Low-temperature physical properties of new orthorhombic compounds $R_4Pt_9Al_{13}$ ($R = Ce, Pr$)

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Abstract. Magnetic, transport, and thermal properties of new orthorhombic compounds $Ce_4Pt_9Al_{13}$ and $Pr_4Pt_9Al_{13}$ have been investigated by the magnetization, the electrical resistivity, and the specific-heat measurements. $Ce_4Pt_9Al_{13}$ is a Kondo-lattice compound and shows a ferromagnetic or ferrimagnetic transition at $T_C = 0.88$ K. $Pr_4Pt_9Al_{13}$ is an antiferromagnetic compound with the transition temperature at $T_N = 2.6$ K.

1. Introduction

Recently, coexistence of ferromagnetism and superconductivity in some U-based compounds have attracted much attention [1]. In contrast to the discovery of the U-based ferromagnetic superconductors, no other systems such as Ce-based or Yb-based ones have been discovered thus far. In order to examine the mechanism of the coexistence more precisely, it is important to examine physical properties of the other systems showing the coexistence. From this view point, we have focused on a new orthorhombic compound $Ce_4Pt_9Al_{13}$ (space group: $Pmnm$, $D_{2h}^{13}$, No. 59) [2]. There are three independent Ce sites in this structure as shown in the figure 1. The physical property measurements down to 1.72 K have revealed that this compound does not show any magnetic transition down to 1.72 K, although the positive paramagnetic Curie temperature (41.6 K) implies ferromagnetic interaction between Ce moments [2]. In this study, magnetic and transport properties of $Ce_4Pt_9Al_{13}$ have been examined down to 0.4 K. Additionally, we have tried to prepare samples of $Pr_4Pt_9Al_{13}$ and examined their physical properties since...
Ce₄Pt₉Al₁₃ is a new compound and no isomorphous compounds with the other rare earths have been synthesized.

2. Experimental methods
Polycrystalline samples of Ce₄Pt₉Al₁₃ and Pr₄Pt₉Al₁₃ were synthesized by arc melting the stoichiometric constituent elements in an Ar atmosphere. The X-ray powder diffraction experiments for these compounds revealed that all of the Bragg peaks in the diffraction patterns can be indexed on the basis of the reported structure. No impurity peaks were detected in the diffraction patterns. The lattice constants were determined to be $a = 4.1739$, $b = 11.4373$, and $c = 19.8125$ Å for Ce₄Pt₉Al₁₃, and $a = 4.1615$, $b = 11.4162$, and $c = 19.7620$ Å for Pr₄Pt₉Al₁₃. The lattice constants of Ce₄Pt₉Al₁₃ agree with the previously reported ones [2] within the experimental precision. The magnetization $M$ was measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS) as functions of the temperature $T$ and magnetic field $H$ between 1.8 and 300 K up to 5 T. The electrical resistivity $\rho$ was measured with a dc four-probe method between 0.4 and 300 K in a laboratory-built $^3$He cryostat. The specific heat $C$ was measured with a thermal relaxation method between 0.5 and 9 K in a $^3$He cryostat.

3. Results and Discussion

3.1 Ce₄Pt₉Al₁₃
The inverse magnetic susceptibility $H/M$ of Ce₄Pt₉Al₁₃ (not shown) above 100 K obeys the Curie-Weiss law $H/M = \frac{(T - \theta_p)}{C_{\text{Curie}}}$, where $C_{\text{Curie}} = 0.894$ emu K/Ce-mol and $\theta_p = -189.8$ K show the Curie constant and the paramagnetic Curie temperature, respectively. The effective magnetic moment $\mu_{\text{eff}}$ calculated from $C_{\text{Curie}}$ is $2.67 \mu_B$/Ce ($\mu_B$: Bohr magneton). Since the calculated $\mu_{\text{eff}}$ is close to the theoretical one for the free Ce$^{3+}$ ion ($2.54 \mu_B$/Ce), we can consider that the Ce ions in this compound are trivalent. The negative $\theta_p$ indicates that the antiferromagnetic interaction acts between the Ce magnetic moments, although the positive $\theta_p$ (ferromagnetic interaction) was reported in the previous report. No anomaly of $H/M$ has been detected above 1.8 K as already reported previously.

Figure 2 shows the temperature dependence of the electrical resistivity $\rho$ of Ce₄Pt₉Al₁₃. $\rho$ decreases

![Figure 2. Temperature dependence of the electrical resistivity $\rho$ of Ce₄Pt₉Al₁₃. The inset represents the low-temperature part of $\rho$ measured in the various magnetic fields.](image)

![Figure 3. Temperature dependence of the specific heat $C$ and the total entropy $S$ of Ce₄Pt₉Al₁₃.](image)
with decreasing temperature, followed by a minimum at 18 K, and shows \(-\ln T\) dependence between 18 K and 7 K. These \(\rho(T)\) behavior indicates that Ce₄Pt₉Al₁₃ is a Kondo lattice compound. In addition, \(\rho\) shows a steep decrease at \(T_c = 0.88\) K, indicating that some phase transition occurs at this temperature. The low-temperature part of \(\rho\) measured in various magnetic fields are shown in the inset of the figure. \(T_c\) shifts to higher temperatures with increasing magnetic field, indicating that the decrease in the \(\rho\) at 0.88 K corresponds to the ferromagnetic transition temperature. No superconductivity has been detected above 0.4 K.

