Crystal field excitations in the singlet ground state compound Pr_3In

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Pr_3In exhibits an antiferromagnetic transition at $\sim$12 K. This transition appears to occur due to the exchange-generated admixture of higher lying crystal field levels into the singlet ground state. It is thus an example of an induced moment antiferromagnet. To provide detailed understanding of the magnetic behavior of Pr_3In, we have measured the magnetic excitation spectrum with inelastic neutron scattering experiments. We observe a clear dispersion of a crystal field excitation at 4 K. Above 100 K, the dispersion of the crystal field excitation has largely vanished and a crystal field scheme for Pr in a cubic site symmetry (in which the lowest states are a Γ_1 singlet and a Γ_4 triplet) provides a good approximation to the data. © *2007 American Institute of Physics*.
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Pr is an example of a 4*f* element with an even number of electrons that when under the influence of the crystalline environment may exhibit a singlet ground state. Surprisingly, a number of singlet ground state systems are observed to order magnetically. The magnetically ordered ground state arises due to the mixing of higher lying crystal field levels into the ground state by the magnetic exchange interaction.[1,2] Recently, we have investigated the magnetic properties of a single crystal sample of Pr_3In.[3] From these investigations and those of previous workers,[4] Pr_3In appears to be an example of an induced-moment antiferromagnet closely related to the well studied ferromagnetic singlet-triplet system Pr_3Tl.[5,6] In this paper, we present inelastic neutron scattering measurements which demonstrate the strong influence of the exchange interaction upon the crystal field levels as well as provide confirmation that Pr_3In is an induced-moment singlet-triplet system.

Pr_3In crystallizes in the cubic Cu_3Au structure (space group $Pm\bar{3}m$) with lattice parameter $a=4.94$ Å at low temperature. Pr_3In orders antiferromagnetically at $\sim$12 K.[3] Although the Cu_3Au structure is cubic, the Pr^{3+} ion sits on a site of tetragonal symmetry where eight of nearest neighbors are Pr and the remaining four are In. The crystal field (CF) Hamiltonian in this case is

$$H_{CF}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4. \quad (1)$$

Here, the B_l^m and O_l^m are the crystal field parameters and Stevens operators, respectively. A reasonable starting point for analysis of H_{CF} for Pr_3In is to assume cubic symmetry.[7] Under cubic symmetry the crystal field Hamiltonian becomes

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

Diagonalizing H_{CF} for cubic symmetry gives four levels,[8] a singlet (Γ_1), a nonmagnetic doublet (Γ_3), and two triplets (Γ_4 and Γ_5). In both the cubic and tetragonal cases, the off diagonal terms in H_{CF} mix the pure states of J_z so that the eigenstates of the Hamiltonian contain admixtures of different values of J_z. The addition of an exchange term to the Hamiltonian affects the crystal field energy levels as well as the admixture of the different values of J_z among the eigenstates. This interplay between the exchange and crystal field splitting is the essence of the physics occurring in induced-moment systems.

Polycrystalline samples of Pr_3In and the nonmagnetic analog La_3In were prepared in an arc furnace. The resulting buttons were annealed and susceptibility measurements of Pr_3In indicate similar behavior to single crystal samples as well as previous polycrystalline samples.[3,4] Neutron scattering measurements were conducted on the time of flight spectrometers LRMECS and HRMECS at the Intense Pulsed Neutron Source at Argonne National Laboratory at a variety

