Magnetic properties of new dilute rare earth compounds
$R_2Ru_3Al_{15}$

Kento YOKOTA$^1$, Takashi NISHIOKA$^{1,2}$, Kentaro KITAGAWA$^1$, Harukazu KATO$^1$, and Masahiro MATSUMURA$^1$

$^1$Graduate School of Integrated Arts and Sciences, Kochi University, 2-5-1 Akebono-cho, Kochi 780-8520, Japan

$^2$Center for Advanced Marine Core Research (KCC), Monobe-B200, Nankoku 783-8502, Japan

E-mail: nisioka@kochi-u.ac.jp

Orthorhombic YbFe$_2$Al$_{10}$-type Kondo semiconductor Ce$T_2$Al$_{10}$ ($T$ = Ru and Os) have anomalous high phase transition temperatures in spite of small Ce content. We have succeeded to synthesize new dilute rare earth hexagonal compounds Ce$_2$Ru$_3$Al$_{15}$-type $R_2Ru_3Al_{15}$ ($R$ = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm) closely related to YbFe$_2$Al$_{10}$-type structure, and investigated their transport and magnetic properties. The electrical resistivity measurements indicate that all the compounds are metal, and $R$ = Ce shows a logarithmic increase below 20 K due to Kondo effect. $R$ = Ce, Nd, Sm, Gd, Tb, Dy, Ho and Er show antiferromagnetic transitions at $T_N$ = 3.5, 27, 9.2, 19.0, 15.7, 7.85, 3.0 and 1.6 K, respectively, and the $T_N$ almost follows the de Gennes’ law except for $R$ = Ce and Sm. $R$ = Pr has nonmagnetic ground state and $R$ = Tm is expected to order magnetically below 1.2 K from the susceptibility measurement. We have found that the Neél temperature of $R$ = Ce is about 20 times larger than an expected value by the de Gennes’ law, indicating that Ce$_2$Ru$_3$Al$_{15}$ is also a member of high magnetic transition temperature materials.

KEYWORDS: Ce$_2$Ru$_3$Al$_{15}$, Pr$_2$Ru$_3$Al$_{15}$, Nd$_2$Ru$_3$Al$_{15}$, Sm$_2$Ru$_3$Al$_{15}$, Gd$_2$Ru$_3$Al$_{15}$, Tb$_2$Ru$_3$Al$_{15}$, Dy$_2$Ru$_3$Al$_{15}$, Ho$_2$Ru$_3$Al$_{15}$, Er$_2$Ru$_3$Al$_{15}$, Tm$_2$Ru$_3$Al$_{15}$, electrical resistivity, ac magnetic susceptibility, magnetization, antiferromagnetic order, Kondo effect

1. Introduction

Orthorhombic YbFe$_2$Al$_{10}$-type CeRu$_2$Al$_{10}$ has received considerable attention since our propose that the phase transition is a novel phase transition which cannot be described by the Doniach’s phase diagram [1–3]. We insisted that the transition temperature $T_0$~27 K is too high compared to an expected value of 0.2 K evaluated from the Neél temperature GdRu$_2$Al$_{10}$ by the de Gennes’ law, and the origin is not magnetic but electrical one. After that, a neutron diffraction experiment using polycrystalline powder sample revealed that the transition is attributed to an antiferromagnetic order, and the Ce moment along the $c$-axis with a moment of 0.3$\mu_B$/Ce at 2 K [4]. This was confirmed by our neutron diffraction study using a single crystal, though the value of ordered moment is somewhat larger value of 0.42 $\mu_B$/Ce [5]. Up to now numerous experimental studies have been performed, but the reason of high transition temperature has not been clarified yet. However, the anomalous magnetic properties of CeRu$_2$Al$_{10}$ are considered to be closely related to the crystal structure from many experimental [6, 7] and theoretical studies [8, 9].

