Crystal-field spectrum and linewidths in the heavy-fermion system $PrInAg_2$

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The heavy-fermion intermetallic compound $PrInAg_2$ has been studied by means of inelastic neutron scattering. In agreement with a previous study, there is clear evidence from both the excitation energies and relative intensities that the crystal-electric-field ground state is the Γ_3 nonmagnetic, non-Kramers doublet, and this, together with enhanced thermodynamic properties at low temperatures, indicates that $PrInAg_2$ is a candidate quadrupolar Kondo material. In addition to the Γ_3-Γ_4 and Γ_3-Γ_5 excitations, which are seen at low temperature, we have observed the other two allowed transitions, Γ_4-Γ_1 and Γ_4-Γ_5, which are visible when the Γ_4 triplet becomes thermally populated. Within the Lea-Leask-Wolf parametrization scheme, we obtain $W = -0.111 \pm 0.006$ meV and $x = -0.079 \pm 0.037$, values that are similar to but slightly different from those previously reported. No magnetic quasielastic scattering is seen, down to ~ 90 μeV, and this provides further evidence that the heavy-fermion behavior is unconventional and has a nonmagnetic origin. However, both the Γ_3-Γ_4 and Γ_3-Γ_5 levels are broadened significantly and to differing degrees. Possible sources of this broadening are discussed.

I. INTRODUCTION

The quadrupolar Kondo model posits that another type of many-body interaction between conduction electrons and f electrons exists and that in certain circumstances it will yield non-Fermi-liquid behavior in metals.[1] The theory states that if the ground state of a $4f$ or $5f$ ion has zero magnetic moment but nonzero quadrupole moment, then conduction electrons interact with this moment in a manner analogous to the traditional, magnetic Kondo effect. Originally proposed to explain the lack of quasielastic neutron scattering in the heavy fermion system UBe_{13},[2] the model was met with skepticism because subsequent measurements of the nonlinear susceptibility indicate a magnetic ground state;[3] furthermore, quasielastic scattering has since been observed in higher-resolution neutron-scattering measurements.[4] Similarly, it has been suggested that the quadrupolar Kondo model may explain the non-Fermi-liquid behavior of $Y_{1-x}U_xPd_3$,[5] but again a strong quasielastic component in the neutron-scattering spectrum indicates a magnetic ground state.[6] A crucial factor in these considerations is the nature of the underlying crystalline-electric-field (CEF) level scheme and whether the renormalized thermodynamic and transport properties, which are characterized by non-Fermi-liquid-like temperature dependences, can be thought of as developing from a nonmagnetic CEF ground state. The uncertainty in this interpretation for U compounds is due to the itinerant nature of $5f$ hybridized states, resulting in heavily damped CEF excitations that are unobservable by neutron scattering.

Given that the uranium compounds are so poorly understood, the better understood lanthanide series offers a tractable alternative path to addressing the same problem. In 1996, Yatskar *et al.*[7] looked for quadrupolar Kondo systems among rare-earth compounds, where the CEF levels are often unambiguous; praseodymium compounds were the most promising because the Pr^{3+} and U^{4+} ions both have $J=4$ Hund's rule ground states. In a cubic CEF, this leads to the possibility of having the Γ_3 nonmagnetic, non-Kramers doublet as a ground state. This reasoning led to the discovery that $PrInAg_2$ is a very strongly correlated metal with a specific-heat anomaly at ~ 0.4 K, which was identified as a Kondo peak, and a Sommerfeld coefficient of $\gamma = 6.5\,\mathrm{J\,mol^{-1}\,K^{-2}}$, placing it among the heaviest of the heavy-fermion compounds. While the general behavior of the specific heat conforms fairly well to Fermi-liquid theory [$C_{4f}(T)/T \rightarrow$ const as $T \rightarrow 0$, where T is the temperature and

C_{4f} the electronic specific heat], other measurements behave more anomalously at low temperatures: in particular, the magnetic susceptibility shows a logarithmic upturn below ~20 K, and there is a weak loss of scattering in the transport below ~0.4 K resulting in a linear temperature-dependent resistivity. Both these observations are inconsistent with a Fermi liquid if they are intrinsic.

