Possible Correlated-Electron Behavior from Quadrupolar Fluctuations in $PrInAg_2$

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(Received 12 July 1996)

The temperature dependent magnetic susceptibility, specific heat, and electrical resistivity were measured on $PrInAg_2$. A broad peak, which is identified as a Kondo anomaly, is observed in the specific heat at ~ 0.4 K with a strongly enhanced linear contribution at lower temperatures. $PrInAg_2$ is a Pr-based heavy-fermion compound and has one of the largest known Sommerfeld coefficients of ~ 6.5 J/mol K^2. A new type of nonmagnetic interaction between the conduction electrons and the non-Kramers doublet ground state of the Pr^{3+} ion may be responsible for this behavior. Related features are also observed in the susceptibility and resistivity. [S0031-9007(96)01532-3]

PACS numbers: 75.30.Mb, 65.40.+g, 71.27.+a, 75.40.Cx

The conventional Kondo effect in Ce-, U-, and Yb-based intermetallic systems involves the formation of a coherent spin-singlet ground state from an antiferromagnetic coupling between the f moments and the conduction electrons [1]. A new type of interaction that leads to correlated behavior at low temperatures has recently been proposed to explain the weak magnetic-field dependence of the thermodynamic properties and the anomalous quasielastic neutron scattering in some U-based systems [2]. If the crystal-electric-field (CEF) ground state of the localized f electron is a nonmagnetic, non-Kramers doublet (Γ_3), the fluctuating quadrupolar moment of this ground state could interact with the conduction electrons to produce strongly correlated properties. Like the conventional Kondo effect, a new small energy scale T_K emerges, and this characterizes the renormalized properties that develop at low temperatures. Because the quadrupolar interaction involves more than one electron channel, the localized electron is overcompensated by the surrounding conduction electron cloud below T_K [2]. The resulting ground state is described as a non-Fermi liquid where the quadrupolar susceptibility and specific heat have logarithmic temperature dependencies [3], and the resistivity varies as $T^{1/2}$ [4]. The magnetic susceptibility arises from virtual excitations between the nonmagnetic ground state and the excited CEF levels (i.e., Van Vleck), and it has a $T^{1/2}$ dependence [5].

Numerous U- and Ce-based systems have now been found that display non-Fermi-liquid properties [2,6]. Unfortunately, there is no experimental verification that the ground state is Γ_3 in these systems [7], and alternative models for non-Fermi-liquid behavior such as fluctuations from a quantum critical point associated with an unknown order parameter [8] or a distribution of Kondo temperatures [9] have been proposed. Many of these systems require doping in order to exhibit non-Fermi-liquid behavior, raising the question of chemical inhomogeneity of the sample.

In order to study the possible interaction between conduction electrons and a degenerate, nonmagnetic CEF level, we have chosen Pr intermetallic compounds as likely candidates for three reasons. First, in the Russel-Saunders coupling scheme Pr^{3+} has the same series of CEF levels as U^{4+} [10]. Second, there is little debate regarding the existence of CEF levels in the more localized $4f$ systems. Finally, the possibility existed for finding a line compound that does not require doping.

In this Letter, we report the discovery of a heavy and apparently Fermi-liquid-like ground state at low temperatures in $PrInAg_2$ with a Sommerfeld coefficient of ~ 6.5 J/mol K^2, making this the first Pr-based heavy-fermion compound [11]. The most intriguing aspect regarding this discovery is the likelihood that the CEF ground state of $PrInAg_2$ is Γ_3. This result follows from previous neutron-scattering experiments [12]. In addition to the elastic peak, two inelastic peaks exist at 5.9 and 8.3 meV. From their intensities, the peaks are identified as transitions from a Γ_3 ground state to Γ_4 and Γ_5 magnetic triplets, respectively. Based on this interpretation, $PrInAg_2$ is not only heavy, but may also be a clear example of an f-electron system where a nonmagnetic interaction is responsible for correlated-electron behavior.

