The heat capacity of PrPd$_3$ in magnetic fields

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Abstract. The specific heat $C(T)$ of polycrystalline PrPd$_3$ has been measured down to 0.37 K in magnetic fields $H_{\text{ext}}$ up to 8 T. Two clear peaks, $T_1$ and $T_2$, were observed in zero field at 0.88 and 0.77 K, respectively. $T_1$ increases very slightly with increasing $H_{\text{ext}}$ initially up to 2 T, and decreases rapidly over 5 T. On the other hand, the peak at $T_2$ weakens with the increase of $H_{\text{ext}}$ and disappears around 3 T. The value of $C(T)/T$ in 0 T is almost constant below 0.7 K with an extremely large one. By applying $H_{\text{ext}}$, $C(T)/T$ at 0.5 K gradually decreases to 5.5 J/mol K$^2$ in 8 T. The nuclear contribution to $C(T)$ is not apparent in the present $C(T)$ even in the fields. The giant $C(T)/T$ at low temperatures indicates presumably that PrPd$_3$ is a Kondo system similar to the diluted system of Pr in Pd. The effect of quadrupole interaction as one possibility might be responsible to the characteristic behaviors of the giant $C(T)/T$ and the $H_{\text{ext}}$-dependence of $T_1$.

1. Introduction
PrPd$_3$ is a member of REPd$_3$ (Rare Earth) series crystallizing in AuCu$_3$ structure. The Pr ions are $3^+$ and occupy the equivalent sites of the cubic point symmetry. Experimental results of the magnetic susceptibility $\chi(T)$ [1] and the specific heat $C(T)$ [2] on PrPd$_3$ have been published earlier. A sharp peak of $C(T)$ was observed at 0.6 K in zero field and was thought to be due to the magnetic phase transition by Machado da Silva [2], however, no direct evidence of the magnetic transition was reported anywhere. The measurements of specific heat from 4 to 16 K in 4 and 8.5 T were also performed by Drewes et al. [3]. The crystal-field parameters of PrPd$_3$ have been determined by the neutron inelastic scattering experiment by Ferrer and Purwins [4]; the ground state is triplet $\Gamma_5$ and the first excited state is doublet $\Gamma_3$. Kucherenco et al. observed giant hybridization effects in the 4$f$ photoemission spectra of Pr transition-metal compositions including PrPd$_3$ [5]. Moreover, in the diluted system of Pr in Pd, Walter and Slebarski concluded that Pr$_{0.015}$Pd is a Kondo system on the basis of their inelastic neutron scattering experiment [6]. In this work we measured the $C(T)$ down 0.37 K in various fields up to 8 T in detail to clarify the nature of PrPd$_3$ at low temperatures.

2. Experimental procedure
The polycrystalline PrPd$_3$ was prepared from 99.9% Pr and 99.95% Pd by arc melting the stoichiometric composition in a water-cooled copper boat in an argon gas atmosphere. The crystal structure was confirmed to be of the cubic AuCu$_3$ type from the X-ray powder diffraction experiment. The lattice parameter was evaluated as $a = 4.136\text{Å}$. The specific heat $C(T)$ was measured by the thermal relaxation method down to 0.37 K in various magnetic fields up to 8
T with a physical property measurement system (PPMS, Quantum Design Ltd.), and the $C(T)$ of LaPd$_3$ as a reference compound was also measured.

3. Results

The specific heat of PrPd$_3$ below 3 K down to 0.37 K at 0 T is shown in figure 1, and $C(T)$ of PrPd$_3$ and LaPd$_3$ up to 300 K are shown in the inset of the figure. At low temperatures below 8 K, $C(T)$ of PrPd$_3$ increases with decreasing temperature and shows two clear peaks with 6.3 and 6.4 J/mol K at 0.88 and 0.77 K, respectively. The two temperatures, 0.88 and 0.77 K, are hereafter denoted as $T_1$ and $T_2$, respectively. No apparent $^{141}$Pr nuclear contribution was observed in $C(T)$ as shown in the figure. The value of $C$ at 0.37 K is extremely large, 3.1 J/mol K, which agrees well with the value reported by Machado da Silva [2]. The reported data [2], however, show only one peak with about 5 J/mol K at 0.6 K.