YbFe$_2$Al$_{10}$-type structure is composed by cage-unit without inversion symmetry along the $c$-axis, in which Yb is surrounded by 16 Al and 4 Fe, where the cage unit forms face-sharing columns. There are many compounds with similar structure, e. g., ThMn$_{12}$-, TbRe$_2$Al$_{10}$- and NdRh$_4$Al$_{13.57}$- [10], Ce$_2$Ru$_3$Al$_{15}$- [11, 12], and Sm$_2$O$_3$Al$_{15}$-type [13]. Among them, hexagonal Ce$_2$Ru$_3$Al$_{15}$-type is
closely related to YbFe$_2$Al$_{10}$-type. The main difference is the cage-unit composed of 14 Al and 4 Ru, and another 2 Al are outside of cage-unit. Ce$_2$Ru$_3$Al$_{15}$-type structure was first found by Tursina et al. [11], and then Morrison et al. modified slightly the crystal structure [12], whose structure is about the same as Sm$_2$Ru$_3$Al$_{15}$-type structure [13]. The existence of Ce$_2$Ru$_3$Al$_{15}$-type (or Sm$_2$Os$_3$Al$_{15}$-) compound has been reported for only Ce$_2$Ru$_3$Al$_{15}$, Gd$_2$Ru$_3$Al$_{15}$ and Sm$_2$Os$_3$Al$_{15}$, and the magnetic properties were reported for the former two compounds. The purpose of this study is to examine the existence of other Ce$_2$Ru$_3$Al$_{15}$-type R$_2$Ru$_3$Al$_{15}$ ($R$ = rare earth element), and investigate the transport and magnetic properties systematically.

2. Experimental

The polycrystalline $R_2$Ru$_3$Al$_{15}$ ($R$ = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb) were prepared by arc-melting of the pure elements in their stoichiometric ratio in an Ar atmosphere on a water-cooled copper hearth. Subsequently, the resulting each ingot was annealed in an evacuated quartz tube at 900 °C for 3 days, followed by quenched into water. The powder XRD indicated the samples except $R$ = Yb were almost single phase. The synthesis of $R$ = Yb was failed. Although the crystal structure of Ce$_2$Ru$_3$Al$_{15}$-type was proposed by two types as mentioned above, the powder XRD cannot distinguish this due to small difference. Figure 1 shows the evaluated lattice constants and volumes, and the numerical data are shown in Table I together with the magnetic and transport data described below. We can see the volume contracts smoothly with increasing atomic number, indicating the valence of rare earth elements of all compounds are 3+. The ac magnetic susceptibility was measured with a standard Hartshorn circuit using OP amplifier [14] in the frequency of 100 Hz and excitation field of 2.0 Oe. The dc magnetization was measured with a hand-made vibrating sample magnetometer (VSM) using cryogen-free supercon-

Table I. Lattice constants, Néel temperature determined by $\rho(T)$ ($T_{N0}$) and $\chi(T)$ ($T_{N1}$ and $T_{N2}$), effective moment $\mu_{\text{eff}}$, and paramagnetic Curie temperature $\theta_p$ for polycrystalline $R_2$Ru$_3$Al$_{15}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$T_{N0}$ (K)</th>
<th>$T_{N1}$ (K)</th>
<th>$T_{N2}$ (K)</th>
<th>$\mu_{\text{calc}}$ ($\mu_B$)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\theta_p$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.157</td>
<td>9.109</td>
<td>1365.77</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.40</td>
<td>2.54</td>
<td>-16.4</td>
</tr>
<tr>
<td>Ce$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.133</td>
<td>9.099</td>
<td>1359.24</td>
<td>3.9</td>
<td>3.5</td>
<td>–</td>
<td>3.50</td>
<td>3.58</td>
<td>-10.3</td>
</tr>
<tr>
<td>Pr$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.100</td>
<td>9.077</td>
<td>1349.17</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.56</td>
<td>3.62</td>
<td>-18.8</td>
</tr>
<tr>
<td>Nd$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.075</td>
<td>9.067</td>
<td>1342.55</td>
<td>3.8</td>
<td>2.7</td>
<td>–</td>
<td>9.24</td>
<td>9.58</td>
<td>-4.5</td>
</tr>
<tr>
<td>Sm$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.044</td>
<td>9.034</td>
<td>1331.34</td>
<td>9.2</td>
<td>9.2</td>
<td>–</td>
<td>7.94</td>
<td>7.94</td>
<td>-1.4</td>
</tr>
<tr>
<td>Gd$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.019</td>
<td>9.039</td>
<td>1328.47</td>
<td>20.5</td>
<td>19.0</td>
<td>–</td>
<td>9.57</td>
<td>9.72</td>
<td>3.7</td>
</tr>
<tr>
<td>Tb$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>13.010</td>
<td>9.020</td>
<td>1322.43</td>
<td>17.2</td>
<td>15.7</td>
<td>12.6</td>
<td>10.33</td>
<td>10.65</td>
<td>-0.3</td>
</tr>
<tr>
<td>Dy$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>12.993</td>
<td>9.004</td>
<td>1316.63</td>
<td>7.0</td>
<td>7.85</td>
<td>5.45</td>
<td>10.28</td>
<td>10.61</td>
<td>1.1</td>
</tr>
<tr>
<td>Ho$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>12.980</td>
<td>9.004</td>
<td>1314.11</td>
<td>5.2</td>
<td>3.0</td>
<td>–</td>
<td>9.24</td>
<td>9.58</td>
<td>-4.5</td>
</tr>
<tr>
<td>Er$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>12.977</td>
<td>9.003</td>
<td>1313.18</td>
<td>3.9</td>
<td>1.6</td>
<td>–</td>
<td>7.43</td>
<td>7.56</td>
<td>-9.0</td>
</tr>
<tr>
<td>Tm$_2$Ru$<em>3$Al$</em>{15}$</td>
<td>12.970</td>
<td>8.994</td>
<td>1310.40</td>
<td>–</td>
<td>&lt;1.2</td>
<td>–</td>
<td>7.43</td>
<td>7.56</td>
<td>-9.0</td>
</tr>
</tbody>
</table>
ducting transverse magnet. The electrical resistivity was measured by the ac four-probe method in 13.7 Hz and 3.16 mA using Lake Shore AC resistance bridge Model 370.

