Low-temperature magnetic properties of Pr(Cu,Ga)$_{12.85}$

Y. Shimura$^1$, T. Sakakibara$^1$, K. Kuga$^1$, J.Y. Cho$^2$ and J.Y. Chan$^2$

$^1$ Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan
$^2$ Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

E-mail: sakaki@issp.u-tokyo.ac.jp

Abstract. Magnetization of a cubic compound Pr(Cu,Ga)$_{12.85}$ was examined at low temperatures down to 0.07 K in fields up to 14.5 T. The magnetic susceptibility $\chi(T)$ exhibits Curie-Weiss behavior down to 1 K. Field variation of the magnetization $M(H)$ at 0.12 K shows a steep initial rise to 1.3 $\mu_B$/Pr at 2 T, followed by a gradual increase in higher fields reaching 1.9 $\mu_B$/Pr at 14.5 T. The results indicate that the crystalline-electric-field ground state of Pr$^{3+}$ is a $\Gamma_5$ magnetic triplet. On cooling below 1 K, $\chi(T)$ tends to saturate and provides no evidence of a phase transition down to $\sim$0.3 K, suggesting onsite as well as intersite fluctuations exist. Below 0.25 K, a weak history dependence is observed in $\chi(T)$, which can be attributed to a spin-glass-like freezing of the Pr moment. A weak magnetic field of $\sim$0.2 T suppresses this spin-glass-like state, and non-Fermi liquid like behavior remains in $M(T)$ down to 0.08 K.

1. Introduction

There is a growing interest in a heavy fermion state in Pr-based compounds. In ordinary Ce-based heavy fermion (HF) compounds, the local magnetic moment of a 4$f^1$ configuration couples with conduction electrons to form a Kondo singlet state, leading to a large electronic specific heat coefficient $\gamma$ at low temperatures. Unlike the case of Ce compounds, however, the ground state degeneracy of the crystalline electric field (CEF) levels in Pr-based compounds ($4f^2$) is not protected by time reversal symmetry. High crystal symmetry is therefore required so that the CEF ground state has degeneracy that plays a key role in the HF formation. Up to present, Pr-based skutterudites (cubic), PrFe$_4$P$_{12}$ [1] and PrOs$_4$Sb$_{12}$ [2] are confirmed to be the HFs, the latter being a superconductor below $T_c = 1.7$ K. The cubic compounds PrAg$_2$In [3] and PrMg$_3$ [4, 5] have also been reported to show the HF behavior in the specific heat $C(T)$ and the magnetic susceptibility $\chi(T)$. Pr based HFs known to date are, however, still not large in number, and the mechanism of the HF formation is not known well. Clearly, further effort is needed to search for the new Pr-based HF systems.

A new member of the cubic compounds, Pr(Cu,Ga)$_{12.85}$, has recently been synthesized and the magnetic properties have been studied [6]. This compound crystallizes in a NaZn$_{13}$-type structure, isostructural to the heavy fermion superconductor UBe$_{13}$. In this structure, each Pr atom is surrounded by 24 neighboring atoms, thereby a large hybridization effect can be expected. $\chi(T)$ of Pr(Cu,Ga)$_{12.85}$ shows Curie-Weiss behavior down to 2 K with an effective moment very close to the value of the free Pr$^{3+}$ ion. No evidence of a phase transition is obtained in $\chi(T)$, $C(T)$ and the electrical resistivity $\rho(T)$ measured down to the lowest temperature of...
Figure 1. Magnetic susceptibility of Pr(Cu,Ga)$_{12.85}$ below 6 K. A field of 0.1 T was applied parallel to the [100] direction. The data points below 1 K were obtained in a field-cooled condition. Solid line is the calculated result based on the CEF scheme $\Gamma_5(0 \text{ K}) - \Gamma_1(20 \text{ K}) - \Gamma_4(30 \text{ K}) - \Gamma_3(37 \text{ K})$.

Figure 2. Field dependence of the magnetization of Pr(Cu,Ga)$_{12.85}$ for $H \parallel [100]$ obtained at 0.12 K. The inset shows the results at 1.9 K for $H$ applied to the three principal directions [100] (circles), [110] (squares) and [111] (triangles).

