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Heavy-electron-like behavior in cubic $PrCu_4Au$

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Abstract
The magnetization $M(H)$, magnetic susceptibility $\chi(T)$, electrical resistivity $\rho(T)$ and specific heat $C(T)$ properties of $PrCu_4Au$ have been investigated. A clear antiferromagnetic transition T_N is observed at 2.5 K in $C(T)$ and $\chi(T)$. The internal magnetic field at the Pr nucleus, H_{HF}, is obtained to be 195 T from the nuclear specific heat observed in $C(T)$ below 0.7 K. The ground state of Pr $4f^2$ in the cubic crystalline electric field is inferred to be a magnetic triplet Γ_5 from the magnitude of the magnetization at 2 K, which coincides with the value of the $4f^2$ magnetic moments deduced from H_{HF}. The large value of the electronic specific heat coefficient, γ, remains at the zero-temperature limit even in external magnetic fields. On the other hand, the entropy up to T_N is somewhat less than $R\ln 3$. These anomalous heavy-electron-like behaviors probably originate in the fact that both the magnetic moments and the quadrupole moments are involved in the ground state of Pr $4f^2$.

1. Introduction

The Pr-based intermetallic compounds have been attracting growing interest with respect to possible strongly-correlated electron behaviors. Strongly-correlated electron behaviors have been intensively studied in Ce-based compounds, in which the 4f electrons and conduction electrons are highly correlated. Another group that has been investigated intensively is U-based compounds, in which 5f electrons are more extended than the 4f electrons. The $4f^2$ electron configuration of Pr^{3+} is compared with the $5f^2$ of U^{4+}. However, $4f^2$ has more localized characters than $5f^2$. So, the effect of the crystalline electric field (CEF) of $4f^2$ is more distinct than that of $5f^2$. It has generally been considered that various interesting behaviors, such as enhanced C/T at low temperatures, can be caused by the interaction between the conduction and f electrons. The state of $4f^2$ electrons is more strictly lifted by the CEF than that of $5f^2$ electrons. The $4f^2$ configuration of Pr^{3+} can have a non-magnetic, non-Kramers Γ_3 doublet as its CEF ground state (GS), and the quadrupole moment of the Γ_3 doublet might interact with the conduction electrons to produce strongly-correlated properties; examples are found in $PrAg_2In$ [1–3], $PrCu_2In$ [4], $PrPb_3$ [5] and $PrMg_3$ [6]. The first two material types are characterized with enhanced Sommerfeld coefficients $\gamma \sim 6.5$ J mol^{-1} K^{-2} and $\gamma \sim 1$ J mol^{-1} K^{-2}, respectively. Another class of materials in which the effect of c–f hybridization and the f^2 multipole degrees of freedom have an important role includes the filled Pr skutterudites, e.g. $PrOs_4Sb_{12}$ [7] and $PrFe_4P_{12}$ [8–10]. The former is the first Pr-based heavy-electron superconductor and shows a field-induced ordered phase due to an antiferroquadrupole (AFQ) origin above 4.5 T at low temperatures. The latter, $PrFe_4P_{12}$, is characterized as the heavy-fermion state at high magnetic fields and shows an anomalous ordered state, which is non-magnetic, at low temperatures below $T_A = 6.5$ K at 0 T.

In the present study, we report the magnetic, electric and thermodynamic properties of a new Pr-based compound $PrCu_4Au$ with a $MgCu_4Sn$-type cubic structure. We focus on the large value of C/T remaining at the zero-temperature limit even in external fields. In this paper, we suggest that the heavy-electron-like behaviors may be caused by the fact that both the magnetic moments and the quadrupole moments are involved in the magnetic triplet Γ_5.