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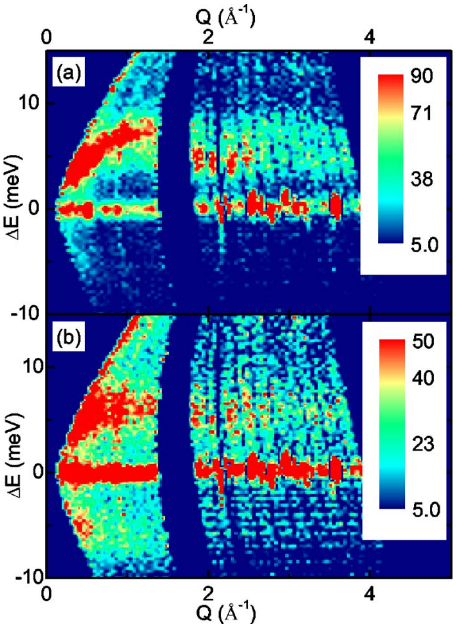

FIG. 1. (Color online) Inelastic neutron scattering data collected with E_i =30 meV with HRMECS. The color scale indicates the scattering intensity in arbitrary units. (a) T=4 K. (b) T=120 K. The data have been smoothed for clarity.

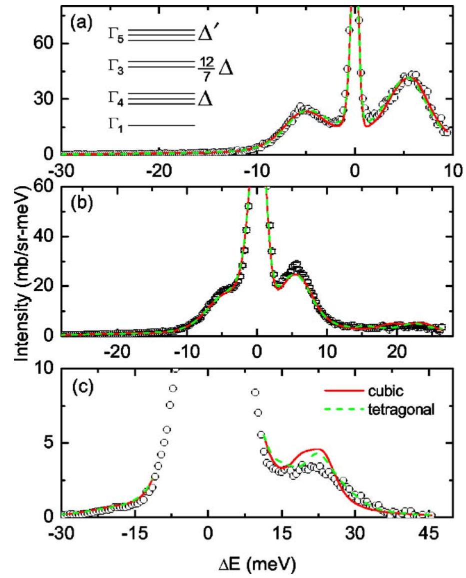

FIG. 2. (Color online) Inelastic neutron scattering data collected with LRMECS. These data represent the magnetic part of the inelastic neutron scattering spectrum for Q=0 determined as described in the text (except for $\Delta E \sim \pm 0.15E_i$, where residual nonmagnetic intensity remains). (a) E_i =15 meV, T=100 K. (b) E_i=35 meV, T=120 K. (c) E_i=60 meV, T =100 K. The error bars are approximately the symbol size and are shown in (b) for completeness. The lines are fits to crystal field models as described in the text.

of incident energies, E_i and temperatures. The nonmagnetic background was determined by measuring the nonmagnetic analog La_3In under identical experimental conditions to Pr_3In. In all cases the nonmagnetic background was found to be small in comparison to the magnetic scattering of Pr_3In. For the detailed crystal field analysis at high temperature, we have corrected the LRMECS data (Fig. 2) for neutron absorption, the nonmagnetic background, the Pr^{3+} form factor, and have normalized with vanadium to put the data on an absolute scale. Thus, the data displayed in Fig. 2 represents the magnetic scattering at Q=0 (Pr^{3+} form factor removed) with the exception of the scattering near the elastic line ($\Delta E \sim \pm 0.15E_i$), where residual nonmagnetic intensity remains.

Figure 1(a) shows the polycrystalline averaged dispersion of the lowest lying crystal field excitation in Pr_3In at 4 K with an E_i of 30 meV. The data conform to the expectations for magnetic scattering at low temperature, with no appreciable scattering on the neutron energy gain side (negative energy transfers). The dispersion is evident at low Q, while at higher Q the dispersion blurs due to the more complete polycrystalline average as scattering in higher Brillouin zones contributes to the neutron scattering response. At the lowest values of Q resolved in these measurements, the energy of the excitation is a minimum at 2.2 meV and Q =0.37 Å^{-1}. Starting at $Q \sim 1$ Å^{-1}, the dispersion begins to flatten significantly with the excitation energy, reaching a maximum value of 7.3 meV. These results are corroborated by similar experiments on LRMECS, where identical magnetic scattering is observed. Figure 1(b) shows data collected on HRMECS at 120 K under the same experimental conditions as the data collected at 4 K. The dispersion observed at low temperature has largely vanished. Instead a relatively flat excitation is now visible at ~6 meV and, due to the thermal population at 120 K, the excitation is also evident on the energy gain side.

