Dilution effect of Ce ion in CeRu$_2$Al$_{10}$

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Abstract. CeRu$_2$Al$_{10}$ causes a mysterious phase transition at $T_0\sim 27$ K. In order to examine the feature of this transition, we have measured the magnetic susceptibility and electrical resistivity of Ce$_{1-x}R_x$Ru$_2$Al$_{10}$ ($R=\text{La, La}_{0.63}\text{Y}_{0.37}$, Y) system in which Ce ions in CeRu$_2$Al$_{10}$ are replaced by non-magnetic rare earth ions with different ionic radii, where the relationship among the ionic radii is $\text{La}^{3+} > (\text{La}_{0.63}\text{Y}_{0.37})^{3+} \sim \text{Ce}^{3+} > \text{Y}^{3+}$. The magnitude of the magnetic susceptibility becomes smaller with decreasing ionic radii, indicating Kondo temperature increases due to the chemical pressure effect. In the La- and La$_{0.63}$Y$_{0.37}$-substituted system, $T_0$ decreases monotonically and disappears smoothly at $x\sim 0.7$, while in the Y-substituted system, $T_0$ decreases more slowly and disappears suddenly between $x=0.4$ and 0.5. These behaviors cannot be understood by a simple magnetic phase transition, suggesting that the change in valence of Ce ion plays an important role in the mysterious phase transition.

1. Introduction

Orthorhombic YbFe$_2$Al$_{10}$-type CeRu$_2$Al$_{10}$ [1] undergoes a phase transition at $T_0\sim 27$ K [2, 3]. Although neutron diffraction experiments have revealed the occurrence of an antiferromagnetic ordered moment with the magnitude of $\sim 0.3 \ \mu_B$/Ce along the $c$ axis below $T_0$ [4], this phase transition seems to be too high as a magnetic transition. This is because the antiferromagnetic transition temperatures of NdRu$_2$Al$_{10}$ and GdRu$_2$Al$_{10}$ with the same crystal structure are $T_N=2.2$ K and 16.5 K, respectively. Magnetic transition temperatures of rare earth compounds are scaled by the de Gennes factor $(g_J-1)^2J(J+1)$ within the molecular field approximation. The Néel temperatures of NdRu$_2$Al$_{10}$ and CeRu$_2$Al$_{10}$ expected from $T_N$ of GdRu$_2$Al$_{10}$ using this scaling law are estimated as 1.93 K and 0.19 K, respectively, which is almost identical in NdRu$_2$Al$_{10}$, while nearly 100 times smaller in CeRu$_2$Al$_{10}$. This might be related to the valence instability of 4$f$ electrons in Ce, which is not considered in the molecular field approximation.

Tanida et al. examined the macroscopic properties of La-substituted system Ce$_{1-x}$La$_x$Ru$_2$Al$_{10}$ in order to investigate the mechanism of the phase transition at $T_0$ [5]. They found that $T_0$ decreases monotonically with $x$ and smoothly disappears, indicating that the origin of this phase transition is based on the interaction between Ce ions. On the other hand, decrease in $T_0$ with respect to $x$ in Y-substituted system Ce$_{1-x}$Y$_x$Ru$_2$Al$_{10}$ is smaller than the La-substituted system [6]. The different behaviors in different non-magnetic ion substitution imply that the chemical pressure effect due to the difference of ionic radii plays an important role in the phase transition. Since the change in lattice volume alters the conduction- and 4f-
exchange interaction $J_{ef}$, the mysterious phase transition should be related to a small change in $J_{ef}$.

The purpose of this study is to examine systematical dilution effect of Ce ion in CeRu$_2$Al$_{10}$ and to clarify the relationship between the phase transition and the lattice volume. In order to achieve this, we have measured the magnetic susceptibility $\chi$ and electrical resistivity $\rho$ of Ce$_{1-x}$R$_x$Ru$_2$Al$_{10}$ ($R$=La, $La_{0.63}Y_{0.37}$, Y) system in which Ce ions in CeRu$_2$Al$_{10}$ are replaced by non-magnetic ion with different ionic radius, where the relationship among ionic radii is La$^{3+}$ > ($La_{0.63}Y_{0.37}$)$^{3+}$ ~ Ce$^{3+}$ > Y$^{3+}$.