2. Experimental procedures

Polycrystalline samples of $PrCu_4Au$ were prepared by an arc-melting method. The purities of the base materials were 99.9% for Pr, 99.99% for Cu and 99.99% for Au, respectively. The

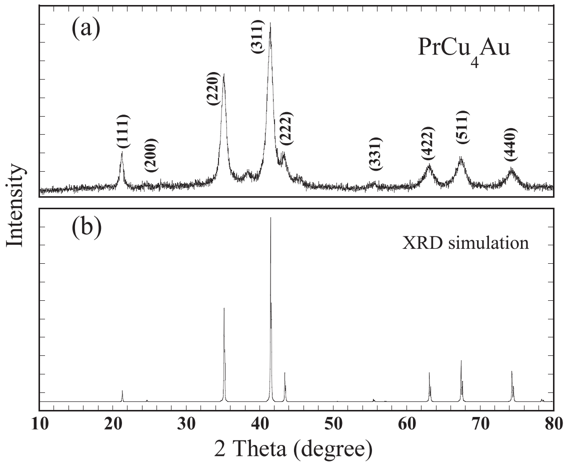

Figure 1. Powder x-ray diffraction pattern of cubic $PrCu_4Au$. (b) A calculated x-ray diffraction profile for $PrCu_4Au$.

samples were annealed at 800 °C for two weeks to obtain a better quality. It has been reported that the silver ternary RCu_4Ag compounds (R = La and Pr) are difficult to prepare in a single phase [11]. However, the $PrCu_4Au$ sample was successfully prepared. The crystal structure was confirmed by x-ray powder diffraction to be of the cubic $MgCu_4Sn$ type, although there remains a weak impurity peak (the intensity is at most less than 3% of $PrCu_4Au$), as shown in figure 1. The lattice parameter a was 7.219 Å.

The electrical resistivity $\rho(T)$ was measured from 2 to 300 K by a conventional four-probe DC method and from 0.5 to 9 K by an AC method. Measurement of the magnetization M and the magnetic susceptibility $\chi(T)$ were performed from 2.0 to 300 K in magnetic fields up to 7 T in a superconducting quantum interference device (SQUID) magnetometer (MPMS-7, Quantum Design Ltd). The specific heat $C(T)$ was measured by the thermal relaxation method down to 0.54 K with a physical property measurement system (PPMS; Quantum Design Ltd), and the $C(T)$ was also measured on a reference compound YCu_4Au.

3. Experimental results

3.1. Magnetic susceptibility

Figure 2 and the inset show the T-dependence of $\chi(T)$ and its inverse $\chi^{-1}(T)$, respectively. $\chi(T)$ increases monotonically with decreasing T and exhibits a clear peak at 2.5 K, which is thought to be an antiferromagnetic transition temperature T_N. The paramagnetic Curie temperature θ_P and the effective Bohr magneton number μ_{eff} deduced from the $\chi^{-1}(T)$ versus T plot from 40 to 300 K are −5 K and 3.50 μ_B, respectively, which is slightly smaller than 3.58 μ_B for a free Pr^{3+} ion.

As shown in figure 3, the magnetization M up to 7 T was measured at various temperatures (2, 5, 10, 20 and 300 K). M increases linearly at high temperatures above 20 K when the external field H_{ext} is increased to 7 T. However, M at 2 K shows a saturation-like behavior at high external fields. At low fields, the slope of M increases slightly with increasing external field as if a weak metamagnetic transition occurs.

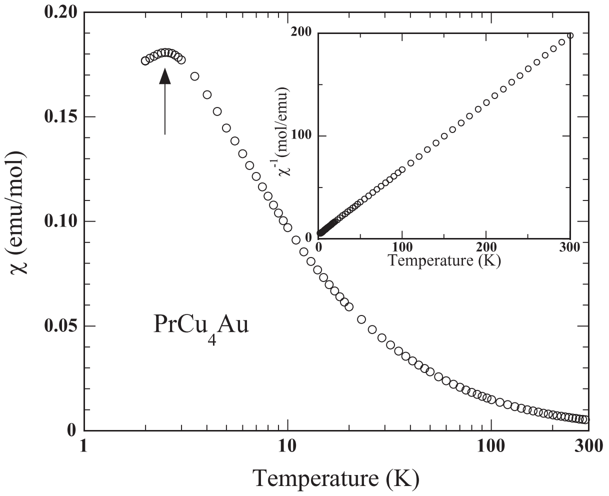

Figure 2. Temperature dependence of the magnetic susceptibility $\chi(T)$ of $PrCu_4Au$ under $H_{ext} = 1$ T. A clear transition peak is observed at 2.5 K. The inset shows the temperature dependence of $\chi^{-1}(T)$.