Despite the uncertain classification of the low-temperature behavior, there is still strong evidence that a nonmagnetic interaction is responsible for the correlated electron behavior in $PrInAg_2$. Previous work, including inelastic neutron scattering by Galera *et al.*,[8] indicated that the CEF ground state is Γ_3. Yatskar *et al.*[5] found that they could fit the high-temperature electronic specific heat assuming the same ordering of the CEF levels reported by Galera. The presence of a nonmagnetic ground state and strongly enhanced thermodynamic properties makes $PrInAg_2$ a candidate quadrupolar Kondo system.

In this paper, we present a detailed neutron-scattering investigation of the CEF spectrum of $PrInAg_2$. With modest corrections, we confirm the previously reported CEF spectrum, we observe all four allowed transitions, and in particular we definitively establish the Γ_3 level as the ground state. Also, we begin to probe the dynamics of the CEF excited states through the excitation linewidths. Higher-resolution neutron-scattering experiments show that two of the inelastic transitions are significantly broadened. We suggest several possible causes for this effect.

II. EXPERIMENT

Inelastic neutron-scattering experiments were performed on the PHAROS (Ref. 9) spectrometer at Manuel Lujan, Jr. Neutron Scattering Center, Los Alamos National Laboratory, and on the QENS (Ref. 10) spectrometer at the Intense Pulsed Neutron Source, Argonne National Laboratory. The sample consisted of 58 g of crushed, polycrystalline $PrInAg_2$; the preparation and characterization of this sample have been described previously.[7]

PHAROS was used to determine the CEF energy levels. The sample was mounted on a three-stage displex refrigerator, and data collected at two temperatures, 6.6 K and 77 K, with incident neutron energies of 25.3 and 36.6 meV. A vanadium plate was used to measure the spectrometer's resolution. The elastic peak was very nearly Gaussian with $\Delta E/E_i=4\%$ full width at half maximum FWHM. To improve the statistics of the experiment, data from the planar array of linear, position-sensitive detectors were summed over the available Q range (0.10 to 0.75 Å^{-1} at the elastic line) and rehistogrammed into constant energy bins.

At 6.6 K, two peaks are observed, at 6.1 and 8.3 meV (see Fig. 1). From the matrix elements calculated by Birgeneau,[11] one expects that two of the six possible inelastic transitions will be forbidden by symmetry. Initial data taken on PHAROS with a higher incident energy showed no additional peaks up to 25 meV. Therefore, a second measurement was performed at 77 K, where the 6.1 meV state would be thermally populated, allowing additional transitions to be observed. The resulting data are shown in Fig. 1; two new peaks appear at 2.2 meV and 9.14 meV.

In order to study the linewidths associated with these

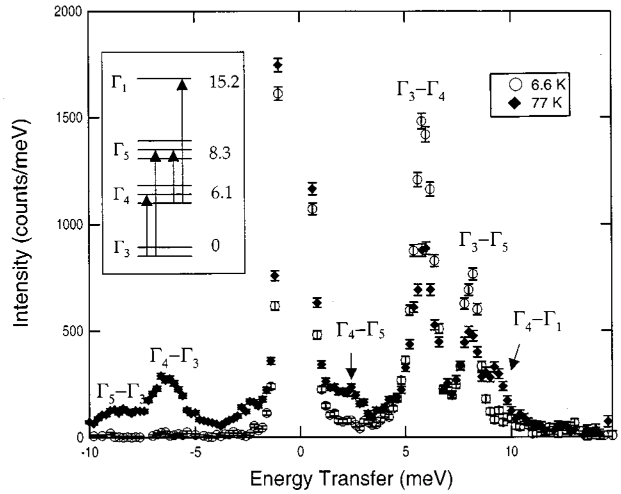

FIG. 1. Inelastic neutron spectra from PHAROS (intensity vs neutron energy loss). $E_i=25.3$ meV, and the Q range at elastic peak is 0.10–0.75 Å^{-1}. Open circles: data taken with the sample at $T=6.6$ K. Diamonds: data, which was normalized to correct for different counting times, taken with the sample at 77 K. At this higher temperature two new peaks have emerged in the spectrum at 2.2 and 9.1 meV. Inset shows the CEF level scheme that is consistent with the data. The energy resolution at the elastic line is ~1.04 meV.

