Anomalous Antiferromagnetic Phase Diagram in HoRu$_2$Al$_{10}$

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Abstract. To investigate an antiferromagnetic (AFM) phase transition of HoRu$_2$Al$_{10}$ with $T_N$ = 5.2 K, we performed specific heat measurements on a single-crystalline sample under magnetic fields $H$. In $H$ along the $b$- and $c$-axes, a sharp peak of the specific heat at $T_N$, indicating the phase transition, shifts to lower temperature with increasing $H$. From these measurements, we clarified a magnetic phase diagram for $H \parallel b$ and $c$ above 2 K. In $H \parallel b$, $T_N$ decreases monotonically with increasing $H$, and the phase boundary closes around 1.0 T, which is a usual behavior for an antiferromagnet. In $H \parallel c$, although $T_N$ shows a monotonic decrease with increasing $H$ at low $H$, the phase boundary exhibits an inflection point around 4.0 T, suggesting that additional interaction are enhanced or induced by $H \parallel c$ in HoRu$_2$Al$_{10}$. From the stand point of fluctuation of quadrupole moments in isomorphic compound HoFe$_2$Al$_{10}$, we propose that the inflection point is originated from a quadrupolar instability.

1. Introduction

Ternary aluminides $LnTr_2Al_{10}$ ($Ln$ = rare earth, $Tr$ = Ru, Os, and Fe) with the orthorhombic YbFe$_2$Al$_{10}$-type structure (space group: $Cmcm$) have attracted many interests of magnetism. At the early stage, CeRu$_2$Al$_{10}$ has been studied intensively. It is the first example which shows an AFM ordering in the Kondo insulating state [1–4]. The AFM transition temperature of CeRu$_2$Al$_{10}$ is one hundred times higher than the expected temperature from the de Gennes law in $LnTr_2Al_{10}$ despite the strongly reduced Ce magnetic moment [3, 4]. In addition, the ordering direction of the magnetic moment in the AFM state is along the magnetically hard axis [3, 4]. The origin of the unusual AFM transition temperature and direction of the ordered moments has not been clarified. Recently, other $LnTr_2Al_{10}$ compounds have been also studied, such as an AFM transition with a valence instability [5], an incommensurate AFM ordering [6], successive magnetic phase transitions, and so on [7–11].

We focus on an AFM transition at $T_N$ in HoRu$_2$Al$_{10}$ which was reported by Mizushima et al. [11]. A sharp peak of the specific heat $C_p$ was observed at $T_N$. The temperature $T$ dependencies of magnetic susceptibility along the all axes decrease below $T_N$, suggesting an
AFM transition at $T_N$ in HoRu$_2$Al$_{10}$. The $H$ dependence of the magnetization $M$ along the $c$-axis at 2 K shows a metamagnetic transition at 0.8 T. In contrast, $M$ along the $a$- and $b$-axes increase almost monotonically with increasing $H$ up to 7 T. The results suggest that the magnetic moments of Ho are oriented toward the $c$-axis below $T_N$. As the Ho$^{3+}$ ion in HoRu$_2$Al$_{10}$ is under the orthorhombic symmetry, degenerated 4f-electronic state of the free Ho$^{3+}$ ion (total angular momentum $J=8$) splits into seventeen singlets by the crystal electric field (CEF). In this situation, it is unlikely that there is a spin-degenerated state. In the present work, to investigate the AFM transition in HoRu$_2$Al$_{10}$, we performed specific heat measurements in $H // b$ and $c$.