2. Experimental

All measurements were carried out using single crystals grown by the Al self-flux method. Single crystals were grown in the following steps. First, polycrystalline samples with stoichiometric ratio were melted using an arc furnace in an argon atmosphere. Then the crushed polycrystalline crystals were grown in the following steps. First, polycrystalline samples with stoichiometric ratios were melted together with Al chips, the composition ratio of R:Ru:Al=1:2:60, were placed in an aluminum tube, and they were vacuum-sealed in a quartz ampoule. They were heated to 1000 $^\circ$C and then cooled to 680 $^\circ$C at a rate of $-5^\circ$C/h and the Al-flux was removed by centrifugation. Slight remaining Al-flux was completely removed by NaOH solution (5M). The resulting single crystals were polyhedron shape. Powder X-ray diffraction confirmed the single phase with YbFe$_2$Al$_{10}$-type. The crystallographic axes were determined from the single crystal surface using a diffractometer. The magnetization was measured using a SQUID magnetometer (Quantum Design, MPMS-XL5). The electrical resistivity was measured using a standard ac four-probe method in a frequency of 40 Hz and in an effective current of 3.16 mA. All measurements were carried out along the a-axis.

3. Results

Figure 1 shows the temperature dependence of $\chi$ of Ce$_{1-x}$R$_x$Ru$_2$Al$_{10}$. The magnitude of $\chi$ above $\sim$100 K decreases monotonically with increasing $x$, which is scaled by Ce concentration, so that expected compounds are considered to be grown. Compared with the same $x$ value, the magnitude of $\chi$ decreases in the order of La, $La_{0.63}Y_{0.37}$, Y. As with CeRu$_2$Al$_{10}$, all substitutions with $x=0.1$ and 0.3 shows a broad peak, followed by a bend at a lower temperature. The bend temperature corresponds to $T_0$. For $x>0.3$, $\chi$ increases accompanied with a shoulder with decreasing temperature. Specific heat measurements of La-substituted system by Tanida et al. have shown that this shoulder corresponds to the phase transition [5]. This anomaly becomes vague with increasing $x$. $T_0$ obtained from these anomalies are indicated by arrows in Fig. 1.

Figure 2 shows the temperature dependence of $\rho$ of Ce$_{1-x}$R$_x$Ru$_2$Al$_{10}$. Arrows in Fig. 2 shows $T_0$ obtained from $\chi(T)$. The behavior of $\rho(T)$ against $x$ is almost similar for all substituted system. As the increase in $x$, semiconducting temperature rise is smaller, and a bend by a sharp increase in $\rho$ due to the phase transition becomes unclear. $T_0$ is difficult to be determined from $\rho(T)$ accurately for $x>0.3$. The magnitude of a broad peak below $T_0$ increases once at $x=0.1$, and then it decreases rapidly with further increasing $x$. Since this broad peak disappears together with vanishment of $T_0$, they seem to be related with each other in some way. In large $x$ region, sudden changes from metallic to semiconducting behavior is observed. This value is between $x=0.5$ and 0.7 for La- and $La_{0.63}Y_{0.37}$-substituted system and between $x=0.7$ and 0.9 for Y-substituted system. Although it is difficult to see from the Fig. 2, an increase in $\rho$ due to Kondo effect is observed below 50 K in all substitution system at $x=0.9$.