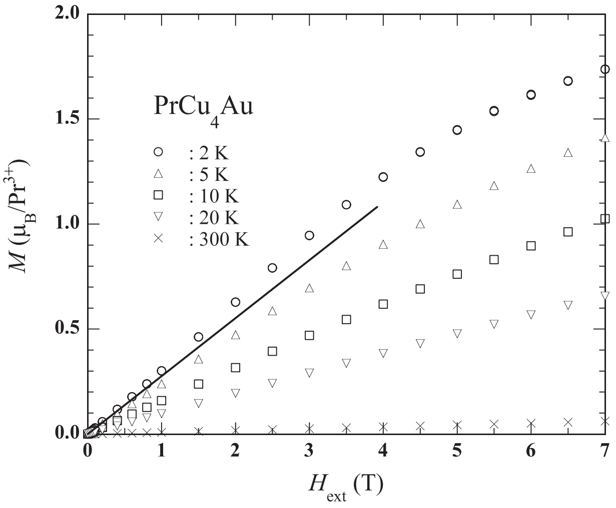

Figure 3. Isothermal magnetization curves $M(H_{ext})$ per Pr^{3+} ion of $PrCu_4Au$ at various temperatures in fields up to 7 T. The solid line denotes the initial slope of M at 2 K below 0.1 T.

In figure 4, $\chi(T)$ at low temperatures below 20 K is shown in various external magnetic fields H_{ext}. T_N shows no apparent dependence on H_{ext} below 1 T. However, it disappears at about 3 T, as shown in the inset of figure 4. $\chi(T)$ at high temperatures above T_N shows no clear dependence on the external field. The inset shows the phase diagram of T_N versus H_{ext} obtained from the H_{ext} dependence of $\chi(T)$ and $C_{4f}(T)$.

3.2. Electrical resistivity and thermoelectric power

As shown in figure 5, $\rho(T)$ decreases monotonically with decreasing T in the high-temperature range above 10 K. However, as expected, $\rho(T)$ decreases rapidly below about 2.5 K as shown in the inset of figure 5. The solid line in the inset represents the simulation of $\rho(T)$ at low temperatures below 2.0 K approximated by $\rho = \rho_0 + AT^2$, with $\rho_0 =$

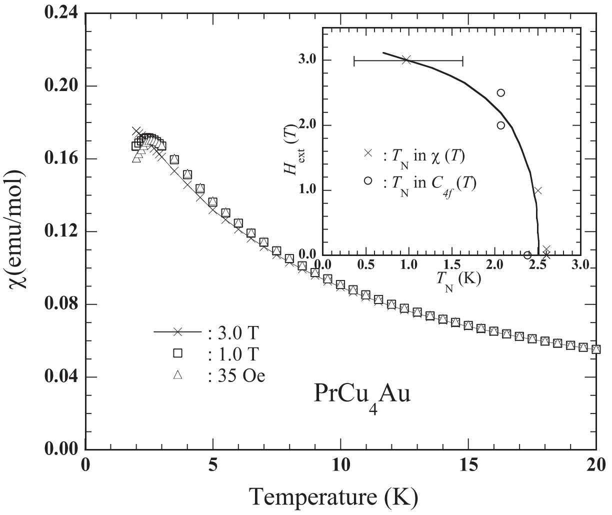

Figure 4. Temperature dependence of $\chi(T)$ at low temperatures under various magnetic fields. The inset shows the phase diagram of H_{ext} versus T_{N} observed in $\chi(T)$ (×) and $C_{4\mathrm{f}}(T)$ (○). The error bar of T_{N} at 3 T shows that the transition temperature is between 0 and 2.0 K.

