Nonmagnetic $\Gamma_3$ doublet ground state in a caged compound PrRh$_2$Zn$_{20}$

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Abstract.

We have prepared single crystals of PrRh$_2$Zn$_{20}$, which is isostructural and isoelectronic to PrIr$_2$Zn$_{20}$ where coexistence of superconductivity and antiferroquadrupolar order has been recently found. The electrical resistivity $\rho$, magnetic susceptibility $\chi$, isothermal magnetization $M$, and specific heat $C$ have been measured. Hysteretic behavior appears in $\rho(T)$ for $170 \text{ K} < T < 470 \text{ K}$, suggesting a structural phase transition. On cooling below 10 K, $\chi$ approaches a constant value, indicating a non-magnetic ground state. Anisotropic behavior in $M(B)$ at 1.8 K for $B > 2 \text{ T}$ and a broad peak in $C(T)$ at around 10 K are reproduced by the two crystal-field levels split by 32 K; a nonmagnetic $\Gamma_3$ doublet ground state and a magnetic $\Gamma_4$ triplet excited state.

1. Introduction

Praseodymium-filled skutterudites show a variety of phenomena owing to the $4f^2$ electronic configuration of the Pr$^{3+}$ ions, such as heavy-fermion superconductivity in PrOs$_4$Sb$_{12}$ [1], scalar-type multipole ordering in PrFe$_4$P$_{12}$ [2, 3, 4], and a metal-insulator transition in PrRu$_4$P$_{12}$ [5]. Recently, another class of Pr encaged compounds PrT$_2$X$_{20}$ (T: transition metal, X: Al, Zn) have been synthesized, which crystallize in the cubic CeCr$_2$Al$_{20}$-type structure with the space group of $Fd\bar{3}m$ [6]. The Pr atom is encapsulated in a highly symmetric Frank-Kasper cage formed by 16 zinc atoms. This leads crystalline electric field (CEF) ground states to be degenerated so that multipolar degrees of freedom remain active and the $4f$ electrons can be hybridized with conduction electrons. Therefore, phase transitions and/or Kondo effect of the multipolar degrees of freedom are expected to occur. Recently, PrIr$_2$Zn$_{20}$ with a nonmagnetic $\Gamma_3$ doublet ground state has been found to undergo a superconducting transition at $T_c=0.05 \text{ K}$ in the presence of antiferroquadrupolar (AFQ) order below $T_Q=0.11 \text{ K}$ [7, 8, 9]. It is suggested that the quadrupolar fluctuations play an important role in the formation of the Cooper pairs. PrT$_2$Al$_{20}$ (T=Ti, V, Nb) also display anomalous temperature dependences of the electrical resistivity and the specific heat which is possibly related to quadrupole Kondo effect [10, 11]. These facts suggest that strong correlation between the $4f^2$ electronic state and the conduction electrons plays a crucial role in forming the unusual ground states of the PrT$_2$X$_{20}$ family.

In the present work, we focus on PrRh$_2$Zn$_{20}$ which is isoelectronic to PrIr$_2$Zn$_{20}$. Because the CEF level scheme is expected to be similar to that for PrIr$_2$Zn$_{20}$, the ground state would be
the $\Gamma_3$ doublet. To study how the ground state changes on going from PrIr$_2$Zn$_{20}$ to PrRh$_2$Zn$_{20}$, we have grown single-crystalline samples of PrRh$_2$Zn$_{20}$ and studied the magnetic and transport properties.

2. Experimental

Single-crystalline samples of PrRh$_2$Zn$_{20}$ were grown by the melt-growth method with high-purity elements of Pr (4N), Rh (3N) and Zn (6N). The CeCr$_2$Al$_{20}$-type structure was confirmed by powder x-ray diffraction method. The lattice parameter at room temperature was refined to be 14.294(8) Å, whose value agrees with the reported one [6]. The crystal compositions were determined by electron-probe microanalysis (EPMA) to be 1 : 1.98(1) : 20.02(5). The EPMA detected binary alloys RhZn$_6$ and Pr$_{14}$Zn whose volume fractions are less than 5 \% in view of back-scattering electron images. The single-crystalline sample was oriented by the back reflection Laue method using an imaging plate camera, IPXC/B (TRY-SE).

The electrical resistivity $\rho$ was measured by a standard four-probe AC method in a laboratory-built system with a Gifford-McMahon-type refrigerator between 30 and 600 K. The specific heat $C$ was measured by a relaxation method using a commercial calorimeter (Quantum Design PPMS) at temperatures between 0.4 and 300 K. The magnetization $M$ was measured using a SQUID magnetometer (Quantum Design MPMS) between 1.8 and 300 K and in magnetic fields up to 5 T.

