperature. From a simultaneous profile refinement of all the spectra, normalized on an absolute intensity scale, we have concluded that the Γ_1 singlet is the ground-state level. Discrepancies with earlier neutron scattering reports [6] are explained by the need for extra terms in the cubic crystal field Hamiltonian that are required by the T_h point group symmetry [14]. Although our data are inconsistent with a quadrupolar Kondo scenario, we conclude that inelastic quadrupolar fluctuations do play a vital role in enhancing the superconducting transition temperature, through aspherical Coulomb scattering of the conduction electrons [15].

We performed our experiments on the same polycrystalline sample that was used for previous neutron scattering measurements; details of its preparation and characterization can be found in Ref. [6]. The inelastic neutron scattering experiments have been performed on the time-of-flight Fermi chopper spectrometer LRMECS at the pulsed spallation neutron source IPNS (Argonne National Laboratory, Argonne), and on the cold-source triple-axis spectrometer SPINS at the NIST Center for Neutron Research. The time-of-flight measurements used incident energies of 6, 25, 35, and 60 meV, and were normalized on an absolute intensity scale using a vanadium standard. The higher energy runs showed no evidence of crystal field excitations above 20 meV. LRMECS has continuous detector coverage from 2.4° to 117.6°. The data at the highest angles ($> 100°$) are dominated by phonon scattering, but extrapolation of the momentum transfer dependence to low angle shows that the phonon contribution below 30° is sufficiently small at all incident energies to be neglected in our analysis. The SPINS data, which were collected with a fixed final energy of 3.7 meV using a cold BeO filter, showed evidence of a well-

resolved transition at 0.7 meV, which decreases in intensity with increasing temperature; i.e., it is a crystal field transition from the ground state.

Figure 1 shows low-angle LRMECS data measured with an incident energy of 35 meV at 1.8, 3.2, 5, and 20 K. The data were summed from 2.4° to 30°, giving an average momentum transfer at the elastic position of 1.2 Å^{-1}. The data in Fig. 1 show that the magnetic spectra are dominated by two crystal field transitions; the 11 meV peak is a ground-state transition, but the 17.2 meV peak occurs only at higher temperature and represents a transition from a low-lying excited state consistent with the 0.7 meV peak observed on SPINS.

The data are sufficiently complete to allow an unambiguous determination of the crystal field potential. The praseodymium ions in $PrOs_4Sb_{12}$ sit on lattice sites with cubic point group symmetry T_h, which lacks two symmetry operations of the more common O_h group (C_4 and C_2') [14]. The crystal field levels in T_h and O_h symmetry have the same degeneracies but different group theory labels and selection rules. In this Letter, we will use the more familiar cubic O_h labels, which can be mapped onto the T_h labels using the following: $\Gamma_1(O_h) \rightarrow \Gamma_1(T_h)$, $\Gamma_3(O_h) \rightarrow \Gamma_{23}(T_h)$, $\Gamma_4(O_h) \rightarrow \Gamma_4^{(1)}(T_h)$, and $\Gamma_5(O_h) \rightarrow \Gamma_4^{(2)}(T_h)$.