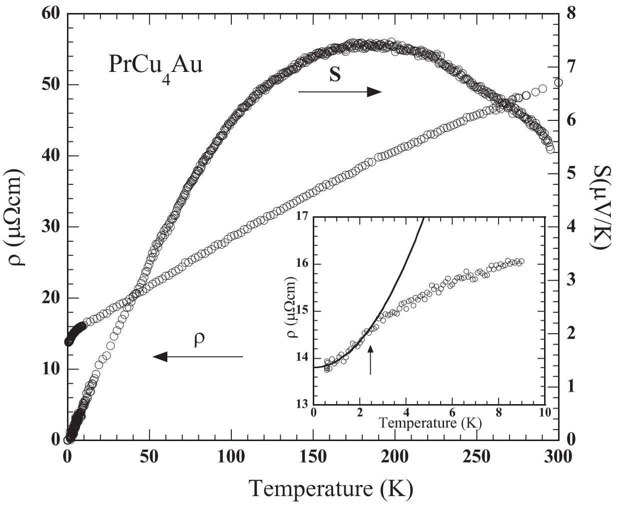

Figure 5. Temperature dependence of the electrical resistivity $\rho(T)$ and the thermoelectric power $S(T)$ of $\mathrm{PrCu_4Au}$. The inset shows $\rho(T)$ at low temperatures below 20 K. The rapid decrease below 2.5 K is due to the presence of a magnetic transition. The solid line in the inset represents the calculation of $\rho = \rho_0 + AT^2$.

13.8 $\mu\Omega$ cm and $A = 0.14\ \mu\Omega\ \mathrm{cm\ T^{-2}}$. The residual resistivity ratio (RRR; $\rho_{300\ \mathrm{K}}/\rho_0$) is 3.6.

The thermoelectric power $S(T)$ is shown in figure 5. A broad peak with an amplitude of 8 $\mu\mathrm{V\ K^{-1}}$ appears around 200 K. In contrast to $\rho(T)$, $S(T)$ shows no apparent anomaly around T_{N}, and goes to zero at 0 K with the slope S/T of 0.07 $\mu\mathrm{V\ K^{-2}}$ at the zero-temperature limit.

3.3. Specific heat

The specific heat $C(T)$ of $\mathrm{PrCu_4Au}$ is shown in figure 6 together with $C(T)$ of $\mathrm{YCu_4Au}$ as a reference sample. As shown in figure 6, $C(T)$ of $\mathrm{PrCu_4Au}$ exhibits a sharp peak at 2.4 K which is a cooperative phase transition temperature and an upturn below 0.7 K which is the nuclear contribution C_{N} of ^{141}Pr (nuclear spin $I = 5/2$ for ^{141}Pr with natural abundance 100%). C_{N} will be analyzed numerically later. The 4f contribution to $C(T)$ is derived from $C_{4\mathrm{f}}(T) = C(T) - C_{\mathrm{YCu_4Au}}(T) - C_{\mathrm{N}}(T)$, where $C_{\mathrm{YCu_4Au}}(T)$, the specific heat of $\mathrm{YCu_4Au}$, is used as the phonon contribution of $\mathrm{PrCu_4Au}$. For $C_{\mathrm{YCu_4Au}}(T)$, the conventional analysis based on the equation $C/T = \gamma + \beta T^2$ at low temperatures yields the two values $\gamma = 10\ \mathrm{mJ\ mol^{-1}\ K^{-2}}$ and $\beta = 0.46\ \mathrm{mJ\ mol^{-1}\ K^{-4}}$.

