Crystal-field effect on anisotropic magnetic properties of CeT$_2$Al$_{10}$ (T = Ru and Os)

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Abstract. The magnetic susceptibility of single crystalline samples of CeT$_2$Al$_{10}$ (T=Ru, Os) showing unusual phase transitions at $T_0 = 27$ K and 29 K, respectively, has been measured up to 700 K along the three principal axes of the orthorhombic structure. The crystal field analysis of the data led to the crystal field scheme with excited levels at 326 K and 530 K for T = Ru and 433 K and 704 K for T = Os. For the ground state, the butterfly-like wave function elongates along the $b$-axis in the distorted hexagon composed of Al(3) and Al(4) atoms in the $b$-$c$ plane. This charge distribution allows the 4$f$ electron state to hybridise with the 3$p$ states of the Al(3) and Al(4) atoms. We propose that this hybridisation plays an important role in both the formation of the hybridisation gap and the enhancement of the antiferromagnetic ordering temperature.

1. Introduction

A family of cerium-based intermetallic compounds CeT$_2$Al$_{10}$ (T = Fe, Ru, Os) attracts much attention because CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ undergo unusual transitions at rather high temperatures $T_0 = 27$ K and 28.5 K, respectively, while CeFe$_2$Al$_{10}$ shows behaviour of a paramagnetic Kondo semiconductor [1-4]. At the initial stage of the studies of CeRu$_2$Al$_{10}$, a structural transition at $T_0$ was proposed by the $^{27}$Al NQR measurement [5]. However, neutron diffraction and $\mu$SR experiments indicate that the magnetic moments on the Ce sites of approximately 0.3 $\mu_B$ order antiferromagnetically below $T_0$ [6-8]. In the ordered phase, the magnetic moments orient along the orthorhombic $c$ axis alternately. [7] This finding of magnetic order raised a question why $T_0$’s are much higher than the Néel points of the Nd- and Gd-counterparts [2, 9].

The magnetic susceptibility $\chi(T)$ for CeT$_2$Al$_{10}$ (T = Fe, Ru, Os) exhibits strong anisotropy, $\chi_a > \chi_c > \chi_b$ in the paramagnetic state [2, 3]. The dominant origin of the magnetic anisotropy may be the crystalline electric field (CEF) effect on the Ce ion which is surrounded by four T atoms and 16 Al atoms in the YbFe$_2$Al$_{10}$-type structure. The CEF of the $m2m$ point symmetry splits the $^2F_{5/2}$ multiplet of the Ce$^{3+}$ ion into three Kramers doublets. However, a rather weak CEF effect on the Pr and Nd ions in the isostructural compounds ROs$_2$Al$_{10}$ was inferred from the small paramagnetic Curie temperatures less than 10 K [9]. This suggests that the hybridisation effect in the Ce compounds is stronger than the CEF effect due to the point charges of the ligand atoms. It is important to determine the crystal field level scheme for the Ce compounds to understand the mechanism of the enhancement of $T_0$. Therefore, we have measured $\chi_a$, $\chi_c$, and $\chi_b$ for single crystals of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ up to 700 K. Our
Figure 1. Inverse magnetic susceptibilities of (a) CeRu$_2$Al$_{10}$ and (b) CeOs$_2$Al$_{10}$ along the three principal axes as a function of temperature. The solid curves represent results of the CEF analysis. The energy levels of 4$f$ electron states are shown in the insets.

results of the CEF level scheme will be compared with those obtained by neutron inelastic scattering experiments and the recent calculation [10, 11].

2. Experimental

Single crystalline samples of CeT$_2$Al$_{10}$ (T = Ru, Os) were grown using an Al self-flux method, which was reported previously [3]. Binary alloys of CeRu$_2$ and CeOs$_2$ were prepared by arc melting of pure elements. The crushed ingots of the alloy together with an excess amount of Al in the ratio 1:2:20 were loaded into an alumina crucible, which was sealed in a quartz tube under an Ar atmosphere of 1/3 atm. The crucible was heated to 1150°C and then cooled slowly to 720°C at which point the molten Al flux was separated by centrifuging. The obtained single crystals have typical size of 4 mm and 2 mm in diameter for T = Ru and T = Os, respectively. No deviation from the ideal stoichiometry of 1:2:10 was detected by electron-probe microanalysis. Powder x-ray patterns confirmed the orthorhombic YbFe$_2$Al$_{10}$-type structure. For the measurement of $\chi(T)$ along the principal axes, the crystal was oriented by the back reflection Laue method using an imaging plate camera.

The measurement of $\chi(T)$ was performed at an external field $B = 1$ T in two temperature ranges using a superconducting quantum interference device magnetometer, MPMS. The lower range is from 2 K to 350 K and the higher one is from 300 K to 700 K. For the latter, the crystal was wrapped in Al foil and placed in an oven installed in the MPMS. The two sets of data were smoothly connected each other in the overlapped range between 300 K and 350 K.

3. Results and Discussions

Figure 1 shows the inverse of $\chi_a$, $\chi_c$, and $\chi_b$ for single crystals of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ up to 700 K. At temperatures above 300 K, the data of $\chi_a$ and $\chi_c$ follow the Curie-Weiss law with an effective magnetic moment of 2.5-2.8 $\mu_B$/Ce, being close to the trivalent free-ion value 2.54 $\mu_B$/Ce. However, the effective magnetic moments for $\chi_b$ are 3.0 and 3.7 $\mu_B$/Ce for T = Ru and T = Os, respectively. The extrapolation of the fitting to the inverse of $\chi_b(T)$ yields large negative values for the paramagnetic Curie temperature; $-550$ K and $-820$ K for T = Ru and T = Os, respectively. Such a large negative value can be attributed to the Kondo effect, which manifests in $\chi(T)$ as a negative molecular field in the CEF analysis [12].

