Electronic State of $PuCoGa_5$ and $NpCoGa_5$ as Probed by Polarized Neutrons

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By using single crystals and polarized neutrons, we have measured the orbital and spin components of the microscopic magnetization in the paramagnetic state of $NpCoGa_5$ and $PuCoGa_5$. The microscopic magnetization of $NpCoGa_5$ agrees with that observed in bulk susceptibility measurements and the magnetic moment has spin and orbital contributions as expected for intermediate coupling. In contrast, for $PuCoGa_5$, which is a superconductor with a high transition temperature, the microscopic magnetization in the paramagnetic state is small, temperature-independent, and significantly below the value found with bulk techniques at low temperatures. The orbital moment dominates the magnetization.

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The isostructural intermetallic compounds of the RTX_5 series with $R =$ (Ce, U, Np, Pu), $T =$ (Co, Rh, Ir, Fe, Ni) and $X =$ (Ga, In) show a wide range of interesting electronic and magnetic properties. Especially the discovery of superconductivity in $PuCoGa_5$ at the surprisingly high temperature of $T_{sc} = 18$ K stimulated considerable research into the interplay of magnetism and superconductivity of these compounds [1].

We report here on polarized-neutron diffraction experiments [2]. Our measurements probe the spatial dependence of the magnetization and reveal the microscopic magnetic properties of the superconductor $PuCoGa_5$ in the *normal* state, as well as those of its neptunium-based homologue $NpCoGa_5$. Important new insights emerge from such a comparison.

$NpCoGa_5$ shows longitudinal-modulated antiferromagnetic (AF) order below $T_N = 47$ K characterized by a propagation vector $\mathbf{q} = (0, 0, 1/2)$ [3]. In the ordered state a moment parallel to the c axis of $\mu = 0.8\ \mu_B$ where μ_B denotes the Bohr magneton $\mu_B = e\hbar/2m_e = 9.274\,10^{-24}$ J/T, and a magnetic form factor consistent with a Np^{3+} ion has been reported. The temperature dependence of the magnetic susceptibility is shown in Fig. 1. In the paramagnetic state at high temperatures a Curie-Weiss-like behavior is observed. Recent NMR experiments [4] in the paramagnetic state indicate a crossover from localized behavior at high temperatures to itinerant magnetic properties below 100 K. Interestingly, the magnetic excitation spectrum investigated by inelastic neutron scattering suggests itinerant behavior in the antiferromagnetically ordered state [5].

No magnetic order has been found down to 1 K in $PuCoGa_5$ [6]. Initial bulk susceptibility measurements [1] are shown in Fig. 1. Subsequent experiments, at ITU as well as at Los Alamos National Laboratory [7], on various single crystalline samples, both $^{239}PuCoGa_5$ and $^{242}PuCoGa_5$, have given a significantly lower value of the susceptibility. These differences are not understood, but may be attributed to impurities, possible additional phases, and difficulties in measuring small susceptibilities on encapsulated samples. Measurements performed at ITU using a SQUID magnetometer with the same $^{242}PuCoGa_5$ sample as used for the neutron experiments, and the field applied in the same direction, are shown also in Fig. 1.

$PuCoGa_5$ and $NpCoGa_5$ crystallize in the $P4/mmm$ tetragonal structure with similar lattice parameters $a = 4.2$ Å and $c = 6.8$ Å and the actinide atoms in the 1a special position [6]. For our neutron scattering experiments a $NpCoGa_5$ single crystal of $m = 126$ mg was grown from a melt of the elements. Because of its high neutron absorption cross section, the most common isotope ^{239}Pu is not optimum for neutron diffraction. The present experiments were performed on a 160 mg $^{242}PuCoGa_5$ sample. The use

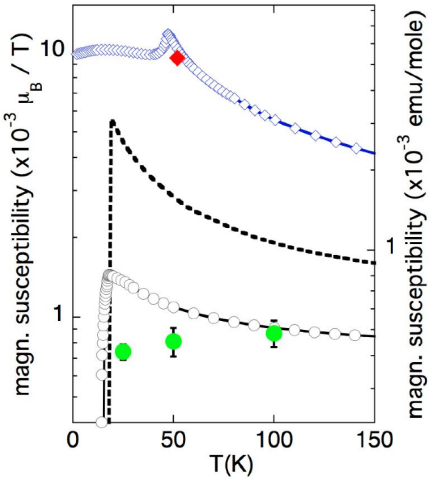

FIG. 1 (color online). Magnetic susceptibility (1 emu/mole = 1.79 μ_B/T) of $NpCoGa_5$ and $PuCoGa_5$ as a function of temperature with $B \parallel a$. Blue open diamonds: $NpCoGa_5$ [3]; red closed diamond: $NpCoGa_5$ deduced from the neutron form factor (this work); dashed line: $PuCoGa_5$ as previously published [1]; open black circles: measured at ITU on the same single crystal of $^{242}PuCoGa_5$ as used for the neutron experiments; green closed circles: deduced from the neutron form factor (this work).