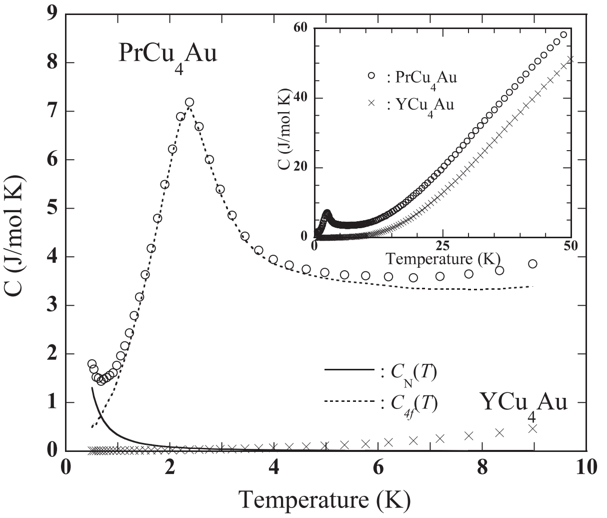

Figure 6. Temperature dependence of the specific heat $C(T)$ of $\mathrm{PrCu_4Au}$ (○) and $\mathrm{YCu_4Au}$ (×) at low temperatures. The solid line and the dotted line represent the ^{141}Pr nuclear contribution and the 4f electron contribution to the specific heat, respectively. The inset shows the specific heat $C(T)$ up to 50 K.

$C(T)$ at low temperatures below 9 K was measured in various H_{ext} up to 6.0 T, and all the data have been corrected by subtracting the ^{141}Pr nuclear contribution $C_{\mathrm{N}}(T)$ and phonon contribution $C_{\mathrm{YCu_4Au}}(T)$, as shown in figure 7. The peak due to T_{N} decreases with the increase of external magnetic field. T_{N} seems to disappear at 3.0 T, and $C_{4\mathrm{f}}(T)$ forms a shoulder without a clear peak. $C_{4\mathrm{f}}(T)$ under all fields crosses around 3.5 K, showing no dependence on the field at this temperature. $C_{4\mathrm{f}}(T)$ around 6.0 K increases with increasing H_{ext} and finally seems to form a new broad peak at 6.0 T.

4. Analysis and discussion

In this section, we discuss the CEF ground state Γ_5 from experimental features; the saturation magnetic moment in high magnetic fields, the value of the internal magnetic field H_{HF} at the Pr nucleus and the 4f contribution to the entropy $S_{4\mathrm{f}}(T)$. Finally, we discuss the anomalies of $C_{4\mathrm{f}}(T)$ and $C(T)/T$ under an external magnetic field.

4.1. Ground state of magnetic triplet Γ_5

First, we discuss what the ground state of $4\mathrm{f}^2$ electrons in $\mathrm{PrCu_4Au}$ is. The degeneracy of $4\mathrm{f}^2$ electrons is lifted to four levels of Γ_1 (singlet), Γ_3 (doublet), Γ_4 (triplet) and Γ_5 (triplet)

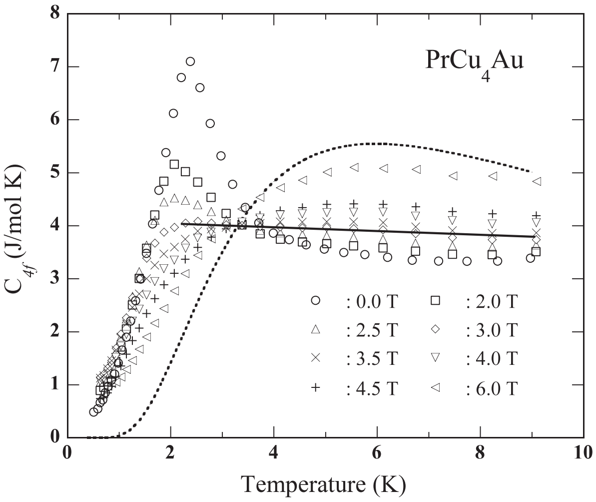

Figure 7. The low-temperature part of $C_{4f}(T)$ of PrCu$_4$Au under various H_{ext} up to 6.0 T. All the data have been corrected by subtracting the ^{141}Pr nuclear contribution $C_N(T)$. The solid line represents the flat behavior of $C_{4f}(T)$ under 3 T. See details in the text. The dotted line represents the calculated specific heat under 6 T taking into account only the Zeeman effect.