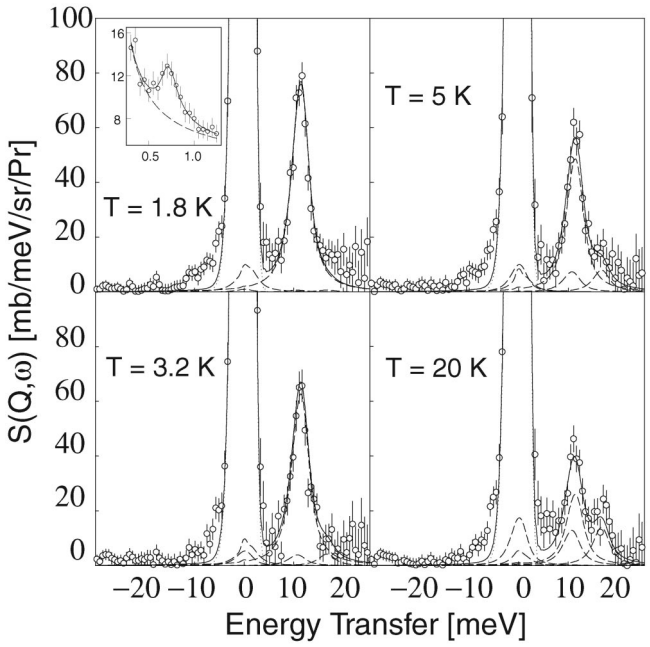

FIG. 1. $S(Q, \omega)$ measured at an average scattering angle of 20° with an incident energy of 35 meV at four temperatures, normalized on an absolute scale. The average elastic momentum transfer is 1.2 Å^{-1}. The solid lines are the fit of the crystal field model described in the text with no adjustment of the intensity scale, and the dashed lines represent the individual crystal field transitions. The inset shows the 0.7 meV transition in the SPINS data (see Ref. [6]).

T_h symmetry requires the addition of an extra crystal field parameter, B_6', to the conventional cubic crystal field Hamiltonian using the Steven's operator formalism:

$$H_{\text{CF}} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) + B_6'(O_6^2 - O_6^6). \quad (1)$$

The extra parameter, B_6', has a relatively small effect on the energies of the crystal field levels, but it mixes the Γ_4 and Γ_5 wave functions so that the usual cubic crystal field selection rules do not apply. Of particular importance is that the dipole matrix element coupling the Γ_1 singlet to the Γ_5 triplet is no longer zero. These dipole selection rules were a major factor in the previous crystal field assignments and explain the discrepancy with the conclusions we outline below.

In order to estimate the importance of this term, we have performed a superposition model analysis of the B_6' parameter for $PrOs_4Sb_{12}$ [16,17]. The starting point of this model is the assumption that the crystal field is the superposition of two-body potentials due to the neighboring ligands.

$$B_l^m = \Theta_l \sum_i A_l(R_i) K_l^m(\theta_i, \phi_i), \quad (2)$$

where Θ_l are reduced matrix elements, $A_l(R)$ are parameters representing the strength of the two-body potential, and $K_l^m(\theta, \phi)$ are geometric functions tabulated in Ref. [16]. The sum is over all the neighboring ligands at (R_i, θ_i, ϕ_i). The point-charge model obeys this superposition principle but makes specific predictions concerning the values of $A_l(R)$ that do not affect our conclusions. If we assume that the crystal field potential is dominated by the nearest-neighbor cage of 12 equidistant antimony ions, the model predicts the ratio of B_6' to B_6^0 without any adjustable parameters. Such a calculation shows that B_6' is substantial in $PrOs_4Sb_{12}$. $B_6'/B_6^0 = -53.4$, so neglecting this term, as previously proposed [12], is not justified.

In $PrOs_4Sb_{12}$, the bulk susceptibility below 5 K indicates that the crystal field ground state is nonmagnetic. Therefore, the ground state is either the Γ_1 singlet or the Γ_3 doublet. Since the LRMECS data are normalized on an absolute scale and comprise measurements at a number of temperatures, there are four ways in which the two models can be distinguished.

(i) Assuming that the 0.7 meV transition is the lowest-lying excitation, the absolute cross section of the $\Gamma_3 \rightarrow \Gamma_5$ transition is considerably larger than the $\Gamma_1 \rightarrow \Gamma_5$ transition and depends sensitively on the value of B_6'. Although the latter transition is not dipole forbidden in T_h symmetry, it is still relatively weak.

(ii) The absolute intensity of the other ground-state transition at 11 meV is very different in the two models. The $\Gamma_3 \rightarrow \Gamma_4$ transition is 25% stronger than the $\Gamma_1 \rightarrow \Gamma_4$ transition.

(iii) The intensities of the ground-state transitions fall with temperature much more strongly with a Γ_1 ground state than with a Γ_3 ground state because of the greater contrast between the ground state and excited level degeneracies. For example, increasing the temperature from 1.8 to 3 K is predicted to reduce the intensity of the 11 meV transition by 15% for the singlet ground state, but only 5% for the doublet ground state.