$PrInAg_2$ was synthesized by placing stoichiometric amounts of Pr, In, and Ag in a Ta crucible, sealed in an evacuated quartz tube, and slowly cooled from 1050 °C to 800 °C over 100 hours and then held at 800 °C for 50 hours. After the sample was quenched, a dense, large-grain ingot was removed from the crucible. Powder x-ray diffraction spectra confirmed that the structure was face-centered cubic with a lattice parameter of 7.075 Å,

consistent with the Heusler crystal structure (BiF_3 structure) reported by Galera *et al.* [12].

A Quantum Design magnetometer was used to measure the static magnetization from 1.8 to 350 K in an applied field of 1 kOe. From 50 to 2 K the specific heat was obtained using a thermal relaxation technique [13], where a sample weighing ~15 mg was attached to a thermometer/heater sapphire platform with a small amount of Apiezon grease. Below 2 K, the specific heat of an ~30 mg sample was determined with a quasiadiabatic technique [14]. The absolute uncertainty in the specific heat is approximately $\pm 2\%$, and in the temperature range where the calorimeters overlap, the data agree within the absolute uncertainty. For resistivity, the sample was polished into a wedge-shaped rod, and leads were attached to it in a four-probe configurations using silver paint. A Linear Research LR400 four-wire ac resistance bridge was used to measure the resistivity from 50 mK to 300 K.

The reciprocal magnetic susceptibility is plotted versus temperature in Fig. 1(a). Above $T \sim 50$ K, a Curie-Weiss temperature dependence is observed. From the high-temperature slope, the effective moment is 3.65 μ_B, a value that is slightly larger than 3.58 μ_B calculated for the Hund's-rule ground state of Pr^{3+}. Since an ordered ground state does not occur in this compound, the Weiss temperature of -22 K indicates that short-range antiferromagnetic correlations are present at temperatures above the first excited CEF level.

At lower temperatures the magnetic susceptibility deviates below the Curie-Weiss behavior extrapolated from high temperatures. As can be seen in Fig. 1(b), the susceptibility starts to level off below ~20 K before turning up at the lowest temperatures. Whether or not the low-temperature upturn is intrinsic is not known, but at 2 K magnetization isotherms are approximately linear to 50 kOe. If one neglects this upturn, the susceptibility appears to saturate at ~0.04 emu/mol. This is consistent with a Van Vleck contribution for excited CEF levels above a nonmagnetic ground state. Assuming the Γ_4 and Γ_5 CEF levels are at the energies seen by inelastic neutron scattering [12], the calculated Van Vleck susceptibility is ~0.043 emu/mol [15]. No anomalies associated with superconducting or magnetic order were observed throughout the measured temperature range.

To determine the importance of electron correlations in this material, the specific heat was measured from 50 K to 50 mK. The phonon contribution was ascertained from a measurement of the isostructural compound $LaInAg_2$. The high-temperature specific heat for both compounds is shown in Fig. 2(a). It is apparent from a comparison of the data that the specific heat of $PrInAg_2$ in this temperature range is dominated by phonon excitations. A deviation from the T^3 approximation of the Debye model for acoustic phonons is observed in the specific heat of $LaInAg_2$ at our lowest measurement temperature of 5 K, indicating very low frequency phonon excitations may exist in these compounds. After subtracting off the data for $LaInAg_2$, the excess specific heat associated with the $4f$ electrons C_{4f} of $PrInAg_2$ is plotted as a function of temperature in Fig. 2(b). This contribution is well