2. Experimental

By using Al self-flux method, we grew a single crystal of HoRu$_2$Al$_{10}$ and polycrystalline LuRu$_2$Al$_{10}$ which is a non-magnetic reference material. Specific heat under $H$ is measured with a relaxation method by using the commercial PPMS system (Quantum Design). $H$ is applied along the $b$- and $c$-axes between 2 and 10 K. Here, we note that the definition of the $b$- and $c$-axes are reverse between our and Mizushima’s samples. To confirm the validity of our definition, we performed X-ray diffraction (XRD) experiments. The XRD patterns on our single-crystalline sample for all planes between 2$\theta$= 70 and 120 degrees, and found the peak position for $\theta=70$ and 120 degrees are shown in Figure 1(a), where $\theta$ is the scattering angle. We observed Bragg peaks for the $a$-plane at 85.48, 85.74, 116.07, and 116.53 degrees, for the $b$-plane at 74.31, 74.52, 98.11, and 98.44 degrees, and for the $c$-plane at 85.12, 85.39, 115.46, and 115.91 degrees, respectively. In addition, we determined the lattice parameters of HoRu$_2$Al$_{10}$ ($a=9.092$ Å, $b=10.206$ Å, and $c=9.117$ Å) by the Rietveld refinement of powder XRD patterns using the program RIETAN-FP [12]. The lattice parameters of HoRu$_2$Al$_{10}$ and LuRu$_2$Al$_{10}$ reported by Sera et al. [13] are shown by closed and open symbols in Figure 1(b), respectively. The lattice parameters of HoRu$_2$Al$_{10}$ are very close to the expected values from the lanthanide contraction. From the lattice parameters of HoRu$_2$Al$_{10}$, we estimated the Bragg peak positions in 2$\theta$ for all planes between 70 and 120 degrees, and found the peak position for $\theta=70$ and 120 degrees are shown in Figure 1(b).
Table 1. The relation between the plane indices and the Bragg peak positions in $2\theta$. We also show the calculated peak positions for each plane index obtained from the Rietveld refinement of powder XRD patterns using the program RIETAN-FP with the lattice parameters ($a = 9.092$ Å, $b = 10.206$ Å, and $c = 9.117$ Å) in HoRu$_2$Al$_{10}$ [12].

| Plan index | Bragg peak position (deg) | Raw data | Calculation |
|------------|---------------------------|----------|-------------|
| (8 0 0)    | 85.48, 85.74              | 85.34, 85.60 |
| (10 0 0)   | 116.07, 116.53            | 115.82, 116.28 |
| (0 8 0)    | 74.31, 74.52              | 74.28, 74.50  |
| (0 10 0)   | 98.11, 98.44              | 98.01, 98.33  |
| (0 0 8)    | 85.12, 85.39              | 85.06, 85.32  |
| (0 0 10)   | 115.46, 115.91            | 115.32, 115.78 |

the plane indices and the peak positions in $2\theta$. The observed peaks are corresponding to each plane index, respectively. This result indicates the validity of our definition for the crystal axis in HoRu$_2$Al$_{10}$. Therefore, we use our definition for the crystal axis.

3. Results and Discussion

Figure 2(a) shows the $T$ dependencies of $C_p$ of HoRu$_2$Al$_{10}$ and polycrystalline LuRu$_2$Al$_{10}$. The absolute value of $C_p$ in LuRu$_2$Al$_{10}$ is almost the same as that in HoRu$_2$Al$_{10}$ above 60 K. We assumed LuRu$_2$Al$_{10}$ as a non-magnetic reference compound to HoRu$_2$Al$_{10}$. We subtracted $C_p$ of LuRu$_2$Al$_{10}$ from that of HoRu$_2$Al$_{10}$ to estimate the magnetic specific heat $C_m$ of HoRu$_2$Al$_{10}$. The $T$ dependence of $C_m$ and magnetic entropy $S_m$ are shown in Figure 2(b). $C_m$ exhibits a sharp peak at $T_N$, and a Schottky peak around 9 K. $S_m$ reaches $1.26R\ln2(=7.26 \text{ J/K mol})$ at $T_N$, where $R$ is the gas constant. $S_m$ saturates around 90 K, suggesting that the CEF splitting in HoRu$_2$Al$_{10}$ is relatively small. The entropy release at $T_N$ indicates that the AFM transition at $T_N$ originates from the pseudo-degenerated state of singlets, though all the CEF states are

![Graph of Cp vs T](image1)

![Graph of Cm vs T](image2)

