T-H Phase Diagram of PrPb₃ in [001] and [110]
Magnetic Field Directions

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Abstract. We have measured the magnetic field dependence of the specific heat in PrPb₃ for H ∥ [001] and [110] up to H = 8 T. At H = 0 T, a sharp λ-type peak due to antiferro-quadrupolar (AFQ) ordering and a small anomaly appears at T_Q = 0.43 K and T* = 0.25 K, respectively. The field dependence of T_Q shows a reentrant behavior and a high-field phase appear above H ∼ 6 T in the both field directions. T* shows a large difference between H ∥ [001] and [110], suggesting that the anomaly is related to the anisotropic feature of the quadrupolar moment in magnetic fields. From these results, we describe the T-H phase diagram PrPb₃ in H ∥ [001] and [110].

1. Introduction
In 4f-electron systems, the spin-orbital interaction is larger than the crystalline-electric-field (CEF) effect so that the magnetic properties of 4f-electrons are characterized by the total angular momentum J(= L + S). In this case, the orbital degrees of freedom can be represented by quadrupolar moments. Five independent quadrupolar moments with two Γ₃-type and three Γ₅-type are defined under cubic(O_h) symmetry. PrPb₃ has a AuCu₃-type cubic structure and a trivalent Pr ion forms 4f² configuration in a crystal. The ninefold degenerate J multiplet ³H₄ of the trivalent Pr ion splits into four levels: a singlet Γ₁, a doublet Γ₃, a triplet Γ₄ and a triplet Γ₅ by the CEF effect. The CEF ground state of PrPb₃ has been studied by various experiments, such as nuclear inelastic scattering [1], specific heat [2] and magnetization measurements [3]. It is established that the CEF ground state is a non-Kramers doublet Γ₃, which carries two quadrupolar moments, O₁(2)= [3J² - J²]/2 and O₂(2)= √3[(Jₓ² - Jᵧ²)/2], and the first exited one is a triplet Γ₄ with an energy gap ∼ 19 K [2]. As the temperature is decreased, PrPb₃ exhibits antiferro-quadrupolar (AFQ) ordering at T_Q = 0.4 K [4].

The T-H phase diagram of AFQ ordering in PrPb₃ was studied by magnetization measurements, which revealed that the field dependence of T_Q is very anisotropic for H ∥ [001], [110] and [111] and the high-field phase appears only in H ∥ [110] [3] [5]. Moreover, the
order parameter of the low-field phase is determined to be $O_2^0$ by inelastic neutron diffraction measurements [6].

In this paper, we report the $T$-$H$ phase diagram of PrPb$_3$ in $H$ $||$ [001] and [110] measured by the specific heat up to $H = 8$ T. At $H = 0$ T, we observe a sharp peak due to the AFQ ordering at $T_Q = 0.43$ K and a small anomaly at $T^* = 0.25$ K. The field dependence of $T_Q$ shows a reentrant behavior and a high-field phase appears above $H \sim 6$ T in the both field directions. $T^*$ shows a large difference between $H$ $||$ [001] and [110], suggesting that the anomaly is related to the anisotropic feature of the quadrupolar moment.

2. Experimental
A single crystal of PrPb$_3$ were prepared by the Bridgman method. The stoichiometric amounts of Pr and Pb metals were heated in a molybdenum crucible sealed by electric beam welding in a vacuum. A high quality single crystal suitable for neutron diffraction experiments was obtained by this method. The specific heat was measured by a pseudo-adiabatic heat pulse method with a $^3$He-$^4$He dilution refrigerator from $T = 0.1$ K to $T = 1$ K and a superconducting magnet up to $H = 8$ T.

3. Results and Discussion

3.1. $H$ $||$ [001]
In Fig. 1(a), we show the temperature dependence of the specific heat at low fields for $H$ $||$ [001]. At $H = 0$ T, a sharp $\lambda$-type peak due to AFQ transition appears at $T_Q = 0.43$ K, while AFQ transition peak is observed at $T_Q = 0.4$ K in the previous studies. We reported that the AFQ transition temperature is suppressed to $T_Q = 0.28$ K only by 1% nonmagnetic La substitution of Pr, which demonstrates that $T_Q$ is very sensitive to sample quality, such as randomness and the presence of grain boundaries. In our previous sample with $T_Q = 0.4$ K, the tail of the neutron reflection peak was broad compared with that of the present sample, implying that the sample included some grain boundaries. From these results, we consider that the increase in $T_Q$ comes from the high quality of the present sample.

In addition, a small anomaly appears at $T^* = 0.25$ K at $H = 0$ T. Although the clear anomaly was not observed in the previous specific heat measurements, the slope in $C/T$ changes at around $T = 0.25$ K. This indicates that the anomaly reflects the essential feature of PrPb$_3$. This anomaly was also observed with ultra sound measurements [7]. It seems that the $T^*$ anomaly

![Figure 1](image-url)

**Figure 1.** (a) Magnetic field dependence of the specific heat in $H$ $||$ [001] up to $H = 1$ T, where the data are shifted by 1 J/(mol K), respectively. (b) Magnetic field dependence of the specific heat in $H$ $||$ [001] between $H = 5$ and 8 T.
stays approximately $T^* = 0.25\,\text{K}$ below $H = 1\,\text{T}$. Above $H = 1\,\text{T}$, the large peak appears at $T_1$, which is due to the first-order transition between the commensurate and incommensurate structures [8]. $T_1$ shows a strong hysteresis in the temperature scan as follows. The anomaly at $T_1$ cannot be observed in the specific heat with decreasing temperature, while we can observe the sharp anomaly at $T_1$ after decreasing the temperature to a value much lower than $T_1$. With increasing magnetic field, $T_1$ shifts to higher temperatures.