3. Results and Discussion

Figure 1 shows the result of $\rho(T)$ for PrRh$_2$Zn$_{20}$. In the temperature range between 170 K and 470 K, hysteretic behavior appears, indicating a first-order phase transition. Hysteretic behaviors were also observed in LaRu$_2$Zn$_{20}$ and PrRu$_2$Zn$_{20}$ at $T_S=150$ and 138, respectively [7]. Since superlattice reflections were observed in PrRu$_2$Zn$_{20}$ below $T_S$, the hysteretic behavior was attributed to a structural modulation. If the local symmetry at the Pr site was lowered in PrRu$_2$Zn$_{20}$, quadrupolar degrees of freedom would vanish below the transition temperature. In PrIr$_2$Zn$_{20}$, on the other hand, no evidence for structural transition was found in $\rho(T)$ from 530 K to 30 K, as shown in Fig. 1. Therefore, the quadrupolar degree of freedom remains active in the $\Gamma_3$ doublet. The inset of Fig. 2 shows $\chi(T)$ of PrRh$_2$Zn$_{20}$ in a magnetic field of

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the electrical resistivity $\rho$ of PrRh$_2$Zn$_{20}$ (solid lines) and PrIr$_2$Zn$_{20}$ (broken lines).

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of the inverse of magnetic susceptibility $\chi(T)$ for PrRh$_2$Zn$_{20}$. The inset shows the Van-Vleck behavior in $\chi(T)$. 

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B=1 T. On cooling below 10 K, χ(T) gradually approaches a constant value, indicating a Van-Vleck paramagnet. This behavior suggests that the CEF ground state is nonmagnetic, either Γ1 singlet or Γ3 doublet. The main panel of Fig. 2 shows χ−1(T) measured at B=1 T. Above 30 K, χ−1 follows the Curie-Weiss law with the effective magnetic moment of 3.55 μB/f.u., which is in agreement with the value of the trivalent Pr free ion. The T-linear behavior of χ−1(T) in the wide temperature range 30 K < T < 300 K suggests the weak CEF effect on the Pr 4f electrons. The paramagnetic Curie temperature \( T_p \) of \( 4.8 \) K indicates that the intersite interaction between the magnetic moments of Pr ions is antiferromagnetic but rather weak.

Figure 3 shows the temperature dependence of the magnetic part of the specific heat divided by temperature, \( C_m/T \). For the lattice part of \( C \) in PrRh\(_2\)Zn\(_{20}\), we used the data of LaIr\(_2\)Zn\(_{20}\) because the more relevant compound LaRh\(_2\)Zn\(_{20}\) does not form. A broad peak manifests itself in \( C_m/T \) at around 10 K. To reproduce this Schottky-like anomaly, we assumed the cubic point group \( T_d \) of the Pr sites. Then, two models as depicted in Fig. 3 are considered for two levels split by Δ=32 K; one is the \( 3 \)-doublet-\( 4 \)-triplet model and the other is the \( 1 \)-doublet-\( 4 \)-triplet model. Here, we neglect the higher excited levels. The solid and broken lines represent the calculations, respectively. The peak at around 10 K is better reproduced by the former than the latter. This fact is favorable to the \( 3 \)-doublet ground state. The \( 3 \)-doublet ground state is also supported by the anisotropic field dependence of \( M(B) \). Figure 4 shows the isothermal magnetization \( M(B) \) for \( B \parallel [100] \) (●) and \( B \parallel [110] \) (□) at 1.8 K. The two data are almost the same up to 2 T, above which two curves gradually diverge. This anisotropic behavior can be well reproduced by the calculation of \( M(B) \) using the \( \Gamma_3-\Gamma_4 \) model, as shown with the solid lines in Fig. 4.

On cooling below 3 K, \( C/T \) continuously increases and reaches 4 J/K\(^2\) mol at 0.4 K as was observed in PrIr\(_2\)Zn\(_{20}\) [7]. This increase of \( C/T \) possibly results from the gradual release of the entropy of the \( \Gamma_3 \) doublet. Since the magnetic properties of PrRh\(_2\)Zn\(_{20}\) at temperatures down to 0.4 K resemble those of PrIr\(_2\)Zn\(_{20}\), we expect that an AFQ order and/or a superconducting transition occur at temperatures below 0.4 K.

It remains as an important question why the \( \Gamma_3 \) doublet ground state is stable in PrRh\(_2\)Zn\(_{20}\) in spite of the possible structural transition above 170 K. Because the \( \Gamma_3 \) doublet is realized only in the cubic point groups, the low temperature phase needs to belong to another cubic point group.
We recall that the metal-insulator transition in PrRu$_4$P$_{12}$ at $T_{MI}=63$ K is accompanied with a structural transition from a body-centered cubic structure in the high-temperature metallic phase to a simple cubic one in the low-temperature insulator phase [13]. In order to determine the structure of the low-temperature phase of PrRh$_2$Zn$_{20}$, x-ray diffraction analysis on a single-crystalline sample is on progress.

4. Conclusion
We performed measurements of $\rho$, $\chi$, $M$, and $C$ on single-crystalline samples of PrRh$_2$Zn$_{20}$. The hysteretic behavior in $\rho(T)$ above 170 K indicates a structural transition. A Van-Vleck behavior in $\chi(T)$ below 10 K, the Schottky anomaly in $C(T)$ at around 10 K and the anisotropic behavior of $M(B)$ above 2 T are consistent with the nonmagnetic $\Gamma_3$ doublet ground state. However, no phase transition attributed to the $\Gamma_3$ doublet has been observed down to 0.4 K. At lower temperatures, an AFQ order and/or a superconducting transition would be observed.

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