of this isotope also avoids effects from radiation damage over the time scale of these experiments. The crystal was grown from the melt using ^{242}PuSb instead of metallic ^{239}Pu as starting material leading to traces of Sb (<1%) in the crystal. The observed superconducting transition temperature is slightly reduced to about $T_{sc} = 15$ K with respect to previous material, but other properties are similar to those reported [6,7]. Both crystals were oriented and encapsulated in a double wall container with a horizontal b-c scattering plane.

The neutron diffractometer D9 of the ILL, Grenoble, France,[8] was used in normal beam geometry to measure about 600 nuclear reflections with a wavelength of $\lambda_1 = 0.84$ Å as well as about 1000 nuclear reflections at $\lambda_2 = 0.43$ Å to determine the crystallographic parameters of $PuCoGa_5$ at $T = 25$ K. The crystallographic parameters are consistent with those reported in the literature [6] and were used in the treatment of the polarized-neutron experiments, together with the relevant corrections for absorption and extinction.

The polarized-neutron experiments on both compounds were performed on the ILL diffractometer D3 [9]. A segmented cryomagnet equipped with a dedicated insert for transuranium samples was used to apply a vertical magnetic field of $B = 9.6$ T parallel to the a axis. We measured flipping ratios $R = I^+/I^-$ at a selection of nuclear Bragg peaks, where I^+ and I^- are measured with the incident neutron beam polarized (at 93%) parallel and antiparallel to the magnetic field, respectively. The selected reflections cover various directions in reciprocal space with different (stronger and weaker) nuclear structure factors. In comparing the data taken on the two samples using different neutron wavelengths, only reflections with structure factors $|F_N| \geq 0.25 \times 10^{-12}$ cm/f.u. were found reliable. During the experiment, many different equivalent reflections were measured. For $PuCoGa_5$ we performed most of our measurements at $T = 25$ K and $\lambda_1 = 0.84$ Å and retained 18 nonequivalent reflections. At $T = 50$ K and $T = 100$ K three reflections (1 0 0), (0 0 2), and (0 0 4) were measured. For $NpCoGa_5$ the experiment was performed at $T = 52$ K and two wavelengths $\lambda_1 = 0.84$ Å (34 nonequivalent reflections) and $\lambda_2 = 0.54$ Å (10 nonequivalent reflections). To extract the magnetic structure factors from the measured flipping ratios all relevant corrections have been applied [9]. Within the statistics of our measurements contributions from Schwinger scattering are not significant and are neglected.

We first report the experimental results on $NpCoGa_5$. Since all analysis methods used to reconstruct the magnetization density map indicate that the only significant magnetization is associated with the neptunium atom, we can examine the results in a more transparent way by plotting the observed structure factors as a function of $Q = 4\pi \sin(\Theta)/\lambda$ (Fig. 2). We then fit the data points to a curve with a Np^{3+} form factor such that $F_M = \mu_{\text{Total}}(\langle j_0 \rangle + C_2\langle j_2 \rangle)$ using the dipole approximation [10]. Assuming intermediate coupling [11] $C_2 = 2.11$ [3,10]. The radial integrals $\langle j_i \rangle$ are calculated from Dirac-Fock solutions of the $5f$ single-electron wave function, and are well known [10]. The fit is shown in Fig. 2 and by extrapolation to $Q = 0$ gives a total induced moment $\mu_{\text{Total}} = 0.091(1)\ \mu_B$ for an applied field of $B = 9.6$ T. This value in the forward direction should correspond exactly to the susceptibility as measured by bulk techniques [3]. We find a value of 9.5(1) $m\mu_B$/T, which is marked by the red diamond in Fig. 1. Considering the methological differences and the required extrapolation to $Q = 0$, this is in good agreement with the susceptibility of 10.3 $m\mu_B$/T as measured with bulk techniques. The Pearson correlation coefficient, R_{PMCC}, which ranges from 0 for uncorrelated data points to 1 for perfect correspondence, is 0.94. Further efforts to refine the data with the inclusion of an induced susceptibility at the Co site and to change C_2 do not result in any significant improvement of the fit. We therefore conclude that the magnetic structure factors observed for $NpCoGa_5$ are well described by a Np^{3+} form factor within an intermediate coupling scheme. These results are consistent with those for other Np intermetallics and in good agreement with recent work on the elements defining the need for intermediate coupling for Np [11]. Nevertheless, they do not exclude hybridization and band effects in such materials as inferred from NMR [4] and inelastic neutron scattering [5] results.