In Fig. 1(b), we show the magnetic field dependence of the specific heat from $H = 5\,\text{T}$ to $H = 8\,\text{T}$. As the magnetic field is increased, a sharp peak at $Q$ broadens, while a new peak becomes obvious at temperatures lower than $Q$. At $H = 7.2\,\text{T}$, for instance, two peaks are clearly observed at $T \sim 0.35\,\text{K}$ and $Q \sim 0.6\,\text{K}$. At $H = 8\,\text{T}$, the new peak develops into a $\lambda$-shaped anomaly, while the peak due to the AFQ ordering disappears. From these results, it is reasonable to consider that a new phase emerges in the high-field region in $H \parallel [001]$. It is noted that the new peak does not show the hysteresis between increasing and decreasing temperatures, implying a second-order transition between the paramagnetic and high-field phases. We have already reported the detail of these results in Ref. [9].

### 3.2. $H \parallel [110]$

Fig. 2(a) shows the temperature dependence of the specific heat at low fields for $H \parallel [110]$. As shown in the figure, $T_Q$ increases gradually to higher temperatures with increasing magnetic field. However, the increase of $T_Q$ in $H \parallel [110]$ is much lower than in $H \parallel [001]$. At $H = 2\,\text{T}$, for instance, $T_Q$ is at $\sim 0.45\,\text{K}$ for $H \parallel [110]$, while it reaches $\sim 0.52\,\text{K}$ for $H \parallel [001]$.

The application of magnetic field induces staggered magnetic dipolar and octupolar moments depending on the field direction with respect to the crystal axis [10]. The induced moments stabilize the AFQ phase, leading to the increase of $T_Q$. Therefore, the field dependence of the increase of $T_Q$ is explained by the difference of the induced moments. The order parameter of the low-field phase is $O^0_2$ for both directions so that the increase of $T_Q$ for $H \parallel [110]$ is lower than that for $H \parallel [001]$.

The anomaly at $T^*$ shifts to a higher temperature with increasing the magnetic field, and is observed up to $H = 2.5\,\text{T}$. We consider that the anomaly is related to changing the structure of the quadrupolar moments. The partially-disordered structure is observed down to $T = 0.1\,\text{K}$ in the neutron experiments [8]. However it is plausible at low temperatures that some of the disordered moments change into an ordered structure at $T^*$ to reduce the entropy and the rest

![Figure 2](image-url)  
**Figure 2.** (a) Magnetic field dependence of the specific heat in $H \parallel [110]$ up to $H = 2.5\,\text{T}$, where the data are shifted by $1\,\text{J/(mol K)}$, respectively. (b) Magnetic field dependence of the specific heat in $H \parallel [110]$ between $H = 5$ and $8\,\text{T}$, which are shifted by $1\,\text{J/(mol K)}$, respectively.
temperatures at H. It is seen that T_Q starts to decrease above H = 5 T, while a new peak appears at high temperatures above H = 7 T, suggesting the emergence of a high field phase.

We describe the T-H phase diagrams for H || [001] and H || [110] in Fig. 3 based on the present results. The AFQ ordering temperatures at T_Q and the first-order transition temperatures at T_1 are in good agreement with those in the previous experiments [3] [8]. We note that the high-field phase appears not only in H || [110] but also in H || [001].

4. Conclusion
We have measured the magnetic field dependence of the specific heat in PrPb_3 for H || [001] and [110] up to H = 8 T. At H = 0 T, two anomalies are observed at T_Q = 0.43 K and T^* = 0.25 K, respectively. The field dependence of T_Q shows a reentrant behavior and a high-field phase appears above H ~ 6 T in the both field directions. T^* shows a large difference between H || [001] and [110]. From these results, we describe the T-H phase diagram PrPb_3 in H || [001] and [110].

Figure 3. The T-H phase diagram of PrPb_3 in H || [001] and H || [110]. Filled and open squares indicate the results obtained by the specific heat measurements at fixed H and by the C/T plot at fixed T, respectively. Filled triangles plot T^*. Open circles are given by the magnetization measurements at fixed T [3]. The solid line draws the phase diagram determined by the experiments, while the dotted line serves as a visual guide.

are frozen by the quadrupole Kondo effect as shown in its diluted system [11]. A large peak due to the first-order transition appears above H = 1.5 T as shown by T_1 in Fig. 2(a). The field dependence of T^* and T_1 are clearly different from those for H || [001]. The difference is likely caused by the anisotropic feature of the quadrupolar moments in magnetic fields.

We show the temperature dependence of the specific heat at high fields for H || [110] in Fig. 2(b). It is seen that T_Q starts to decrease above H = 5 T, while a new peak appears at high temperatures above H = 7 T, suggesting the emergence of a high field phase.

We describe the T-H phase diagrams for H || [001] and H || [110] in Fig. 3 based on the present results. The AFQ ordering temperatures at T_Q and the first-order transition temperatures at T_1 are in good agreement with those in the previous experiments [3] [8]. We note that the high-field phase appears not only in H || [110] but also in H || [001].

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