Semiconducting behaviour in CeT$_2$Al$_{10}$ (T=Fe and Ru)

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Abstract. We present results of the magnetic susceptibility, electrical resistivity and thermopower for CeT$_2$Al$_{10}$ (T=Fe and Ru) crystallizing in the orthorhombic YbFe$_2$Al$_{10}$-type structure. The magnetic susceptibility for CeFe$_2$Al$_{10}$ shows a maximum at 70 K which is a characteristic of a valence fluctuation system. The electrical resistivity below 20 K exhibits semiconducting behaviour with an energy gap of 15 K. On the other hand, CeRu$_2$Al$_{10}$ displays Curie-Weiss behaviour of Ce$^{3+}$ in the susceptibility down to 30 K, and undergoes an antiferromagnetic transition at $T_N=27$ K. The semiconducting behaviour of the resistivity between 70 K and 30 K is described by a gap of 50 K. On cooling below $T_N$, however, the resistivity exhibits a peak at 23 K and falls down. The thermopower shows two maxima at 22 K and 6 K. These findings suggest that the magnetic order induces a semiconductor-to-metal transition in CeRu$_2$Al$_{10}$.

1. Introduction

The formation of an energy gap in the quasi-particle density of states via the hybridization between the localized 4f and conduction electrons is one of the attracting physical phenomena in the rare-earth based Kondo-lattice systems. Such a system is called “Kondo insulator” or “Kondo semiconductor”[1]. Most Kondo semiconductors based on Ce have particular cubic structures like Ce$_3$X$_4$T$_3$ (X=Sb and Bi, T=Pt, Cu and Au) with the Y$_3$Sb$_4$Au$_3$-type structure and CeT$_4$P$_{12}$ (T=Fe, Ru and Os) with the filled skutterudite one[2,3]. In contrast, CeNiSn, CeRhSb and CeRhAs crystallizing in the ε-TiNiSi-type are rare examples of the orthorhombic Kondo semiconductors[4,5]. These orthorhombic Ce compounds are valence fluctuation systems and have a rather narrow energy gap in the order of 10-100 K.

In this paper, we present new systems of orthorhombic Kondo semiconductors CeT$_2$Al$_{10}$ (T=Fe and Ru). These compounds crystallize in the YbFe$_2$Al$_{10}$-type structure where the rare-earth ion is surrounded by the T-Al polyhedron[6,7]. Both compounds show semiconducting behaviour in an activation type temperature dependence of the electrical resistivity. However, the valence states are largely different. CeFe$_2$Al$_{10}$ is a valence fluctuation system while CeRu$_2$Al$_{10}$ shows the stable trivalency of Ce and an antiferromagnetic transition at 27 K.

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2. Experimental
Polycrystalline samples of CeFe$_2$Al$_{10}$, CeRu$_2$Al$_{10}$ and their La counterparts were synthesized by arc-melting the stoichiometric amounts of constituent elements under an argon atmosphere, and then annealed at 800 °C for one week in an evacuated quartz tube. Powder x-ray diffraction analysis confirmed that both compounds crystallize in the YbFe$_2$Al$_{10}$-type structure (space group Cmcm, No. 63). From the least-square refinement, the lattice parameters are obtained as $a=8.992$ Å, $b=10.216$ Å and $c=9.065$ Å for CeFe$_2$Al$_{10}$ and $a=9.1246$ Å, $b=10.281$ Å and $c=9.1878$ Å for CeRu$_2$Al$_{10}$. These parameters agree with those reported for CeFe$_2$Al$_{10}$ by Thiede et al. [6] and for CeRu$_2$Al$_{10}$ by Tursina et al.[7]. The stoichiometry of the samples was examined by the electron-probe microanalysis (EPMA).

Magnetic susceptibility $M/B$ was measured by using a commercial SQUID magnetometer (Quantum Design MPMS) from 2 K to 400 K. Electrical resistivity $\rho$ measurements between 1.8 K and 300 K were performed by an ac four-probe method in a Quantum Design PPMS cryostat. Thermopower $S$ was measured by a differential technique from 4.2 K to 300 K with a temperature gradient 0.05-0.5 K.

3. Results and Discussion

3.1. CeFe$_2$Al$_{10}$
The magnetic and transport properties of CeFe$_2$Al$_{10}$ are summarized in Fig. 1. $M/B$ shown in Fig. 1(a) obeys a Curie-Weiss law from 300 K to 100 K. The effective magnetic moment $\mu_{\text{eff}}$ and the paramagnetic Curie temperature $\theta$ are obtained as $2.8$ $\mu_B$/f.u. and $-440$ K, respectively. The broad maximum at 70 K as well as the large negative value of $\theta$ indicates that CeFe$_2$Al$_{10}$ is a valence fluctuation compound. A Curie tail below 9 K may result from a small amount (~0.1%) of paramagnetic impurities involving trivalent Ce ions.

Figure 1(b) shows the temperature dependence of $\rho$. The $-\log T$ dependence from 300 K to 100 K is a characteristic of a Kondo system. Passing through a broad maximum at 70 K, $\rho(T)$ increases rapidly with decreasing $T$ below 20 K. The semiconducting behaviour $\rho(T)\times\exp(\Delta/2k_BT)$, where $\Delta$ is the energy gap, is manifested in the $\ln \rho$ vs $1/T$ plot (a solid line in the inset of Fig. 1 (b)). The slope between 20 K and 10 K gives the value $\Delta=15$ K. Both the dependence of $\rho(T)$ and the gap energy are similar to the features of the orthorhombic Kondo semiconductor CeRhSb[1,4].