by CEF in cubic symmetry, where the former two levels are non-magnetic and the latter two are magnetic. We conclude that magnetic transition exists at 2.5 K from the maximal value of $\chi(T)$, the maximal value of $C_{4f}(T)$ and the inflection point of the temperature dependence of resistivity. Furthermore, we explain this transition as an antiferromagnetic one because the temperatures due to the magnetic transition in $\chi(T)$ together with $C_{4f}(T)$ decrease with increasing external magnetic field as shown in the inset of figure 4. Therefore, it is apparent that the ground state of PrCu$_4$Au is magnetic.

As shown in figure 3, $M(H)$ shows a tendency of saturation to the value 2.0 μ_B/Pr^{3+} in high magnetic fields. By a simple calculation of CEF, the value of M is calculated as 2.0, 0.4, 0 and 0 μ_B/Pr^{3+} when the CEF GS is Γ_5, Γ_4, Γ_3 and Γ_1, respectively. We can therefore make the reasonable prediction that the CEF GS in PrCu$_4$Au is a magnetic triplet Γ_5. On the other hand, below T_N some magnetic order occurs. Consequently, the ordered magnetic moment causes an internal magnetic field H_{HF} at the position of the Pr nucleus via a hyperfine interaction between the 4f^2 electrons and the Pr nucleus. Thus, H_{HF} results in the splitting of Pr nuclear spin levels, and the ^{141}Pr nucleus contributes to the specific heat as C_N at low temperatures, as shown in figure 6, which is consistent with the conclusion that the GS of 4f^2 is magnetic.

4.2. Nuclear specific heat C_N

The contribution of $C_N(T)$ at low temperatures is analyzed as $C_N = \alpha/T^2$ and the value of α is obtained to be 0.33 J K mol^{-1}. $C_N(T)$ is shown by the solid line in figure 6. From the value of α the internal magnetic field at the Pr nucleus could be obtained as H_{HF} = 195 T based on the following equation:

$$H_{HF} = \{3\alpha k_B^2/\hbar^2\gamma_N^2 RI(I+1)\}^{1/2},$$

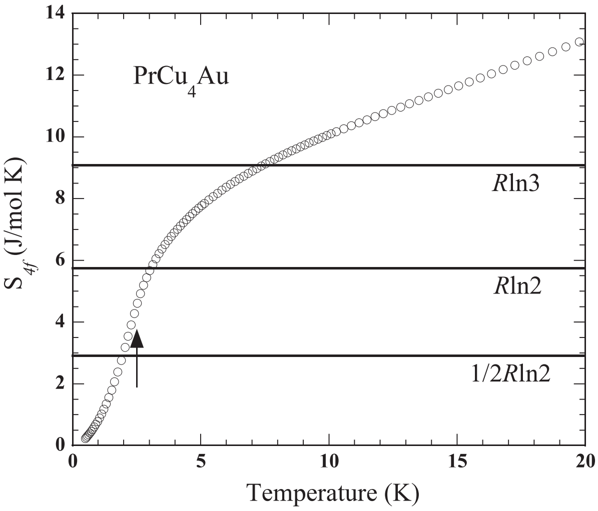

Figure 8. Temperature dependence of $S_{4f}(T)$, the 4f contribution to the entropy of PrCu$_4$Au. The arrow indicates T_N.

where I and γ_N are the ^{141}Pr nuclear spin and the gyromagnetic ratio, respectively. The other definitions are conventional. The value of H_{HF} is 56% of the hyperfine field caused by a free 4f^2 Pr ion (H_{HF} = 350 T) [12], suggesting that the magnetic moment of the Pr^{3+} ion in PrCu$_4$Au is correspondingly reduced from 3.2 μ_B/Pr ion (magnetization for a free Pr ion) to 1.8 μ_B/Pr ion (3.2 × 56%) which is in good agreement with the measured magnetic moment (shown in figure 3). It can be concluded, therefore, from the analysis of the C_N appearing at low temperatures, that the CEF GS of Pr 4f^2 is confirmed again to be a magnetic triplet Γ_5.