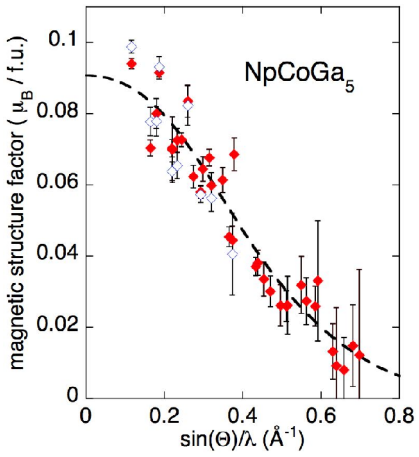

FIG. 2 (color online). Magnetic structure factors of $NpCoGa_5$ plotted as a function of $Q/4\pi = \sin(\Theta)/\lambda$ at $T = 52$ K with a magnetic field $B = 9.6$ T applied parallel to the a axis. The data are taken with two different wavelengths $\lambda_1 = 0.84$ Å (closed diamonds) and $\lambda_2 = 0.54$ Å (open diamonds). The dashed line is a fit to a Np form factor as discussed in the text.

We now turn to the results on $PuCoGa_5$. The 18 measured magnetic structure factors F_M are plotted as a function of $\sin(\Theta)/\lambda$ in Fig. 3. The smaller value of the susceptibility, 1 order of magnitude less than $NpCoGa_5$, see Fig. 1, implies worse statistics. Moreover, when dealing

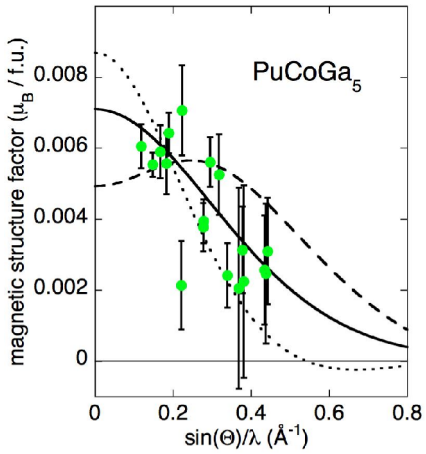

FIG. 3 (color online). Magnetic structure factors of $^{242}PuCoGa_5$ plotted as a function of $Q/4\pi = \sin(\Theta)/\lambda$ at $T = 25$ K with a magnetic field $B = 9.6$ T applied parallel to the a axis. The data are taken with $\lambda_1 = 0.84$ Å. The dashed, dotted, and solid lines are different fits to a Pu form factor as discussed in the text.

with such small induced moments the diamagnetic contributions [12] of the core electrons of all elements are relevant. Diamagnetic contributions amount to $\chi = -15 \times 10^{-6}$ emu/mole and $\chi = -40 \times 10^{-6}$ emu/mole [13] for the argon (on the Co and Ga sites) and radon (on the Pu site) core electrons, respectively, and lead to changes of ≈10% in the position of the data points in Fig. 3.

To start the quantitative analysis an induced paramagnetic moment on the plutonium site is assumed. The dashed line in the figure is the best fit when using a free-ion form factor for Pu^{3+} with an intermediate coupling scheme, e.g. $C_2 = 3.8$. This Pu^{3+} form factor [10,14] has a characteristic maximum at $\mathbf{Q} > 0$, but gives a poor fit and this is confirmed with $R_{\mathrm{PMCC}} = 0.28$. We next fix $C_2 = 0$, which corresponds to a model with spin-only, i.e., no orbital moment, and this is shown as a dotted curve. The fit is again poor, with $R_{\mathrm{PMCC}} = 0.36$. Allowing C_2 to vary gives the solid curve fit with $C_2 = 1.3(3)$, which is a considerable improvement and significant with $R_{\mathrm{PMCC}} = 0.78$. The inclusion of additional parameters such as an induced paramagnetic moment on the Co site gives no significant improvement in the fit.

The extrapolation of the best fit leads to a susceptibility of 0.74(5) $m\mu_B/T$ at $T = 25$ K on the actinide site, which is marked as a solid green point in Fig. 1. All possible values of the intercept in Fig. 3 are considerably (by about 50%) below the value of the susceptibility as measured by bulk magnetization on the *same* sample. The neutron value represents the contribution from the periodic moment arrangement in $PuCoGa_5$ only, and is insensitive to impurities. To investigate further the discrepancy between the microscopic induced moment and the induced magnetization from bulk measurements we measured some flipping ratios at 50 and 100 K. Within the precision of these measurements, no significant temperature dependence is observed; the extrapolation assuming the same form factor as at 25 K, i.e., $C_2 = 1.3$, gives 0.81(10) and 0.87(10) $m\mu_B/T$ at 50 and 100 K, respectively. This small, temperature-independent, value is a major result of our experiment, and puts into question current models of the *normal* state in $PuCoGa_5$.