Figure 3 shows the temperature dependence of the specific heat \(C\) of Ce₄Pt₉Al₁₃. The \(\lambda\)-type anomaly at \(T_c\) indicates that the second-order ferromagnetic transition occurs at \(T_c\). Figure 3 also shows the temperature dependence of the total entropy \(S\) derived by integrating \(C/T\) in \(T\). Since the symmetry of the crystalline electric field is monoclinic for Ce1 site, and orthorhombic for Ce2 and Ce3 sites, the six-fold ground multiplet of Ce³⁺ splits into three doublets for these Ce sites. In this case, it is expected that the entropy released at \(T_c\) reaches \(R\ln2\) (\(R\): gas constant). However, the \(S\) value at \(T_c\) is only 45% of \(R\ln2\) (2.6 J/Ce·mol K). Such a large reduction of \(S\) from \(R\ln2\) cannot be explained only by the Kondo effect. The reduced \(S\) is mainly ascribable to the short-range magnetic correlation below 4 K. In fact, the \(C\) increases gradually below 4 K and the \(S\) value reaches 99% of \(R\ln2\) at 4 K.

There are three independent Ce sites in the crystal structure of Ce₄Pt₉Al₁₃ as described above. In such structure, the magnitude of Ce magnetic moments and/or the magnetic interaction are not necessarily identical among these Ce sites. We therefore cannot decide from the present study if the magnetic structure is simple ferromagnetic or ferrimagnetic. As the next step, we have to determine magnetic structure by neutron diffraction experiment.

### 3.2 Pr₄Pt₉Al₁₃

Figure 4 shows the temperature dependence of the inverse magnetic susceptibility \(H/M\) of Pr₄Pt₉Al₁₃ measured at 0.1 T. \(H/M\) above 100 K follows the Curie-Weiss law (see the solid line in the figure. 4). The \(\mu_{\text{eff}}\) and the \(\theta_P\) derived by the Curie-Weiss fitting are 3.53 \(\mu_B/\text{Ce}\) and -91.4 K, respectively. Since the derived \(\mu_{\text{eff}}\) is close to the theoretical one for the free Pr³⁺ ion (3.58 \(\mu_B/\text{Ce}\)), we can consider that the Pr ions in Pr₄Pt₉Al₁₃ are trivalent. The negative \(\theta_P\) indicates that the antiferromagnetic interaction acts between the Pr magnetic moments. The magnetic susceptibility \(M/H\) shows a cusp at \(T_N = 2.6\) K as

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**Figure 4.** Temperature dependence of the inverse magnetic susceptibility \(H/M\) of Pr₄Pt₉Al₁₃ measured at 0.1 T. The inset represents the low-temperature part of \(M/H\).

**Figure 5.** Temperature dependence of the specific heat \(C\) and the total entropy \(S\) of Pr₄Pt₉Al₁₃.
shown by the arrow in the inset of the figure. The cusp of $M/H$ and the negative $\theta_P$ indicate the occurrence of antiferromagnetic transition at $T_N$.

The electrical resistivity $\rho$ of Pr$_4$Pt$_9$Al$_{13}$ (not shown) decreases with decreasing temperature and shows an increase below $T_N$. The increase below $T_N$ is probably due to the formation of a superzone gap accompanied by the antiferromagnetic transition.

Figure 5 represents the temperature dependence of the specific heat $C$ of Pr$_4$Pt$_9$Al$_{13}$. The $\lambda$-type anomaly at $T_N$ indicates that the second-order antiferromagnetic transition occurs at $T_N$. The total entropy $S$ calculated by the same method for Ce$_4$Pt$_9$Al$_{13}$ is also shown in the figure. The $S$ value at $T_N$ is 78% of $R\ln2$ and exceeds $R\ln2$ above 3.8 K. The nine-fold ground multiplet of Pr$^{3+}$ splits into nine singlets under the crystalline electric field with orthorhombic or monoclinic symmetry. The abovementioned $S$ value suggests that the first excited and/or the second excited singlets are located at the vicinity of the ground singlet. We therefore consider that the pseudo doublet ground state is responsible for the antiferromagnetic transition. The increase in $S$ below 0.8 K is probably attributed to the nuclear specific heat of Pr$^{3+}$ ions.

4. Conclusion
In this study, polycrystalline samples of new orthorhombic compounds R$_4$Pt$_9$Al$_{13}$ (R = Ce, La) have been synthesized and their physical properties down to 0.4 K have been examined.

Magnetic-susceptibility measurement has revealed that the Ce ions in Ce$_4$Pt$_9$Al$_{13}$ are trivalent. Ce$_4$Pt$_9$Al$_{13}$ is a ferromagnetic or ferrimagnetic Kondo-lattice compound with the transition temperature at $T_C = 0.88$ K. No superconductivity has been detected above 0.4 K.

We have found that Pr$_4$Pt$_9$Al$_{13}$ exists as the isomorphic compound of Ce$_4$Pt$_9$Al$_{13}$. Magnetic-susceptibility measurement has revealed that the Pr ions in Pr$_4$Pt$_9$Al$_{13}$ are trivalent. The pseudo doublet ground state of Pr$^{3+}$ is responsible for the antiferromagnetic transition at 2.6 K.

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