peaks, and to search for any quasielastic scattering, higher-resolution measurements were conducted on QENS,[10] which has an instrumental resolution of ~90 μeV at the elastic line. We used the same sample, mounted in a helium cryostat. The sample was wrapped in Al foil and then rolled into an annulus, thereby minimizing the absorption from the In and Ag atoms, while keeping sufficient scattering mass in the beam. Data were taken at 4.4 K and 10 K. The three detector arms on QENS were placed at 40°, 90°, and 130° from the transmitted beam.

III. DETERMINATION OF CRYSTAL-FIELD LEVELS AND PARAMETERS

According to Hund's rules, the Pr^{3+} ion has $J=4$, and in $PrInAg_2$ it occupies a cubic symmetry site ($m\bar{3}m,a=7.076$ Å). As a consequence, the crystalline electric field splits the $4f$ state into four states: Γ_1 (singlet), Γ_3 (doublet), Γ_4 (triplet), and Γ_5 (triplet) (see inset to Fig. 1). Neutrons may induce transitions among different states of the manifold, resulting in peaks in the inelastic spectrum. The intensities of these peaks are proportional to the matrix elements $|\langle\Gamma_i|J_z|\Gamma\rangle|^2$ calculated by Birgeneau;[11] the relative magnitudes of these matrix elements, along with the fact that two of them are zero by symmetry, allow an unambiguous determination of the CEF scheme. Of the six possible inelastic transitions, the four allowed by symmetry are $\Gamma_1\leftrightarrow\Gamma_4$, $\Gamma_3\leftrightarrow\Gamma_4$, $\Gamma_3\leftrightarrow\Gamma_5$, and $\Gamma_4\leftrightarrow\Gamma_5$, as shown in the inset to Fig. 1. A simple Hamiltonian diagonalized by Lea, Leask, and Wolf[2] gives the energy splitting and ordering of the CEF manifold as a function of two parameters: *x*, roughly the ratio of fourth- to sixth-order terms in the CEF Hamiltonian, and *W*, which sets the overall energy scale.

The CEF spectrum is determined completely by the PHAROS data shown in Fig. 1. We fit the two inelastic

TABLE I. $PrInAg_2$ crystal-field energies and linewidths (HWHM) in meV.

	E_{Γ_1}	$\Delta E_{\Gamma_3-\Gamma_1}(4.4\,K)$	$\Delta E_{\Gamma_3-\Gamma_1}(10\,K)$
Γ_1	15.24 ± 0.04		
Γ_5	8.324 ± 0.012	0.133 ± 0.049	0.121 ± 0.024
$\Gamma 4$	6.100 ± 0.016	0.301 ± 0.017	0.300 ± 0.017
Γ_3	0		

peaks observed at $T=6.6$ K with Gaussians with widths fixed to the instrument resolution to obtain the intensities of each transition; this yields a ratio of intensities for the $\Gamma_3\rightarrow\Gamma_4$ transition to that of the $\Gamma_3\rightarrow\Gamma_5$ transition of 2.34 ± 0.08. The calculated intensity ratio[8] of these two transitions is 2.33, which is closer to the observed ratio than other possible combinations. The corresponding ratio with a Γ_4 or Γ_5 ground state is 2.67 or 1.14, respectively. Furthermore, Γ_4 can only be the ground state at $x=0.85$; at this value of x, the Γ_4, Γ_5, and Γ_3 states are degenerate, which would leave only one inelastic transition. If Γ_1 were the ground state, then there would be only one inelastic peak corresponding to the only allowed transition, $\Gamma_1\rightarrow\Gamma_4$. One might argue that if the Γ_4 triplet were sufficiently low lying, it might be thermally populated, the $\Gamma_1\rightarrow\Gamma_4$ transition would be lost in the elastic peak, and the two inelastic peaks observed are really transitions from Γ_4. This interpretation runs afoul on two points: the ratio of intensities is still inconsistent with the data, and only one new transition ($\Gamma_3\rightarrow\Gamma_5$) would remain to appear at higher temperatures, as opposed to the two observed. Therefore, Γ_3 is assigned as the ground state, Γ_4 as the first excited state at 6.1 meV (71 K), and Γ_5 at 8.3 meV (96 K). At 77 K, the Γ_4 level is thermally populated, allowing us to observe additional transitions from this level. It follows that the two new peaks observed at higher temperature correspond to $\Gamma_4\rightarrow\Gamma_5$ (2.2 meV) and $\Gamma_4\rightarrow\Gamma_1$ (9.1 meV), which puts the Γ_1 state at 15.2 meV above the ground state. The resulting level scheme is shown as the inset in Fig. 1, and the eigenenergies listed in Table I.