The specific heat has been measured under external magnetic fields H_{ext}, which will be discussed later. Here, we focus on the fact C_N is not affected qualitatively by H_{ext} up to 6 T, which indicates that H_{HF} is extremely large compared to H_{ext}.

4.3. Magnetic entropy S_{4f}

Figure 8 shows the 4f contribution $S_{4f}(T)$ to the entropy. The initial value of S_{4f} at 0.54 K is obtained as 0.25 J mol^{-1} K^{-1}, assuming that the gradient of $C_{4f}(T)/T$ versus T is constant below 0.54 K. The entropy at T_N is considerably smaller than $R\ln 3$, and $S_{4f}(T)$ approaches $R\ln 3$ around 7 K. In general, in the vicinity of T_N, magnetic fluctuations extend above T_N and thus the entropy at T_N is usually less than the value estimated from the degree of freedom of the magnetic ground state. However, the entropy remaining above T_N in PrCu$_4$Au seems to be quite large. As shown in figure 6, the feature of $C_{4f}(T)$ above T_N is not a tail due to the magnetic fluctuation, but a plateau. The quadrupole fluctuations may cause a plateau of $C(T)/T$ at low temperatures, as has been observed in PrAg$_2$In [2] and PrCu$_2$In [4], in which the ground states have quadrupole moments and $C(T)/T$ is enhanced at low temperatures.

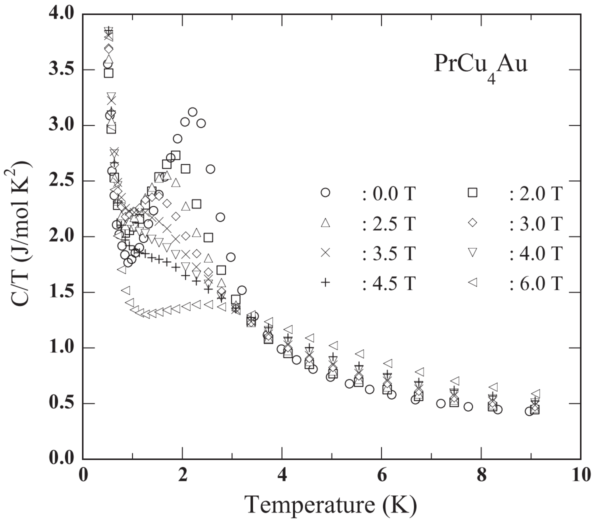

Figure 9. The low-temperature part of $C(T)/T$ of PrCu$_4$Au under various H_{ext} up to 6.0 T. None of the data are corrected.

4.4. Anomalies of $C_{4f}(T)$ and $C(T)/T$ under H_{ext}

All the $C_{4f}(T)$ under different H_{ext} cross at about 3.5 K as shown in figure 7. With the increase in the external magnetic field, the magnetic ordering temperature T_N goes down accompanied by the decrease of the peak intensity of $C(T)$. On the other hand, $C_{4f}(T)$ around 6 K is largely enhanced with increasing external field, and forms an additional broad peak at 6 T. The behavior of $C_{4f}(T)$ under 6 T resembles a Schottky-type specific heat. Thus, we calculated the $C(T)$ to compare the experimental $C_{4f}(T)$ under 6 T based on a simple model that the degeneracy of the triplet ground state is lifted by the Zeeman effect with the splitting energy of about ±10 K. The energy of 10 K is estimated from the equation $\Delta E = -MH_{ext}$, where M and H_{ext} are 2 μ_B and 6 T, respectively. In this simple calculation, the magnetic exchange interaction is neglected. The calculated $C(T)$ is shown by the dotted line in figure 7. The calculated $C(T)$ is qualitatively in good agreement with the experimental $C_{4f}(T)$ under 6 T, although the discrepancy between them is fairly large in the low-temperature region. The value of the magnetic moment 2 μ_B is, however, consistent with the expectation value of the CEF GS being the magnetic triplet Γ_5.