(iv) There should be an excited state transition at $\sim$16.5 meV in the case of the Γ_1 ground state. No such transition is predicted for a Γ_3 ground state below 100 K.

This gives us confidence that it is possible to establish the crystal field level scheme unambiguously by using all the neutron data in a simultaneous refinement of the crystal field parameters, using the technique discussed in Ref. [17] . We used the four spectra shown in Fig. 1 and an additional spectrum at 10 K, which is not shown, with the additional constraint of requiring the lowest transition to be at 0.7 meV. The peak line shapes were Lorenzians convolved with the instrumental resolution. The linewidths did not vary significantly with temperature and were constrained to be equal in the final refinement. In the least-squares fitting procedure, the only adjustable parameters were the crystal field potential, the elastic intensity, and the common linewidth. The reliability of the absolute normalization was such that we did not need to adjust the overall intensity scale.

We performed several refinements with starting parameters consistent with both ground states. However, it was clear that only the Γ_1 ground state was consistent with our data. As Fig. 2 shows, the temperature dependence of the ground-state transitions is too strong to be reproduced accurately with the Γ_3 ground state. The intensity of the 0.7 meV peak is too weak in the 6 meV data (not shown). Furthermore, the Γ_3 model does not reproduce the excited state transition at 17 meV observed above 10 K.

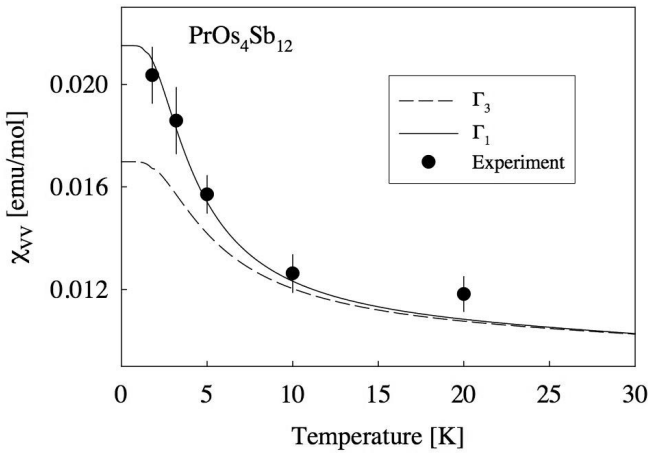

FIG. 2. Temperature dependence of the static magnetic susceptibility derived from the 11 meV peak intensity (see Ref. [26] for details), compared to the Van Vleck susceptibility of the two possible crystal field models.

The results of the refinement are shown in Fig. 1, where all the transitions, from both ground and excited states, are plotted as dashed lines. It is clear that the Γ_1 model is able to reproduce all the observed transitions. The crystal field potential has the following parameters: $B_4 = 0.20(1) \times 10^{-2}$ meV, $B_6 = 0.11(2) \times 10^{-3}$ meV, and $|B_6'| = 0.90(5) \times 10^{-3}$ meV. The ratio, $B_6'/B_6 = 8.2$, is smaller than predicted by the superposition model, which can be explained by adding a contribution to the crystal field potential from the osmium sublattice, which contributes to B_6, but not to B_6'.

The conclusion that the Γ_1 level is the crystal field ground state in $PrOs_4Sb_{12}$ means that the quadrupolar Kondo effect cannot be responsible for the observed conduction electron mass enhancement. Nevertheless, it does not rule out other models in which the quadrupolar degrees of freedom of the rare earth f electrons are important. As we now discuss, the properties of $PrOs_4Sb_{12}$ can be explained by a delicate balance between two types of interaction, magnetic dipolar and quadrupolar, between the conduction electrons and the praseodymium f electrons.