The energies of the Γ_4 and Γ_5 states are close to those reported by Galera *et al.*,[8] the only difference being that in the present experiment the Γ_4 state lies ~0.2 meV higher. Our level scheme is qualitatively similar to that which Yatskar *et al.*[7] derived from the specific heat (the present experiments are compared with the specific-heat measurements below). Our data are consistent with the model of Lea *et al.*[12] with $W=0.111\pm0.006$ meV and $x=-0.079\pm0.037$. When compared to the values given by Galera *et al.*[8] of $W=-0.103\pm0.017$ meV and $x=0\pm0.02$, the discrepancy in x is due to both the slight difference in the measured energy of the Γ_4 state as well as our inclusion of the Γ_1 state in the determination.

IV. LINEWIDTHS OF CRYSTAL-FIELD STATES

It is clear from the QENS data shown in Fig. 2 that both the 6.1 and 8.3 meV inelastic peaks are substantially broadened beyond the instrument resolution, indicating a finite lifetime for the CEF excitations, even at the lowest measured temperature. To investigate the broadening, each inelastic peak was fit with a convolution of a Lorentzian, given by

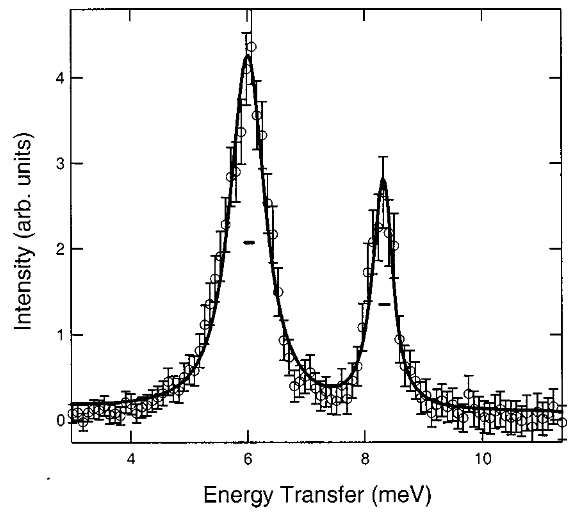

FIG. 2. Inelastic-scattering data obtained with the high-angle detector bank ($Q=2.24-2.53$ Å^{-1} at elastic line) on the QENS spectrometer. The sample temperature was 4.4 K. The solid line is the fit to the data described in the text. The horizontal lines show the calculated instrument resolution at their respective energies. The energy resolution at the elastic line is ~90 μeV.

$$S(\omega)=\frac{I}{\pi}\frac{\Gamma}{\Gamma^2+\hbar^2(\omega-\omega_0)^2}, \qquad (1)$$