In figure 9, $C(T)/T$ is shown in various external magnetic fields. We analyzed the C/T in $H_{ext} = 0$ by assuming that $C/T = \alpha/T^3 + \gamma + \beta T^2 + cT^2$ in a narrow temperature range below 1.8 K down to 0.5 K, where the last term is assumed to be a magnetic contribution. β, the contribution of phonon, is assumed to be the same value as in YCu$_4$Au discussed above. From this equation, $\alpha = 0.33$ J K mol^{-1} and $\gamma = 0.77$ J mol^{-1} K^{-2} are obtained. α has already been discussed. This large γ means that the 4f^2 electrons behave like heavy electrons. The tendency of this large γ does not change when H_{ext} is applied. We therefore concluded that this large γ can be accounted for by electric factors.

Finally, we must note the quadrupole fluctuation model proposed by Isikawa *et al* [2], which has been applied to explain the large C/T of PrCu$_2$In and PrAg$_2$In at low temperatures [1, 4]. These compounds have an extremely small thermoelectric power coefficient S/T at low temperatures, and the relationship predicted by Behnia *et al* [13, 14] between C/T and S/T does not hold (where S denotes the thermoelectric power, not the entropy). From these facts, Isikawa *et al* suggested that the large C/T was not due to the heavy electrons but the quadrupole fluctuation. In the present compound, S/T is also extremely small and the relationship does not hold either. Therefore the heavy-electron-like behavior in PrCu$_4$Au is considered to be related to the electric quadrupole fluctuation. PrCu$_4$Au is a complex system because the compound has both magnetic fluctuation leading to an antiferromagnetic order and quadrupole fluctuation which does not make a quadrupole order in this case. The details are not clear at the present time. Theoretical studies are needed to solve the anomalous behaviors in this fantastic compound with both fluctuations.

5. Summary

We have prepared a new cubic PrCu$_4$Au compound and measured $M(H)$, $\chi(T)$, $\rho(T)$, $S(T)$ and $C(T)$. PrCu$_4$Au is an antiferromagnetic compound with $T_N = 2.5$ K. The phase diagram of T_N versus H_{ext} is established. The ground state of the Pr 4f^2 electrons is concluded to be the magnetic triplet Γ_5. The magnetization tends to be saturated to 2.0 μ_B at 2 K in a high external field. This saturation moment is in good agreement with the theoretical value deduced from GS of Γ_5. The Pr nuclear specific heat is observed at low temperatures, and the internal field at the position of the Pr nucleus is analyzed to be 195 T. The value of this internal field is reduced to 56% of the hyperfine field caused by a free 4f^2 ion. From this reduction, correspondingly, the free 4f^2 magnetic moment is reduced to 1.8 μ_B, which is in good agreement with the expected M from Γ_5. While the entropy at T_N is considerably smaller than $R\ln 3$, C_{4f}/T seems to remain at 0 K with fairly large value even under high H_{ext}. At zero external magnetic field, $\gamma = 0.77$ J mol^{-1} K^{-1} is obtained. These anomalous heavy-electron-like behaviors in PrCu$_4$Au are considered to be related to the electric quadrupole fluctuation and magnetic interaction. PrCu$_4$Au is a complex system because the compound has both the magnetic fluctuation leading to an antiferromagnetic order and the quadrupole fluctuation which does not make a quadrupole order in this case.

Acknowledgments

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