The features of $S(T)$ in Fig. 1(c) also resemble that of CeRhSb[4]. The broad peak at 130 K in $S(T)$ results from the Kondo effect. As shown in the inset of Fig. 1(c), $S(T)$ decreases below 20 K and changes the sign to negative, suggesting the formation of $T$-dependent gap at the Fermi energy.

3.2. CeRu$_2$Al$_{10}$
The magnetic and transport properties of CeRu$_2$Al$_{10}$ are summarized in Fig. 2. Figure 2 (a) shows the temperature dependence of $M/B$. As shown by a solid line, the Curie-Weiss behaviour is observed from 300 K down to 30 K. We obtained $\theta=-100$ K and $\mu_{\text{eff}}=2.6$ $\mu_B$/f.u. whose value is close to the value $2.54$ $\mu_B$ for the Ce$^{3+}$ free ion. A sharp kink at 27 K indicates an antiferromagnetic transition[8]. The origin of a Curie tail below 14 K is attributed to an undefined Ce-Ru-Al impurity (possibly CeRu$_{3-x}$Al$_{10+x}$[9]) observed by EPMA.

Figure 2(b) demonstrates the unusual behaviour of $\rho(T)$ for CeRu$_2$Al$_{10}$, which contrast sharply with the metallic behaviour for LaRu$_2$Al$_{10}$. The two insets show, respectively, $-\log T$ behaviour above 70 K and activation-type one with $\Delta=50$ K below 70 K. Below $T_N=27$ K, $\rho(T)$ exhibits a sharp peak at 23 K and then falls to a value of 1 m$\Omega$cm. This means that the gap is destroyed in part by the antiferromagnetic order.

Temperature dependence of $S$ for CeRu$_2$Al$_{10}$ displays three maxima at 150 K, 22 K and 6 K as shown in Fig. 2(c). The peak at 150 K should result from the Kondo effect because $\rho$ shows the $-\log T$
Figure 1. Temperature dependence of (a) $M/B$, (b) $\rho$ and (c) $S$ for CeFe$_2$Al$_{10}$. A solid line in (a) denotes the Curie-Weiss fit. The insets of (b) and (c) represent the $\ln \rho$ vs $1/T$ plot and the low-temperature part of $S$, respectively.

Figure 2. Temperature dependence of (a) $M/B$, (b) $\rho$ and (c) $S$ for CeRu$_2$Al$_{10}$. A solid line in (a) represents the Curie-Weiss fit. The insets of (b) show $\rho \propto -\log T$ (right) and $\ln \rho \propto 1/T$ (left). The inset of (c) represents $\rho(T)$ and $S(T)$ for $T<30$ K.

behaviour. At 50 K where $\rho(T)$ shows the semiconducting behaviour, $S(T)$ vanishes and increases on further cooling. This feature suggests that the semiconducting state has electron-hole symmetry[10]. The low-temperature two maxima occur at the same temperatures with those in $\rho(T)$.

The magnetic measurements demonstrate that the Ce 4f states are contrasting between CeFe$_2$Al$_{10}$ and CeRu$_2$Al$_{10}$. The valence instability in CeFe$_2$Al$_{10}$ should originate from the strong 4f hybridization with the Fe 3d band. As was indicated in CeT$_4$P$_{12}$ for T=Fe and Ru[3], the 3d band has the large and narrow density of states near the Fermi level relative to the Ru 4d one.

Within the isostructural Kondo semiconductors, the magnitude of the hybridization gap tends to increase with increasing the hybridization strength[11]. For CeT$_2$Al$_{10}$, on the contrary, the antiferromagnet CeRu$_2$Al$_{10}$ with weaker hybridization possesses larger energy gap than in CeFe$_2$Al$_{10}$. The reason for this contradiction may be related to the rather high $T_N$ relative to other Ce antiferromagnets ($T_N \leq 5$ K) as well as the two maxima in $\rho(T)$ and $S(T)$. In order to clarify the anomalous behaviour in CeRu$_2$Al$_{10}$, microscopic studies by nuclear magnetic resonance and neutron scattering experiments are in progress.

4. Summary
We have synthesized Ce-based cage-like compounds CeT$_2$Al$_{10}$ (T=Fe and Ru) and studied the magnetic and transport properties by measuring the magnetic susceptibility, electrical resistivity and
thermoelectric power. CeFe$_2$Al$_{10}$ shows valence fluctuation behaviour while CeRu$_2$Al$_{10}$ with trivalent Ce states orders antiferromagnetically at 27 K. Nevertheless, both compounds display semiconducting behaviour in the electrical resistivity. The Kondo effect manifests itself as the large negative value of the paramagnetic Curie temperature, the logarithmic temperature dependence in the resistivity and the broad peak in the thermopower. The fact that the La counterparts are good metals indicates that the semiconducting behaviour for CeT$_2$Al$_{10}$ results from the hybridization between the Ce 4f electrons and the conduction electrons. The narrow energy gaps of 15 K for CeFe$_2$Al$_{10}$ and 50 K for CeRu$_2$Al$_{10}$ are also comparable to that for Ce-based Kondo semiconductors crystallizing in the orthorhombic structure.

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