3. Results and Discussion

Figure 2 shows the temperature dependence of the electrical resistivity $\rho$ of $R_2\text{Ru}_3\text{Al}_{15}$ scaled by the value of 300 K. The room temperature values of $R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{ Tb}, \text{ Dy}, \text{ Ho}, \text{ Er}, \text{ Tm}$ are 135, 140, 90, 100, 132, 58, 122, 150, 135 and 190 $\mu\Omega$cm, respectively, and the errors are about 10 %. Figure 3 shows a log-log plot of the temperature dependence of the dc magnetic susceptibility $\chi$ of $R_2\text{Ru}_3\text{Al}_{15}$. From Figure 2, $\rho$ of all $R_2\text{Ru}_3\text{Al}_{15}$ decreases with decreasing temperature, indicating that $R_2\text{Ru}_3\text{Al}_{15}$ are metals. $R = \text{Ce}$ shows a logarithmic increase in the resistivity due to Kondo effect below 20 K. The resistivity shows a bend and a drop at a certain temperature except $R = \text{La}, \text{Pr} \text{ and Tm}$, which is due to the decrease in the spin order resistivity. Since the susceptibility also shows a bend at around the temperature, the anomalies are attributed to an antiferromagnetic transition. Compared with the other ordered compounds, the bend is quite broad and the magnitude of the drop are quite large for $R = \text{Ce}$. In the log-log plot of $\chi(T)$, the Curie law appears as a straight line. From Fig. 3, the slope of the susceptibility above 50 K is $-1$ except for $R = \text{Sm}$, indicating the Curie-Weiss law with small the paramagnetic Curie temperature $\theta_p$ holds in the temperature region. This indicates that the influence of the crystal field is small, which can be expected in a substance with the cage-unit. The effective magnetic moment $\mu_{\text{eff}}$ and $\theta_p$ obtained from the method of the least squares fit are shown in Table I. Since the $\mu_{\text{eff}}$ is close to the theoretical value of the trivalent ion, the $4f$ electron is to be well localized, which is consistent with smooth lanthanoide contraction in the cell volume in Fig. 1.