Very interestingly, $\rho(T)$ shows the $AT^2$ dependence at low $T$ with a large $A$ coefficient of 0.0727 $\mu\Omega \text{ cm/K}^2$, and a relatively large $C/T$ value of 97 mJ/mol-K$^2$ is obtained around 2 K. These results suggest that Pr(Cu,Ga)$_{12.85}$ is a HF system. In fact, a Kadowaki-Woods ratio, $A/\gamma^2$, of $0.727 \times 10^{-5} \mu\Omega \text{ cm-molK}^2 \text{ mol}^{-2}$ is in the order of the expected range for many HFs. In order to examine the ground state magnetic properties of Pr(Cu,Ga)$_{12.85}$, we measured the magnetization down to below 0.1 K.

2. Experimental

Single crystalline samples of Pr(Cu,Ga)$_{12.85}$ were grown by the Ga-flux method. Ga atoms mix into the crystal since the NaZn$_{13}$ structure is only stabilized in the presence of Ga [6]. The atomic ratio of Ga and Cu, as determined from the electron probe microanalysis, is 7.0:6.3 [6]. DC magnetization measurements below 1.9 K in magnetic fields up to 14.5 T were done using a capacitive Faraday magnetometer with a dilution refrigerator [7]. Magnetization above 1.9 K was measured by a SQUID magnetometer (MPMS, Quantum Design).

3. Results and Discussion

Figure 1 shows the magnetic susceptibility $\chi(T)$ of Pr(Cu,Ga)$_{12.85}$ below 6 K down to the base temperature of 0.08 K. It has been reported in the previous paper that $\chi(T)$ above 2 K well follows a Curie-Weiss law, with an effective moment of 3.32 $\mu_B$/Pr and a small negative Weiss temperature of -1.27 K [6]. Our data shows that $\chi(T)$ continues to increase down to below 1 K. This fact strongly indicates that a magnetic triplet is the ground state or in the very low-lying states of the CEF scheme. In this figure, the data points below 1 K were obtained in a field-cooled (FC) condition. Well below 1 K, $\chi(\text{FC})$ tends to saturate to a finite value. No evidence of a phase transition is obtained in $\chi(\text{FC})$ down to 0.08 K.

Figure 2 shows the field dependence of the magnetization $M(H)$ of Pr(Cu,Ga)$_{12.85}$ for $H \parallel [100]$ measured at 0.12 K. $M(H)$ in low fields shows a steep rise to the value 1.3 $\mu_B$/Pr at
Figure 3. Thermal variation of the magnetization of Pr(Cu,Ga)$_{12.85}$ in a field of 0.03 T (||[100]) obtained in field-cooled (FC) and zero-field-cooled (ZFC) conditions. Inset shows the full-loop magnetization to ±0.6 T measured at 0.07 K.

Figure 4. Thermal variation of the magnetization of Pr(Cu,Ga)$_{12.85}$ in fields of 0.15 and 0.25 T (||[100]). Open (closed) circles are the ZFC (FC) data. Inset shows the $H - T$ diagram for the irreversibility in $M(T, H)$.

2 T, followed by a gradual increase at higher fields. The moment value reaches 1.9 $\mu_B$/Pr at 14.5 T. In the $M(H)$ data, no anomaly that could be related to a phase transition can be seen up to 14.5 T, suggesting that the system is in the paramagnetic state in this field range. The inset shows the $M(H)$ data measured at 1.9 K for the three principal directions $H \parallel [100]$, [110] and [111]. $M(H)$ is isotropic in low fields below 1 T as expected for cubic symmetry. At higher fields, a small but distinct anisotropy develops in the magnetization: $M_{[100]} < M_{[110]} < M_{[111]}$.