**Figure 2.** $T$ dependencies of (a) the specific heat $C_p$ of HoRu$_2$Al$_{10}$ and LuRu$_2$Al$_{10}$, and (b) the magnetic specific heat $C_m$ and the magnetic entropy $S_m$ of HoRu$_2$Al$_{10}$. The inset displays the same data in an expanded scale of $C_p$ in HoRu$_2$Al$_{10}$ and LuRu$_2$Al$_{10}$ below 20 K.
singlets as mentioned above. Here, the pseudo-degenerated state means electronic states with energy separations which can be regarded as a degenerated state from the following viewpoint. If the system is in a condition at a certain temperature which has a higher energy scale than the energy separation, the energy separations may be ignored in the energy scale. In the case of HoRu$_2$Al$_{10}$, the entropy release at $T_N$ is about $\Delta S_{\text{CEF}}$, indicating that the CEF ground and first excited states seem to degenerate above $T_N$. Thus, we mention that the pseudo-degenerated state at $T_N$ is a pseudo-doublet. The energy splitting between the CEF ground and first excited states is most likely less than $T_N$.

Figure 3(a) and (b) show the $T$ dependencies of $C_p$ in $H // b$ and $c$, respectively. In $H // b$ and $c$, the sharp peak of $C_p$ shifts to lower $T$ with increasing $H$, and then the peak is not observed above 0.7 and 5.5 T, respectively. The Schottky specific heat for $H // b$ increases with increasing $H$. In contrast, the Schottky specific heat for $H // c$ decreases. These behaviors are expected to originate from the change of the Schottky peak which depends on the energy scale. In the case of HoRu$_2$Al$_{10}$, the entropy release at $T_N$ is about $\Delta S_{\text{CEF}}$, indicating that the CEF ground and first excited states seem to degenerate above $T_N$. Thus, we mention that the pseudo-degenerated state at $T_N$ is a pseudo-doublet. The energy splitting between the CEF ground and first excited states is most likely less than $T_N$.

The $H$-$T$ diagram for $H // b$ and $c$ in HoRu$_2$Al$_{10}$. Closed and open symbols denote our and Mizushima’s data [11], respectively.

Figure 3. $T$ dependencies of the specific heat $C_p$ for (a) $H // b$ and (b) $H // c$ in HoRu$_2$Al$_{10}$. 

Figure 4. $H$-$T$ diagram for $H // b$ and $c$ in HoRu$_2$Al$_{10}$. Closed and open symbols denote our and Mizushima’s data [11], respectively.
an inflection point around 3.0 K. This result suggests that additional interactions are enhanced or induced by $H // c$. We have reported that isomorphic compound HoFe$_2$Al$_{10}$ shows elastic softening originating from inter-level transition of quadrupole in the low energy range [14, 15]. Considering the result of HoFe$_2$Al$_{10}$, we assume that the inflection point of the $H$-$T$ diagram for $H // c$ is caused by enhancement of an instability due to the fluctuating quadrupole moments in $H // c$. To investigate the quadrupolar instability around $T_N$ in HoRu$_2$Al$_{10}$, ultrasonic measurements in $H$ along the all axes are in progress.

4. Conclusion
We performed specific heat measurements under $H // b$ and $c$. The sharp peak of $C_m$ is observed at $T_N$. $S_m$ exceeds $Rln2$ at $T_N$, indicating that the AFM transition at $T_N$ originates from the pseudo-degenerated state of singlets. The peak of $C_m$ shifts to lower $T$ with increasing $H // b$ and $c$. From the results, we clarified the $H$-$T$ diagram of HoRu$_2$Al$_{10}$ for $H // b$ and $c$ above 2 K. In $H // b$, the phase boundary closes around 1 T. Meanwhile, in $H // c$, we found the inflection point of the phase boundary around 4 T, which is an anomalous behavior for antiferromagnet. Considering the result that fluctuation of quadrupole moments exist in isomorphic compound HoFe$_2$Al$_{10}$, we propose that the inflection point of the $H$-$T$ diagram for $H // c$ in HoRu$_2$Al$_{10}$ arises from the quadrupolar instability.

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