The facts that the dispersion has largely vanished at 120 K and that the enhancement of the static susceptibility by the exchange diminishes above 100 K (Ref. 3) indicate that at high temperatures it may be possible to deduce the crystal field part of the Hamiltonian. Figure 2 shows INS data at various temperatures collected with LRMECS. Incident energies of 15, 35, and 60 meV have been employed to cover a large range of energy transfers. The crystal field excitation at 6 meV is clearly visible at incident energies of 15 and 35 meV. In the 60 meV data (and less obviously in the 35 meV data), a transition at 20 meV is present. In contrast to the ground state crystal field excitation at 6 meV, the 20 meV transition is not observed at low temperature (data not shown) and thus represents a transition between the crystal field level at 6 meV and a higher lying level. Examining the possible cubic crystal field levels in Ref. 8 allows many crystal field level schemes to be excluded. For example, since the Γ_5 has significant matrix elements with all of the other crystal field levels, any crystal field level scheme with Γ_5 as the ground state can be excluded due to the small number of crystal field excitations observed in the inelastic neutron scattering spectrum. Moreover, the Γ_4 is not allowed to be the ground state except when it is degenerate with Γ_1 *and* Γ_3. With these facts in mind, we have attempted to fit the neutron scattering data with a cubic crystal field level model. A great number of possibilities have been examined to ensure that the small number of observed crystal field excitations and the broadness of the lines did not lead to local minimum in the least squares fits. The result of simultaneously fitting the inelastic neutron scattering data with E_i

TABLE I. Selected parameters from fits to a cubic crystal field model.

χ^2	Δ (meV)	Δ' (meV)	B_4 (meV)	B_6 (meV)
7.2	6.3	30	−0.0096(1)	−0.000 017(1)

=15 meV at 100 K, E_i=35 meV at 120 and 200 K (data not shown), and E_i=60 meV at 100 K is shown as the solid line in Fig. 2. Several important fitting parameters are displayed in Table I, and the level ordering is displayed in the inset of Fig. 2(a). The fits reproduce the data reasonably well, with the exception of the overestimation of the intensity of the peak at 20 meV which is most evident in the 60 meV data. No other plausible cubic model yields a better fit to the 20 meV peak. Two likely possibilities for the deficiency of the cubic crystal field model in fitting the 60 meV data are (1) tetragonal distortions and (2) the fact that the exchange interaction is already mixing the crystal field levels at high temperatures. In an attempt to address (1), we have evaluated numerous tetragonal crystal field level schemes. For completeness a tetragonal fit is shown as the dashed line in Fig. 2. No plausible tetragonal model was found which was able to significantly improve the fit of the 20 meV peak. Given that no tetragonal crystal field model offers a significant improvement over a cubic model and that the cubic crystal field model reproduces the inelastic neutron scattering data reasonably well, the assertion that Pr_3In is an induced-moment singlet-triplet (Γ_1-Γ_4) system is validated. Theoretical calculations including crystal field level splitting and the exchange interaction are underway to provide further insight into the behavior of Pr_3In.[9]

In summary, Pr_3In exhibits a strong dispersion of the Γ_1-Γ_4 crystal field excitation characteristic of the presence of strong magnetic exchange interactions. Fits to the high temperature inelastic neutron scattering data are in agreement with previous work that Pr_3In is an induced-moment singlet-triplet system. Further work is in progress on a single crystal sample to elucidate the behavior of Pr_3In.

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[7]This assumption is based on the Pr and In ions possessing similar charges as well as on the screening due to the conduction electrons limiting the effect of any difference between the ions. A similar assumption was made in the related and well studied singlet-triplet system Pr_3Tl, for example, see Refs. 5 and 6
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