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the specific heat $C(T)$ of PrPd$_3$ (∙) from 0.37 to 3 K in 0 T. The inset shows the $C(T)$ of PrPd$_3$ (∙) and LaPd$_3$ (○) at temperatures up to 300 K.

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of $C(T)/T$ of PrPd$_3$ from 0.37 to 10 K under zero field. The inset shows a flat behavior of $C(T)/T$ observed at low temperatures below 0.7 K.

Figure 2 and the inset show the $T$-dependence of $C(T)/T$ and its low-temperature part, respectively. $C(T)/T$ increases monotonically with decreasing $T$ and exhibits a flat behavior with 8.5 J/mol K$^2$ below 0.7 K down to 0.37 K. The temperature of 0.37 K is sufficiently low compared to $T_2$. From the flat behavior of $C(T)/T$, we would expect that a large value of the coefficient of the electronic specific heat $\gamma (T \rightarrow 0)$ might exist in PrPd$_3$.

$C(T)$ in various external magnetic fields $H_{\text{ext}}$ up to 8 T is shown in figure 3 at low temperatures below 9 K. As shown in the figure, $C(T)$ above 1.6 K is largely enhanced with increasing $H_{\text{ext}}$ and finally makes a new broad peak around 3 K under 8 T. All the $C(T)$ curves under different $H_{\text{ext}}$ cross at about 1.6 K showing that no dependence on external field at this temperature. At low temperatures below 1.4 K, $C(T)$ is shown in the inset of figure 3 in an expanded scale. With the increase of $H_{\text{ext}}$, the peak at $T_1$ does not change clearly in $H_{\text{ext}}$ below 5 T. However, in 6 T, the value of $C$ at the peak is weakened to 5.6 J/mol K almost at the same temperature. Furthermore, with increasing $H_{\text{ext}}$, the $C$ is rapidly lowered to 3.0 J/mol K, and $T_1$ decreases to 0.7 K under 8 T. On the other hand, the peak at $T_2$ is easily weakened by $H_{\text{ext}}$ and disappears around 3 T. Characteristic behaviors of the dependence of $T_1$ and $T_2$ on $H_{\text{ext}}$ are different from each other, indicating that the two peaks are caused by some different origin. In
the present study, we cannot determine whether the magnetic transition peak reported earlier [2] is one of the two peaks in our study.

The phonon contribution $C_{ph}(T)$ in PrPd$_3$ is expected to be similar to the $C(T)$ of LaPd$_3$. As shown in figure 3, it is considerably small at least at temperatures below 5 K. However, the $C(T)$ of LaPd$_3$ exceeds the $C(T)$ of PdPd$_3$ around 9 K, which is unusual although similar result has been reported before [2]. By using the data of LaPd$_3$ below 6 K, the Debye temperature $\theta_D$ for LaPd$_3$ is calculated as 176 K, which is in good agreement with the reported one [2].

**Figure 3.** The low-temperature part of $C(T)$ of PrPd$_3$ under various $H_{ext}$ up to 8 T. $C(T)$ of LaPd$_3$ in 0 T is also shown for comparison. The inset shows the dependence on $H_{ext}$ of the two peaks in $C(T)$ in an expanded scale.

**Figure 4.** Temperature dependence of the entropy $S(T)$ of PrPd$_3$ under various fields. Initial value of $S(T)$ at the lowest temperature is different in each field as shown in the figure.

Figure 4 shows the entropy $S(T)$ of PrPd$_3$ under 0, 6 and 8 T. The corresponding initial values of $S(T)$ in these fields were appropriately estimated because $C(T)/T$ is different from each other under the magnetic fields. As shown in figure 4, it is clear that $S(T)$ approaches $R \ln 3$ at 1 K under zero field and this indicates that the crystalline electric field (CEF) ground state (GS) is a triplet. A further increase in $S(T)$ is observed above 1 K, which is ascribed to the contribution from the CEF excited states. The $S(T)$ is lowered by the external magnetic field as shown in figure 4. This result can be understood qualitatively by considering the Zeeman effect, by which the magnetic triplet of the CEF GS $\Gamma_5$ is lifted in the external magnetic field.