and the instrument response function, where the Lorentzian models the scattering function with I and Γ as fitting parameters. The thermal factor $\langle n(\omega)+1\rangle=e^{\beta\hbar\omega}/e^{\beta\hbar\omega}-1$ was omitted as it does not differ appreciably from unity at these energy transfers and temperatures. The instrument response function must incorporate both the variation of energy resolution with energy transfer as well as asymmetry due to the moderator pulse shape. This was done by using elastic-scattering data from a nonmagnetic sample as the instrument response function; in this case we used YBe_{13} data taken with the same spectrometer and sample configurations. Monte Carlo estimates give the FWHM at the elastic line as 90 μeV, increasing to 140 μeV and 160 μeV at 6.1 meV and 8.3 meV, respectively. To account for this variation, the YBe_{13} data set's energy-transfer axis was dilated by 140/90 and 160/90 for the 6.1 and 8.3 meV peaks, respectively (the change in resolution across each peak was ignored). Because indium and silver nuclei are strong neutron absorbers, the fits were performed on data from the high-angle bank (2.23 Å$^{-1}\leqslant Q\leqslant2.53$ Å^{-1}). The resulting intrinsic linewidths are given in Table I. The same intrinsic broadening, especially of the 6.1 meV excitation, is visible in both the 6.6 K and 77 K data taken on PHAROS (see Fig. 1). In fact, this excitation broadens slightly, by ~50% in the intrinsic linewidth, between 6.6 and 77 K. This clearly rules out the linear Korringa-type relaxation, and it also seems to be inconsistent with the $\sqrt{T}$ dependence more typical of Kondo systems.

There are various scenarios that could produce the observed broadening. The first possibility would be that the crystal-field states exhibit dispersion, due to intersite exchange. Normally, single crystals are needed to see this ef-

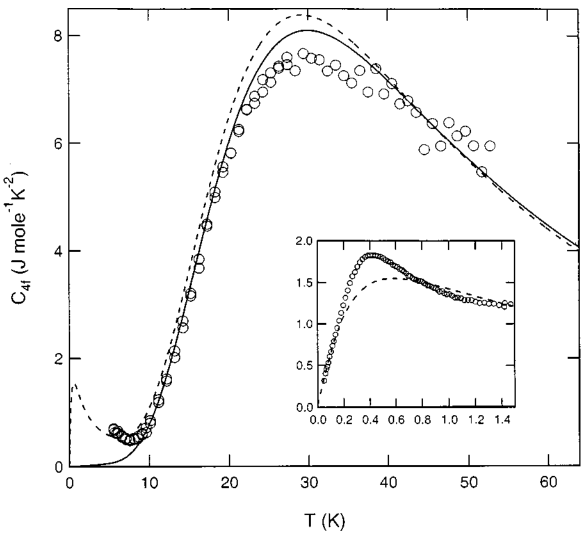

FIG. 3. The electronic specific heat C_{4f} from Yatskar *et al.* (Ref. 7) (circles) plotted as a function of temperature. The lines show calculations, described in the text, with parameters from the present experiment. Solid line: $\alpha=0$. Dashed line: $\alpha=120\,\mu$eV. The inset shows the same calculations with the specific-heat data taken below 1.4 K.

fect, as a function of **Q**, and it is not easy to measure dispersion in polycrystalline samples like ours. In fact, our PHAROS data all lie within the first Brillouin zone, and the broader 6.1 meV peak is observed over ~30% of the zone. There is no observable dispersion (to within 100 μeV) over this Q range, at either 6.6 K or 77 K, so the intrinsic full width of 600 μeV FWHM listed in Table I is probably not due to dispersion. A second possibility would be that the local site symmetry (point group) is reduced, perhaps by a structural distortion. There is no evidence for any splitting of the triplet excited states in our data, nor of any phase transitions in the specific heat. A third possibility would be that the conventional magnetic Kondo effect acts on the Γ_4 and Γ_5 excited states, which do indeed possess dipole moments. Normally, this gives a $\sqrt{T}$ dependence of the linewidth at high temperatures and would seem to be in better agreement with our data than the linear Korringa-type temperature dependence. Finally, in the neutron-scattering experiment, we observe widths associated with transitions between two states, i.e., a joint density of states, and not just the excited state. Therefore, any ground-state broadening associated with the quadrupolar-Kondo effect, or whatever else is giving the huge low-temperature specific heat, must be present in our observations of the excited states, and it should be equal in both the Γ_3-Γ_4 and Γ_3-Γ_5 transitions. For a doublet ground state, the observed low-temperature specific heat ($\gamma=6.5\,\mathrm{J\,mol^{-1}\,K^{-2}}$) would imply[13] a quasielastic half width for the ground state of $\alpha\sim120\,\mu$eV, and this is very close to the observed linewidth of the Γ_3-Γ_5 transition listed in Table I. While this is very suggestive, there must be a different interaction that gives a larger intrinsic width for the Γ_4 level, as it is so much broader. The specific heat can be calculated assuming the observed transition linewidths, with and without intrinsic broadening of the ground state, i.e., $\alpha=0$ and 120 μeV. The results are shown in Fig. 3, along with the observed specific data of Yatskar *et al.*[7] Above 10 K, both