In CeT$_2$Al$_{10}$, the Ce ion with total angular momentum $J = 5/2$ occupies the site with the $m2m$ ($C_{2v}$) point symmetry. Hence, the Stevens operators $O_n^m$ for $n = 6$ are zero, and therefore the CEF Hamiltonian is described by five terms as
Figure 2. Spatial charge distribution of the ground-state wave function of the Ce 4f electron in (a) CeRu$_2$Al$_{10}$ and (b) CeOs$_2$Al$_{10}$. The atomic coordination of Al(3), Al(4), Ru and Os is drawn.

\[ H_{\text{CEF}} = B_x^0 O_x^0 + B_y^2 O_y^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_8^0 O_8^0 \]  

(1)

where $B_n^m$ stand for CEF parameters describing the strength of the interaction [13]. In the mean-field approximation, $\chi_i(T)$ (i = a, b, c) is expressed as $\chi_i(T) = \chi_{\text{CEF}}(T)/[1 - \lambda \chi_{\text{CEF}}(T)]$, where $\lambda$ is the mean-field parameter. We took the $c$ axis as the quantization axis although $b$ axis was chosen by Hanzawa [11]. The expression for $\chi_{\text{CEF}}(T)$ based on the CEF model is given by

\[ \chi_{\text{CEF}} = \frac{(g|\mu_B|^2)}{\sum_m e^{-E_m/k_BT}} \left( \sum_m |(m|m|n)|^2 e^{-E_m/k_BT} + \sum_m \sum_n |(n|m|n)|^2 e^{-E_n/k_BT} - e^{-E_n/k_BT} \right) \]  

(2)

where the notations of the symbols are given in our previous report [14]. The solid lines in Figs. 1(a) and 1(b) are the calculated curves using the parameters obtained by a least-squares fitting to the data above 80 K. The obtained CEF parameters and 4f level schemes are listed in Table 1. We confirmed that our CEF parameters for CeRu$_2$Al$_{10}$ are comparable with those obtained by Hanzawa [11] when the quantization axis is converted from the $c$ axis to $b$ axis. The dominant term is $B_x^0$ whose value is $-39$ K for both compounds. The rather large molecular field parameters of $-90$ and $-60$ mol/emu for T = Ru and T = Os, respectively, can be attributed to the strong Kondo effect in addition to the inter-site antiferromagnetic interaction. The energies of the excited doublets $\Delta_1$ and $\Delta_2$ are, respectively, 326 K and 530 K for T = Ru and 433 K and 704 K for T = Os, whose values agree with those obtained by inelastic neutron scattering experiments [10]. It is worth noting that the overall splitting is rather large compared to other Ce-based intermetallic compounds. Because $\Delta_1$ exceeds 300 K, we consider that only the ground state doublet takes part in the magnetic order below $T_0$ as well as the unusual magnetic excitations at 8 and 11 meV for T = Ru and T = Os, respectively, which develop below $T_0$ [10, 15].

The crystal field parameters allow us to draw the spatial charge distribution of the ground-state wave function. As shown in Fig. 2, the butterfly-like wave function lies in the $b$-$c$ plane. This distribution is consistent with the easy magnetization axis along the $a$ axis in the paramagnetic state. The wave function elongates along the $b$-axis in the distorted hexagon made of Al(3) and Al(4) atoms in the $b$-$c$ plane. This charge distribution suggests that the 4f electron state hybridises strongly with the
Table 1. Crystal field parameters, molecular field coefficient, energy levels, and wave functions of the Ce 4f electron in CeRu$_2$Al$_{10}$ (left) and CeOs$_2$Al$_{10}$ (right).

| Energy levels | CeRu$_2$Al$_{10}$ Wave functions | Energy levels | CeOs$_2$Al$_{10}$ Wave functions |
|---------------|----------------------------------|---------------|----------------------------------|
| E(K)          | +5/2>                           | E(K)          | +5/2>                           |
| 530           | 0                               | 704           | 0                               |
| 530           | 0.049                           | 704           | -0.043                          |
| 326           | 0.676                           | 704           | 0.740                           |
| 326           | 0.576                           | 704           | 0.043                           |
| 0             | 0.728                           | 433           | 0.532                           |
| 0             | -0.28                           | 433           | -0.585                          |
| 0             | 0.490                           | 0             | 0.331                           |
| 0             | -0.28                           | 0             | 0.419                           |

3p states of the Al(3) and Al(4) atoms. This hybridisation should play an important role in both the enhancement of the ordering temperature and the formation of the hybridisation gap. Hanzawa, on the other hand, pointed out that onsite 4f-5d mixing may occur due to the lack of inversion symmetry at the Ce site [11]. It was suggested that the 4f-5d mixing may enhance the Ruderman-Kittel-Kasuya-Yoshida interaction which causes the magnetic ordering of Ce magnetic moments. The onsite 4f-5d and inter-site 4f-3p hybridisations would be observed by the undergoing photoemission and linear-polarised soft-x-ray absorption experiments. Remaining problems to be clarified are the mechanisms for the enhancement of $T_0$ and for the change in the direction of the magnetic moments from the a axis in the paramagnetic state to the c axis in the ordered state. To answer these problems, further studies are necessary which take into account the anisotropic hybridisation based on the CEF scheme obtained by this work.

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