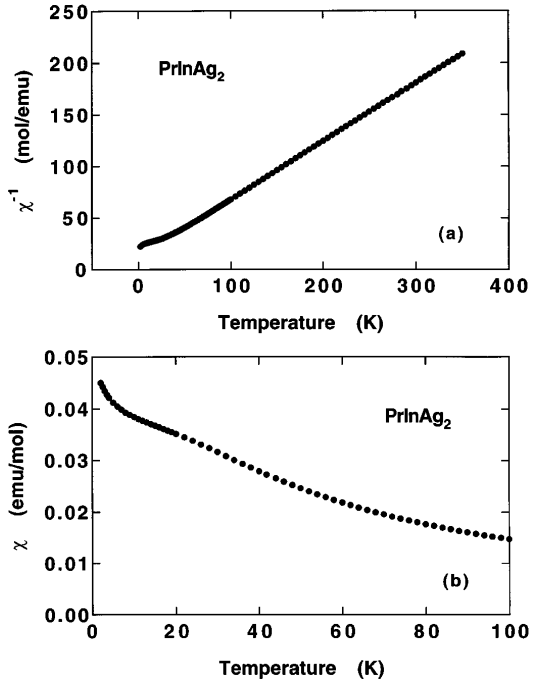

FIG. 1. (a) Inverse magnetic susceptibility χ^{-1}, normalized per mole Pr, versus temperature for $PrInAg_2$. The measurement was performed with a field of 1 kOe. (b) Magnetic susceptibility χ at lower temperatures.

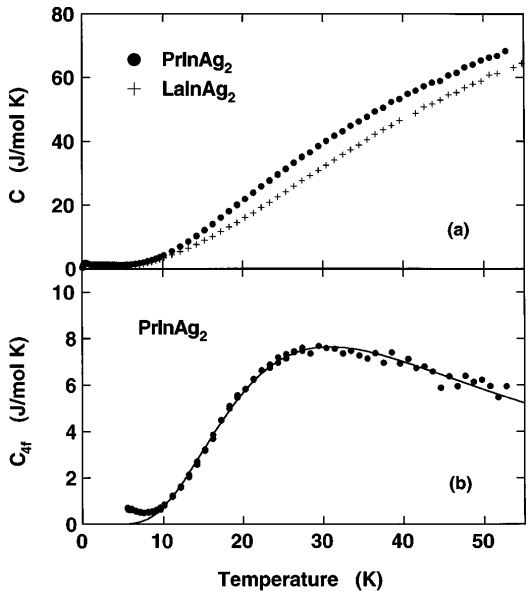

FIG. 2. (a) The high-temperature specific C versus temperature for $PrInAg_2$ (solid circles) and $LaInAg_2$ (crosses). The data are normalized per mole rare earth. (b) The $4f$ contribution to the specific heat C_{4f} for $PrInAg_2$ as a function of temperature. The solid line in (b) is a calculation based on a doubly degenerate ground state with two triply degenerate and one singly degenerate CEF levels at 5.7, 9.8, and 19.2 meV, respectively.

described [solid line in Fig. 2(b)] by a model that is based on two triply degenerate and one singly degenerate CEF levels at 5.7, 9.8, and 19.2 meV, respectively. The first two of these levels are reasonably close to the two CEF excitations observed by neutron scattering [12].

The low-temperature specific heat is plotted in Fig. 3(a). A pronounced peak at $T \sim 0.4$ K is visible, evolving into a linear temperature dependence at lower temperatures. A fit to the data below ~200 mK yields a Sommerfeld coefficient γ of ~6.5 J/mol K^2, and the dramatic increase and eventual saturation of $\gamma = C/T$ is evident when the data are plotted as C/T versus T as in Fig. 3(b). This specific heat anomaly is similar to the prediction of the Coqblin-Schrieffer model for a single-channel Kondo impurity [16]; the maximum value of the peak is slightly larger than the calculation for $J = \frac{1}{2}$ with a $T_K = 0.8$ K [solid line in Fig. 3(a)]. Using the single impurity relation $T_K = 1.29\pi R/6\gamma$, where R is the gas constant, the Kondo temperature is estimated to be 0.86 K [16]. Not only is this a Pr-based heavy-fermion compound, but its Sommerfeld coefficient is close to the largest ever observed (~8 J/mol K^2 for YbBiPt over a similar temperature range [17]).