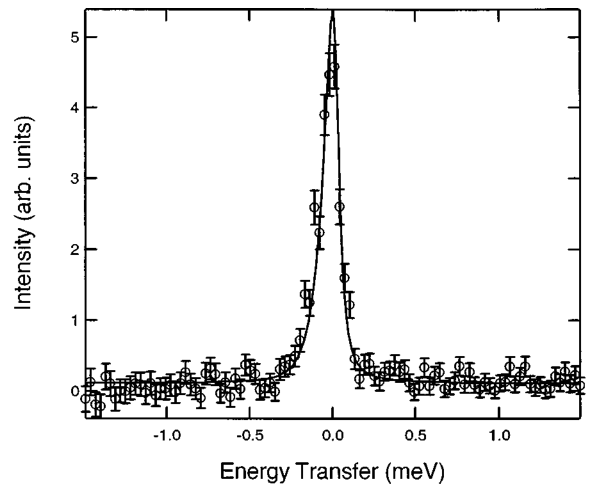

FIG. 4. Scattering data, centered on the elastic peak, obtained with the low-angle detector bank ($Q=0.83$–$0.99\,\mathrm{Å}^{-1}$ at the elastic line) on the QENS spectrometer. The sample temperature is 4.4 K. The solid line is the fit to the data described in the text.

models agree pretty well with observation, and there is not much difference between them. However, the broadened ground state is necessary to reproduce any of the specific heat below 10 K as shown in the inset.

Because the Γ_3 ground-state level is not magnetic, quasielastic scattering is not expected in a neutron-scattering experiment. To check this assertion, a procedure similar to that used to fit the inelastic peaks was employed. YBe_{13} data were again used as the instrument response function I. We compare two models: the first assumed that $d\sigma/dE\propto cI+IS'$, where c is a constant determined by fitting, $S'=\omega[\langle n(\omega)+1\rangle]S$, and S is the Lorentzian given by Eq. (1). The first term represents purely elastic scattering, while the second term models the quasielastic response of a paramagnet. The second model simply took $d\sigma/dE\propto cI$. In this case, the low-angle ($0.83\,\mathrm{Å}^{-1}\leqslant Q\leqslant0.99\,\mathrm{Å}^{-1}$) data measured with QENS (Fig. 4) were analyzed because data close to the elastic peak taken with higher-angle detectors contained spurious scattering from the cryostat. We found that the first model did not work: there is no evidence in the data for quasielastic scattering at either 4.4 K or 10 K. This sets an upper limit of 90 μeV (FWHM), the resolution of QENS, on any quasielastic scattering.

V. CONCLUSION

We have confirmed definitively that the heavy-fermion compound $PrInAg_2$ has a nonmagnetic Γ_3 CEF ground state by observing all four allowed cubic CEF excitations. No quasielastic scattering was seen, placing an upper bound of 90 μeV on the linewidth of any such phenomenon. However, the inelastic peaks at low temperatures are significantly broadened. While one excited state is broadened more strongly, the narrower Γ_3-Γ_5 excited state has a width that is comparable with that of the ground-state fluctuation associated with the observed linear specific heat. In addition, although we have relatively few temperature points, it is clear that the linewidths do not increase linearly with temperature, and it is possible that the $\sqrt{T}$ dependence found in regular Kondo systems applies.

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[13] Experiments on cerium-based heavy-fermion systems, where quasielastic scattering is observed, show $\Gamma\gamma \sim 0.8\,\mathrm{J\,meV\,mol^{-1}\,K^{-2}}$ (again, Γ is the quasielastic HWHM, γ the Sommerfeld coefficient). On this basis, we expect $\alpha \sim 120\,\mu\mathrm{eV}$, which is still consistent with the observed linewidths.