4. **Summary and discussion**

In this experiment, the two clear peaks at $T_1$ and $T_2$ have been found in $C(T)$. The magnetic field dependence of $T_1$ and $T_2$ in PrPd$_3$ is summarized in figure 5. $T_1$ seems to increase very slightly with increasing $H_{ext}$ initially although the error bar is not sufficiently short. On the contrary, $T_2$ decreases with increasing $H_{ext}$ and disappears around 3 T. The behavior of the $H_{ext}$ dependence of $T_1$ is not similar to that of usual magnetic phase transition but to that of usual quadrupolar phase transition. It is, therefore, inferred that $T_1$ may be a quadrupolar phase transition.

We discuss the origin of $T_1$ and $T_2$ whether they are due to the magnetic interaction. The energy scheme due to the CEF effect has been already determined by the neutron inelastic scattering experiment (INS) [4] and specific heat experiment (SH) [2]; from the INS experiment, the triplet $\Gamma_5$ is the ground state separated by 14 meV from the excited states $\Gamma_1$, $\Gamma_3$ and $\Gamma_4$. The phonon contribution $C_{ph}(T)$ in PrPd$_3$ is expected to be similar to the $C(T)$ of LaPd$_3$. As shown in figure 3, it is considerably small at least at temperatures below 5 K. However, the $C(T)$ of LaPd$_3$ exceeds the $C(T)$ of PdPd$_3$ around 9 K, which is unusual although similar result has been reported before [2]. By using the data of LaPd$_3$ below 6 K, the Debye temperature $\theta_D$ for LaPd$_3$ is calculated as 176 K, which is in good agreement with the reported one [2].

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and from the SP experiment, the energy separation between the ground state $\Gamma_5$ and the first excited state $\Gamma_3$ was concluded to be 4.2 K, the latter energy scheme of which is consistent with the present experiment. The ground $\Gamma_5$ state is magnetic with magnetic moment of 2 $\mu_B$/Pr ion. At the same time, the $\Gamma_3$ state has a quadrupole moment. Therefore, we have to consider the two effects as the origin of the two peaks appearing at $T_1$ and $T_2$, whether the two peaks are due to the magnetic interaction or quadrupole interaction. At first, we assume simply that the peak, one of the two peaks, is due to the magnetic phase transition and consequently that the magnetic Pr ion makes hyperfine field at the Pr nucleus at temperatures below the magnetic phase transition. This assumption is, however, inconsistent with the present experimental result because the nuclear contribution to $C(T)$ is not observed apparently at 0.37 K. Moreover, in this assumption, the Zeeman interaction of $4f^2$ with $H_{ext}$ yields Zeeman splitting and then makes a Schottky-type broad peak in $C(T)$. The experimental result is, however, inconsistent with this assumption; the broad peak appearing around 3 K is suppressed to about one half of the simple calculation based on the Zeeman effect. Therefore, it is concluded that in PrPd$_3$ the quadrupole interaction also has to be taken into account to understand the characteristic behaviors in $C(T)$.

Finally, we consider the characteristic flat behavior with a giant value of 8.3 J/mol K$^2$ of $C(T)/T$ at low temperatures down to 0.37 K. Recently, Kucherenko et al. [5] have observed the giant hybridization effects in 4f photoemission spectra of Pr and Nd transition-metal compounds. According to them, in case of PrPd$_3$, the deviation of $n_f$ from 2 is mainly due to an admixture of about 3% of the $4f^3$ configuration to the ground state, and the hybridization is of the same order as in Ce systems. On the other hand, Koga at al. [7] investigate the CEF triplet ground state with dipolar and quadrupolar couplings to conduction electrons, and lead to a new nontrivial, non-Fermi-liquid point. Therefore, these effects are presumably responsible for the giant $C(T)/T$ of PrPd$_3$ at low temperatures.

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