Even more fascinating is the possible source of this correlated-electron behavior. While the projection of the magnetic moment J_z onto the Γ_3 ground state in $PrInAg_2$ is zero, the electric-quadrupolar moment $3J_z^2 - J(J+1)$ does not vanish. The conduction electrons can in principle interact with the internal degrees of freedom associated with the quadrupolar moment of the Pr ion, and this interaction, which has a characteristic temperature, can lift the ground state degeneracy as the system is cooled through this temperature. Unlike the prediction of the quadrupolar Kondo model [3], however, the specific heat of $PrInAg_2$ appears to be a Fermi liquid ($\lim_{T\to 0} C(T)/T = \text{const}$). Furthermore, when the entropy is calculated by integrating C/T, it tends to saturate around 3–6 K before increasing again because of thermal and CEF excitations. At $T \sim 4.4$ K, the entropy is $R \ln 2$, implying the full degeneracy of the ground state is lifted by the interaction. This is not consistent with the presence of a fractional residual entropy of $\frac{1}{2}R \ln 2$ predicted for the quadrupolar Kondo model.

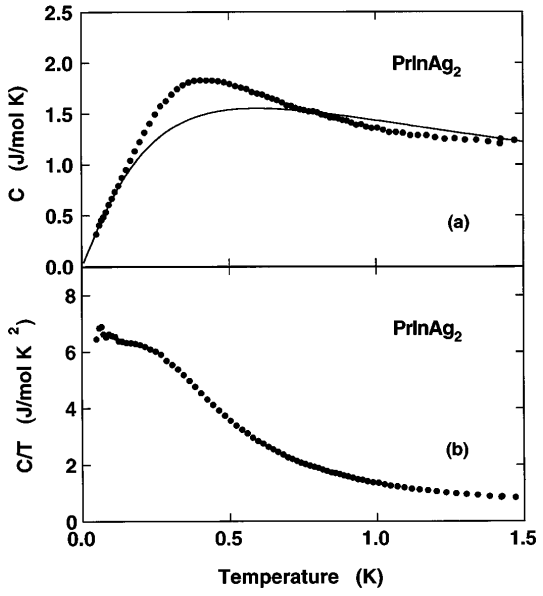

FIG. 3. (a) The specific heat C, normalized per mole Pr, at low temperatures for $PrInAg_2$. The solid line is a calculation for the Coqblin-Schrieffer model with $J = \frac{1}{2}$ and $T_K = 1.29T_0 = 0.8$ K [16]. (b) C/T versus temperature for the data in (a).

A periodic lattice containing Pr^{3+} ions with a non-Kramers doublet ground state should be unstable to some type of cooperative Jahn-Teller effect. In practice, these effects manifest themselves as either first- or second-order phase transitions [18]. For $PrInAg_2$ there is no evidence of a phase transition in the specific heat or resistivity down to 50 mK. It is possible that a competition exists between a broken symmetry and an enhanced Fermi-liquid ground state which depends on the strength of the exchange parameter, similar to the magnetic analog [19]. In this case the system quadrupolarly orders as in $PrPb_3$ at $T_Q = 0.35$ K [20] when the exchange is weak, while a Fermi-liquid ground state prevails in $PrInAg_2$ because the exchange is larger. Also, the quadrupolar susceptibility for a single impurity diverges at low temperatures if a two-channel interaction is important [2]. The Fermi-liquid-like behavior in $PrInAg_2$ may indicate that the two-channel symmetry of the quadrupolar interaction is lifted.