Our experiments establish significant differences in the microscopic magnetic properties of $NpCoGa_5$ and $PuCoGa_5$: the paramagnetic form factor of Np in $NpCoGa_5$ is consistent with a Np^{3+} form factor expected for intermediate coupling and is similar, as expected, to the form factor observed in the ordered state [3].

The situation is different for $PuCoGa_5$. At 25 K, just above T_{sc}, the microscopic magnetization as deduced from the neutron measurements appears to be ≈50% of that found with bulk measurements on the same crystal. Only the latter shows a temperature dependence, the measured bulk and neutron values agree at higher temperatures. The absolute value of the susceptibility observed with neutrons [$0.74(5)\ m\mu_B/T = 0.41(3) \times 10^{-3}$ emu/mole at $T = 25$ K] is close to the values found in Pu metal (0.50×10^{-3} emu/mole) [15] and PuTe (0.30×10^{-3} emu/mole) [16]. Both these materials show an almost temperature-independent susceptibility, as found also for $PuCoGa_5$ with neutrons, and neither have localized $5f$ states or order magnetically.

The value of $C_2 = +1.3(3)$ derived here may be directly related to the ratio of orbital (μ_L) to spin (μ_S) moments, as $C_2 = (\mu_L)/(\mu_L + \mu_S)$. The value of C_2 greater than one shows that μ_L and μ_S are antiparallel. A simple derivation suggests that $\mu_L/\mu_S \approx -4$. A dominant orbital moment is found also for PuTe,[13] where $C_2 \approx 1$. PuTe is understood as an intermediate-valence system, either on the basis of atomiclike $5f$ states [16] or within a band picture in which the $5f$ and conduction electrons (mostly $6d$) are strongly hybridized [17]. Thus, from a discussion of the C_2 coefficient, a model of localized $5f$ states in $PuCoGa_5$ is incompatible with the neutron form factor as shown in Fig. 3.

As expected given the wide interest in the RTX_5 compounds, there have been many theoretical papers published describing the electronic state of Pu in $PuCoGa_5$. Most theories have at least started from the local spin-density approximation (LSDA) model [18] and find that the dominant contribution to the Pu state comes from the $5f^5$ manifold (i.e. trivalent Pu^{3+}). Adding Coulomb correlations to the model (LSDA + U) [19,20] then starts to include other manifolds, in particular, the $5f^6$ (i.e., divalent Pu^{2+}) state, which is nonmagnetic, and the result is a partial quenching of the magnetism. Whereas all these theories calculate photoemission spectra close to those observed, they all have the Pu ion close to magnetic order. In addition, in the one calculation giving possible C_2 values

[19], the value is predicted to be negative, a situation never found in neutron experiments on any f-electron system.

The theoretical problem of treating the electronic state of Pu in $PuCoGa_5$ appears to be similar to that encountered in Pu metal [21]. Starting with a localized model with five $5f$ electrons may not, in fact, be a good first approximation, as shown by our experiments.

In summary, the experiments reported here have shown that the *normal* state of $PuCoGa_5$ is substantially different from that anticipated from a conventional Pu^{3+} ion, which would exhibit Curie-Weiss-like behavior in the normal state. Instead, the susceptibility is small, temperature-independent, and dominated by orbital effects. These constraints on the model for the normal state are vital input for theory. In the superconducting state, which is not addressed by our experiments, current models [22,23] involve d-wave pairing but the nature of the mediating bosons has not been established [24]. Since our measurements probe $\mathbf{q} = 0$, as does the magnetic susceptibility, we are insensitive to any antiferromagnetic fluctuations, and therefore our results do not address directly this issue. However, the absence of a sizeable paramagnetic moment on the Pu sites is a new fact that must be considered by theories assuming Cooper pairing mediated by spin-fluctuations. The itinerant system UGa_3 develops an ordered AF state from an almost temperature-independent susceptibility and with a value of $C_2 \approx 1$ in the paramagnetic state [25]. Therefore it is still possible that superconductivity develops out of AF fluctuations, perhaps orbital in nature, within the itinerant ground state of $PuCoGa_5$. This needs to be substantiated by experiments, and further measurements to probe the strongly hybridized [21] or intermediate-valence [26] nature of this fascinating material are urgently required.

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