Figure 4 shows the low temperature portion of $\rho$ and $\chi$ for $R_2\text{Ru}_3\text{Al}_{15}$. The susceptibilities shown

![Fig. 2. Temperature dependence of electrical resistivity ratio $\rho/\rho_{300K}$ (300 K) of $R_2\text{Ru}_3\text{Al}_{15}$. Origin of the y-axis is shifted for clarity.](image1)

![Fig. 3. Temperature dependence of the dc magnetic susceptibility per mol of rare earth ions on $R_2\text{Ru}_3\text{Al}_{15}$. The slope of solid straight line indicates $-1$. The symbols are the same as those used in Fig. 2.](image2)
Fig. 4. Low temperature portion of $\rho$ and $\chi$ of $R_2$Ru$_3$Al$_{15}$. The $\chi$ of (a), (b), (d) and (j) are dc measurement, and others are ac measurement. The magnetic fields of dc measurements are indicated. The arrows denote the temperatures at which anomalies of $\rho$ and $\chi$ take place.
here are ac measurements except $R = \text{Ce}$ and Sm with small susceptibility and $R = \text{Pr}$ and Tm without showing magnetic order. The anomaly temperatures of $\chi_{dc}$ below 1 T are nearly the same as those of $\chi_{ac}$. The anomaly temperatures of $\rho$ and $\chi$ are roughly the same, but complete concidence is for $R = \text{Sm}$ and Gd only. The difference is large for $R = \text{Nd}$, Ho and Er. The reason of the different anomaly temperature is that the phase transition is not pure antiferromagnetic transition due to the short range order which comes from structural disorder. The $\rho$ indicates only one anomaly, while $\chi$ indicates two anomalies for $R = \text{Dy}$ and Tb. This suggests that spin-reorientation occurs in the ordered state for $R = \text{Dy}$ and Tb. The metamagnetism was observed at 3 K (not shown) for the ordered materials except for $R = \text{Gd}$ whose orbital angular moment is zero, suggesting strong magnetic anisotropy exists in the ordered state. The ground state of $R = \text{Pr}$ is singlet, because $\chi(T)$ saturates at low temperatures. $R = \text{Tm}$ should show magnetic order below 1.2 K, because $\chi$ follows Curie-Weiss law down to 1.2 K. The results of $R = \text{Ce}$ and Gd are nearly the same as Ref. [12].

The anomaly temperatures in $\rho$ and $\chi$ are plotted against the atomic number in Fig. 5. The solid line indicates that expected magnetic ordering temperatures by the de Gennes’ law using the transition temperature of $R = \text{Gd}$. The Néel temperatures are in good agreement to the de Gennes’ law except for $R = \text{Ce}$, Pr, Sm and Tm. $R = \text{Pr}$ has nonmagnetic ground state and $R = \text{Tm}$ should order magnetically below 1.2 K as mentioned above. Slight larger Néel temperature for $R = \text{Sm}$ is probably due to excited LS multiplet levels. We note here that the transition temperature of $R = \text{Ce}$ is about 20 times larger than the expected value 0.23 K by de Gennes’ scaling, indicating CeRu$_2$Al$_{15}$ is also anomalous high transition temperature material as CeRu$_2$Al$_{10}$. The enhancement should be strong $J_{cf}$, because clear Kondo effect was observed. The transition temperature difference of five times of CeRu$_2$Al$_{10}$ and CeRu$_2$Al$_{15}$ may be related to the semiconducting behavior CeRu$_2$Al$_{15}$.

4. Summary

We have synthesized hexagonal CeRu$_2$Al$_{15}$-type $R_2$Ru$_3$Al$_{15}$ ($R = \text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Yb}$) whose structure are closely related to YbFe$_2$Al$_{10}$-type. Compounds except $R = \text{Ce}$ and Gd were first synthesized in this study. All compounds are metal, and $R = \text{Ce}$ shows Kondo effect at low temperatures. Compounds except for $R = \text{La, Pr and Tm}$ show magnetic orderings, and the Néel temperatures follow the de Gennes’ law except for $R = \text{Ce, Pr, Sm and Tm}$. The ground state of $R = \text{Pr}$ is nonmagnetic singlet. $R = \text{Tm}$ should order magnetically below 1.2 K. We have found that the transition temperature of $R = \text{Ce}$ is about 20 times larger than the value expected by de Gennes’ law, which is probably related to strong $J_{cf}$ expected from the observation of Kondo effect. The high magnetic transition temperature may be related to the cage-unit.
Acknowledgment

This work was partially supported by a Grant-in-Aid of the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant No. 23102719 and 21540367).

References