A theory of conduction electron mass enhancement due to inelastic scattering by crystal field transitions in a singlet ground-state system was developed over 20 years ago [18]. According to Fulde and Jensen [18], the mass enhancement due to the inelastic transition at energy Δ between two levels, labeled i and j, is given by

$$\frac{m^*}{m_0} = 1 + (g_J - 1)^2 J_{sf}^2 N(0) \frac{2|\langle i|J|j\rangle|^2}{\Delta}, \qquad (3)$$

where g_J is the Landé factor, J_{sf} is the exchange integral coupling the conduction electrons to the f electrons, $N(0)$ is the bare conduction electron density of states at the Fermi level, and $\langle i|J|j\rangle$ is the magnetic dipole matrix element calculated using the derived crystal field parameters. If we assume that $N(0)$ is the same as in the isostructural lanthanum compound, then we can use the measured Sommerfeld coefficient in $LaOs_4Sb_{12}$, $\gamma = 45$ mJ/mol K^2 (averaging over the two published values [7,19]) in order to estimate that $N(0) = 3\gamma/2\pi^2 k_B^2 = 9.6 \times 10^{-3}$ meV^{-1}. We have no reliable estimate for J_{sf}, but, if we assume that the value derived in praseodymium metal, 0.085 eV [18], represents a reasonable order of magnitude, we obtain a mass enhancement of $\sim$20. Given the uncertainty in the value of J_{sf}, this is in reasonable agreement with experiment, falling between the estimates based on specific heat (~ 50 [5]) and de Haas–van Alphen measurements (≤ 7.6 [7]).

The same $s - f$ exchange that is responsible for the mass enhancement will tend to suppress superconductivity through magnetic pair breaking [20]. However, the superconducting transition temperature in $PrOs_4Sb_{12}$,

$T_c = 1.85$ K, is 2.5 times larger than the nonmagnetic $LaOs_4Sb_{12}$, $T_c = 0.74$ K [7]. We propose that the resolution of this apparent discrepancy involves quadrupolar interactions that conserve time-reversal symmetry and therefore enhance pair formation [15]. This effect, known as aspherical Coulomb scattering, is believed to reduce the rate of suppression of T_c versus praseodymium concentration in the singlet ground-state system $La_{1-x}Pr_xSn_3$ [21,22]. However, $La_{1-x}Pr_xOs_4Sb_{12}$ would be the first systems in which T_c is *increased* by praseodymium substitution [23].

Fulde *et al.* predict that aspherical Coulomb scattering will produce the strongest enhancement of T_c when Δ/T_c is ~ 10 [15]. In the case of $La_{1-x}Pr_xSn_3$, this ratio occurs only when T_c has already been substantially suppressed by magnetic pair breaking [22]. However, if we assume that the crystal field potential is nearly constant in the $La_{1-x}Pr_xOs_4Sb_{12}$ series, the optimum ratio occurs at $x \rightarrow 0$ without requiring any suppression of T_c [23]. The strongest pair breaking arises from the $\Gamma_1 \rightarrow \Gamma_4$ transition, because it has the strongest dipole matrix elements. This is at much higher energy (11 meV) than the $\Gamma_1 \rightarrow \Gamma_5$ transition (0.7 meV), which has a weak dipole but strong quadrupole matrix element, and is therefore responsible for the quadrupolar pair enhancement. In $La_{1-x}Pr_xSn_3$, these two transitions have comparable energies. The crystal field level scheme in $PrOs_4Sb_{12}$ is much more favorable for increasing T_c through this mechanism.

In conclusion, we have performed comprehensive inelastic neutron scattering measurements of the temperature dependence of the crystal field transitions in $PrOs_4Sb_{12}$, which strongly suggest that the Γ_1 singlet is the ground state. This would rule out the quadrupolar Kondo effect as the mechanism for the heavy fermion state, but favors another scenario in which the observed mass enhancement would arise from inelastic exchange scattering of the conduction electrons by the low-lying crystal field levels. We argue that inelastic quadrupolar scattering, also known as aspherical Coulomb scattering, provides an explanation for the enhancement in the superconducting transition temperature compared to the isostructural lanthanum compound. The importance of quadrupole interactions in $PrOs_4Sb_{12}$ is evident in the antiferroquadrupolar order observed in high magnetic field [24,25]. Our results suggest that it plays a vital role in the superconducting phase as well.

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