Even though the specific heat is fairly typical of a heavy Fermi liquid, the electrical resistivity is more uncharacteristic. In Fig. 4(a) the electrical resistivity is displayed as function of temperature. Similar to that reported by Galera *et al.* [12], the resistivity monotonically decreases with decreasing temperature with no indication of a coherence peak. The residual resistivity ratio calculated with the resistivities at 300 and 4 K is ~6.5, implying the sample has relatively few defects. Above ~150 K, the resistivity is linear in temperature. The resistivity drops below the high-temperature linear extrapolation as the temperature is lowered through a range where the CEF levels exist and then levels off below ~10 K. Above ~10 K the resistivity is dominated by inelastic scattering from phonons and CEF excitations. The resistivity at low temperature is plotted in Fig. 4(b). Below ~1.6 K, the resistivity starts to decrease again and continues to do so down to our lowest measurement temperature of 50 mK where its value is only ~5 $\mu\Omega$ cm. The maximum change occurs at ~0.3 K, which is just below the temperature of the specific heat peak in Fig. 3(a). This low-temperature behavior is highly unusual and probably originates from the same source as the heat capacity anomaly. It is difficult to characterize the exact low-temperature dependence of the resistivity because the coherent regime is very narrow as expected from the small T_K. If the data below 0.4 K are fit to a T^2 expression, the coefficient is more than an order of magnitude smaller than expected from the size of the Sommerfeld coefficient [21].

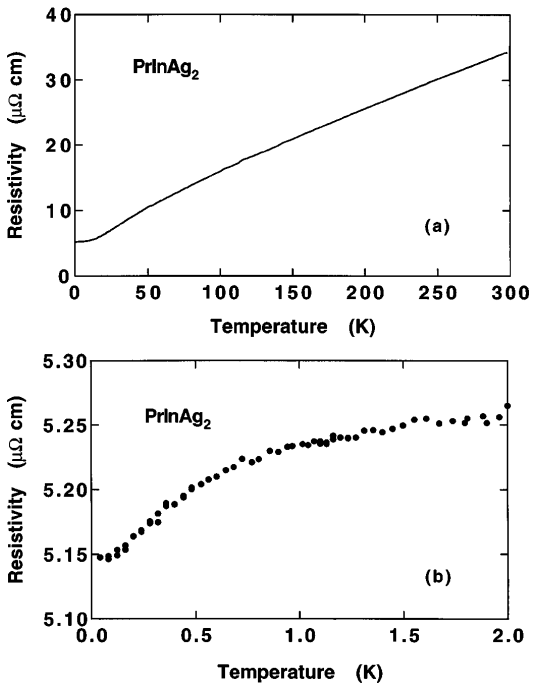

FIG. 4. (a) The temperature dependent resistivity for $PrInAg_2$. To illustrate a small downturn in the resistivity at low temperatures, the data below $T = 2$ K are plotted in (b). Note that the resistivity axis is greatly expanded and offset from zero.

In summary, we report the discovery of the first Pr-based heavy-fermion compound with a very large Sommerfeld coefficient of ~ 6.5 J/mol K^2. This heavy Fermi liquid seems to result from a new type of nonmagnetic interaction between the conduction electrons and the non-Kramers Γ_3 doublet ground state of the Pr^{3+} ion. From the specific heat data we estimate $T_K \sim 1$ K. The magnetic susceptibility exhibits Curie-Weiss behavior at high temperatures, while the low-temperature behavior is consistent with a Van Vleck contribution from a nonmagnetic ground state and a small Curie tail, which could be extrinsic. The temperature-dependent electrical resistivity monotonically decreases with temperature in a fashion atypical for a correlated-electron material, but manifests a loss of scattering when cooled through T_K. Finally, there is no evidence of a phase transition in the measured properties above 50 mK.

Further experiments are needed to fully characterize the unusual properties thought to arise from quadrupolar interactions in $PrInAg_2$. Since the ground state is nonmagnetic, the thermodynamic properties should be insensitive to applied magnetic fields, and measurements of the field dependence are now in progress. We are also investigating other Pr intermetallic compounds for evidence of correlated behavior. In some cases preliminary results, which will be reported in subsequent publications, indicate that $PrInAg_2$ is not unique in its correlated-electron behavior.

We are grateful to N. K. Budraa for his assistance with the specific heat measurements and to A. Panchula and S. L. Bud'ko for their help in growing and characterizing the samples. We also acknowledge D. L. Cox and D. E. MacLaughlin for helpful discussions. This research was supported by the National Science Foundation under Grant No. DMR-9624778. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. Work at Ames and Los Alamos National Laboratories were performed under the auspices of the Director for Energy Research, Office of Basic Energy Sciences.

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