Now we discuss the CEF scheme of Pr(Cu,Ga)$_{12.85}$. In a cubic environment, the $J = 4$ multiplet of Pr$^{3+}$ splits into four states: $\Gamma_1$ singlet, $\Gamma_3$ non-magnetic doublet, and two magnetic triplets $\Gamma_4$ and $\Gamma_5$. The results of the magnetic measurements in Figs. 1 and 2 indicate that a magnetic triplet is involved in the CEF ground state. The $\Gamma_4$ triplet becomes the low-lying state only in a very narrow CEF parameter region where it degenerates with a $\Gamma_1$ singlet and a $\Gamma_3$ doublet [8]. In this situation, it can be shown that the magnetization becomes strongly anisotropic with a [100] easy axis, $M_{[100]}/M_{[111]} \sim 1.6$ for $H > 3$ T, contrary to the experimental results in Fig. 2. By contrast, the $\Gamma_5$ triplet makes an isolated CEF ground state in a much wider parameter range [8], and gives an isotropic moment of 2 $\mu_B$/Pr close to the value observed in Fig. 2. The weak anisotropy observed in high fields can be well explained by admixing with a $\Gamma_3$ doublet in CEF excited states [9]. From these, we consider that CEF ground state of this system is a $\Gamma_5$ triplet. While it is not easy to fully determine the CEF scheme from the magnetization data alone, we tentatively adopt $\Gamma_5(0 \text{ K})$-$\Gamma_4(20 \text{ K})$-$\Gamma_3(30 \text{ K})$-$\Gamma_3(37 \text{ K})$ to reproduce $\chi(T)$ as well as the anisotropy. The solid line in Fig. 1 shows the calculated susceptibility $\chi_{\text{CEF}}(T)$ assuming the level scheme above, which reproduces the experimental result above 1 K reasonably well. More details of the CEF analysis of this compound will be published elsewhere. Below 1 K, however, $\chi(\text{FC})$ significantly deviates from $\chi_{\text{CEF}}(T)$ and levels off. Moreover, $M(H)$ at low $T$ reaches the $\Gamma_5$ moment value only in very high fields. These observations imply that the $\Gamma_5$ moment at low $T$ is significantly suppressed below the full value, possibly due to onsite as well as intersite fluctuations of the $\Gamma_5$ moment which could be related with the heavy fermion behavior.
observed in this system [6].

While no clear evidence of a phase transition is obtained in $\chi(FC)$, we found that a weak history dependence develops in the magnetization in a very low $T - H$ region below 0.25 K and 0.2 T as shown in Fig. 3. Here the field-cooled magnetization $M(FC)$ taken in a field of 0.03 T is compared with the magnetization $M(ZFC)$ obtained in a zero-field-cooled condition. A clear difference appears between $M(ZFC)$ and $M(FC)$ below 0.25 K; while $M(FC)$ is nearly $T$-independent below 0.25 K, $M(ZFC)$ shows a slight decrease. The inset shows the full loop of $M(H)$ to $±0.6$ T measured at 0.07 K after zero-field cooling the sample to the temperature. A small hysteresis can be seen in $M(H)$ at low fields $|H| < 0.2$ T. These results give strong evidence that the CEF ground state of this compound indeed has a magnetic moment which undergoes a freezing in a spin-glass-like state at low $T$. This state is easily destroyed by applying a small field $H_c \sim 0.18$ T. At this field, the induced moment value is only $\sim 25\%$ of the saturation value. The inset of Fig. 4 shows the phase diagram for the spin-glass-like state, where open (closed) squares denote the position where the irreversibility disappears in the $M(T)$ ($M(H)$) measurements. Outside the border (solid line), the system is in the paramagnetic state. In Fig. 4, we show $M(T)$ in the paramagnetic region near $H_c$. Interestingly, we found that the magnetization does not stay constant but shows nearly $T$-linear increase on cooling down to below 0.1 K (Fig. 4), which could be related to quantum critical behavior.

To summarize, low temperature magnetization measurements on Pr(Cu,Ga)$_{12.85}$ indicate that the CEF ground state is a $\Gamma_5$ triplet carrying a magnetic moment, which undergoes a spin-glass-like freezing below 0.25 K. Under a small field of 0.2 T, the system remains in a paramagnetic state down to the lowest temperature of 0.07 K with unusual temperature variation of the magnetization. How the entropy $R \ln 3$ of the $\Gamma_5$ state is released in this region is highly of interest, and we are carrying out the specific heat measurements whose results will be published elsewhere.

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