Figure 3 indicates a plot of $T_0$ obtained from $\chi(T)$ and $\rho(T)$ with respect to $x$. For La- and $La_{0.63}Y_{0.37}$-substituted system, $T_0$ decreases monotonically with $x$, and disappears smoothly at $x \sim 0.7$. However, suppression of $T_0$ against $x$ for La-substituted system is slightly larger than that of $La_{0.63}Y_{0.37}$-substituted system. On the other hand, suppression of $T_0$ for Y-substituted
Figure 1. Temperature dependence of the magnetic susceptibility along the $a$-axis of $\text{Ce}_{1-x}\text{La}_x\text{Ru}_2\text{Al}_{10}$ ($R=\text{La}$, $\text{La}_{0.63}\text{Y}_{0.37}$, $\text{Y}$) at a field of 1 T.

Figure 2. Temperature dependence of the electrical resistivity of $\text{Ce}_{1-x}\text{La}_x\text{Ru}_2\text{Al}_{10}$ ($R=\text{La}$, $\text{La}_{0.63}\text{Y}_{0.37}$, $\text{Y}$). The current direction is along the $a$-axis.

The system is gradual compared to La- and La$_{0.63}$Y$_{0.37}$-substituted system, and disappears suddenly between $x=0.4$ and $0.5$.

4. Discussion

Kondo temperature $T_K$ is expected to increase in the order of La-, La$_{0.63}$Y$_{0.37}$-, $\text{Y}$-substitution, because the magnitude of $\chi$ decreases in this order. Therefore, shrinkage of the spin due to the Kondo effect is expected to be large in the order of La-, La$_{0.63}$Y$_{0.37}$-, $\text{Y}$-substitution. Since magnetic transition temperature is nearly proportional to the square of the magnitude of the spin in the molecular field approximation, if the phase transition at $T_0$ is usual magnetic one, then the reduction of $T_0$ against $x$ should increase in the order of La-, La$_{0.63}$Y$_{0.37}$-, $\text{Y}$-substitution. It can be understood from the molecular field theory that the reduction of $T_0$ for La-substituted system is slightly larger than that for La$_{0.63}$Y$_{0.37}$-substituted system. However, small reduction of $T_0$ for $\text{Y}$-substituted system cannot be understood. $T_0$ in CeRu$_2$Al$_{10}$ increases with pressure despite of shrinkage of spin [3]. Since the similar thing is expected to happen in the $\text{Y}$-substituted system, the reduction of $T_0$ is considered to be suppressed. The reason why $T_0$ increases under pressure and decreases with $\text{Y}$-substitution should be that $\text{Y}$-substitution dilute the concentration of...
Ce. Comparing the change of $T_0$ in the same amount of replacement, it is recognized that the changes in $T_0$ is very similar to the behavior under pressure. For example, at $x=0.3$, $T_0$ is 13 K in La-substitution, little change in La$_{0.63}$Y$_{0.37}$-substitution, but rises to 23 K in Y-substitution. This tendency is also seen at $x=0.1$, though the size is small, which is probably attributed to small pressure effect due to small substitution. Behavior that $T_0$ disappears suddenly in the Y-substitution between $x=0.4$ and 0.5 is similar to the sudden disappearance of $T_0$ at around 4 GPa under pressure of CeRu$_2$Al$_{10}$. Therefore, the phase transition at $T_0$ is considered to involve mechanism related to the change in the lattice volume, which cannot be described by a simple molecular field approximation. This phase transition is considered to be related with the valence instability of Ce due to large $J_{ef}$.

5. Summary
We have measured the magnetic susceptibility and electrical resistivity of pseudo ternary compounds in which Ce ion in CeRu$_2$Al$_{10}$ is replaced by non-magnetic rare earth ion with different ionic radii. The magnitude of $\chi$ decreases with ionic radii, which is attributed to increase in Kondo temperature due to chemical pressure effect. Although $T_0$ for La- and La$_{0.63}$Y$_{0.37}$-substitution decreases monotonically and smoothly disappears, $T_0$ for Y-substitution decreases slowly and disappears suddenly between $x=0.4$ and 0.5. These results suggest that the change in valence plays an important role in this phase transition.

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