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We have carried out a powder X-ray diffraction investigation on antiferromagnetic Kondo semiconductors CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ at low temperatures and under high pressures as well as the structural investigation on single crystal of these compounds. The results of powder X-ray studies of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ indicate that these compounds do not have structural transition at its antiferromagnetic ordering temperature. The results of single crystal structural refinement indicate that the b-axis of this crystal structure is insensitive not only to pressure but also to temperature and that the effect of cooling to Ce–Ce distance for CeRu$_2$Al$_{10}$ is the same as that for CeOs$_2$Al$_{10}$.

1. Introduction

CeT$_2$Al$_{10}$ (T = Ru, Os) crystallizes in orthorhombic structure (space group *Cmcm* No. 63) [1]. These compounds have been reported to exhibit antiferromagnetic (AFM) ordering at ordering temperatures (T_N) of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ are 27.3 and 28.7 K, respectively [2, 3]. These compounds are also reported as a Kondo semiconductor, the gap of which is due to the strong c–f hybridization. Optical conductivity studies have confirmed the c–f hybridization gap in CeRu$_2$Al$_{10}$ and in CeOs$_2$Al$_{10}$ are 35 and 45 meV, respectively [4, 5].

These compounds have been extensively studied because of the coexistence of AFM ordering and c–f hybridization gap. Neutron scattering have confirmed the existence of antiferromagnetic ordering in both CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ [6–8]. These T_N values are about 100 times higher than that would be expected from the de Gennes law [3]. The electronic instability, which accompanies structural instability, is one possible drive force for the high T_N of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$.

The T_N of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ suddenly disappear at a critical pressure (P_C) ≈ 4 GPa and 2.5 GPa, respectively [3, 9]. This sudden disappearance, like a first-order transition, implies the possibility of a pressure-induced structural transition near P_C. This study focuses on T_N and on P_C at room temperatures and the effect of cooling to the structure.

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In this paper, we report the synchrotron X-ray studies of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ around T_N and as well as those under pressure. We also report the analysis of single crystal structure at 110 K and 300 K.

2. Experimental details

CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ were grown by Al self flux method. For the analysis of single crystal structure, we use a piece of single crystal of CeRu$_2$Al$_{10}$ with 50 μm × 40 μm × 20 μm and that of CeOs$_2$Al$_{10}$ with 70 μm × 50 μm × 20 μm. The measurements of single crystal structure were performed on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo K_α radiation.

For the experiment of synchrotron powder X-ray diffraction, the single crystals were grinded into a fine powder. The uniform grain was obtained by using sedimentation method. The pressure was applied by diamond anvil pressure cell (DAC). The measurement down to 10 K was cooled with GM refrigerator. The sample was exposed by the beam with a size of Φ100 μm in diameter and with a wave length $\lambda \approx 0.62$ Å. Imaging plate was used as a detector. In order to eliminate remaining spots of the Debye ring, a stage of the DAC was oscillated during synchrotron X-ray exposure. The mixture of methanol and ethanol with 4:1 ratio was used as pressure transmission. The pressure was evaluated by ruby fluorescence method.

3. Results and discussions
3.1. Powder X-ray diffraction

Figure 1 shows the X-ray diffraction pattern of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ around P_C at room temperature. The diffraction pattern of CeRu$_2$Al$_{10}$ at 4.2 GPa is

not changed from that at 3.1 GPa except a slight change of peaks position due to the contraction of lattice parameters. Because the P_C of CeRu$_2$Al$_{10}$ is from 3 GPa to 4 GPa, this result indicates the lack of structural change around P_C at room temperature. In addition, the intensity ratio of the peaks does not change from 3.1 GPa to 4.2 GPa, which implies the lack of structural deformation around P_C at room temperature.
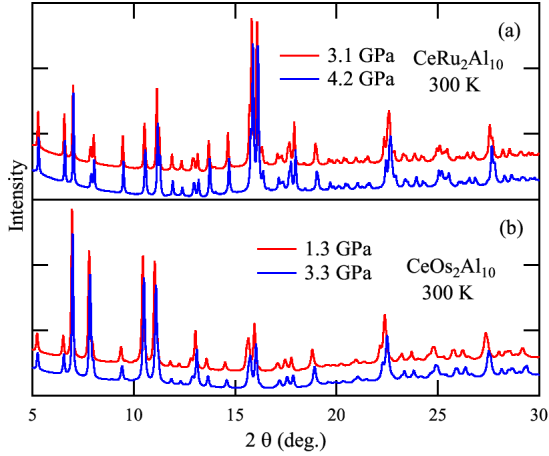

Fig. 1. X-ray diffraction pattern of (a) CeRu$_2$Al$_{10}$ and (b) CeOs$_2$Al$_{10}$ at the pressure below P_C (top) and above P_C (bottom).

Similar results can be seen in the X-ray diffraction patterns of CeOs$_2$Al$_{10}$. The diffraction pattern of CeOs$_2$Al$_{10}$ at 3.3 GPa is not changed from that at 1.3 GPa except a slight change of peaks position. In addition, the intensity ratio of the peaks does not change from 1.3 GPa to 3.3 GPa. Because the $P_C \approx 2.5$ GPa for CeOs$_2$Al$_{10}$, these results imply the lack of structural change and deformation around P_C at room temperature.

Although the angles of the peaks of CeRu$_2$Al$_{10}$ are not so different from that of CeOs$_2$Al$_{10}$ due to the similar lattice constant, the relative peak intensity of each peaks is considerable different as can be seen in Fig. 1. This difference is due to the difference of the atomic position.

Figure 2 shows the X-ray diffraction pattern around T_N below P_C. Neither peak disappearance nor peak splitting are observed. Furthermore, the intensity of the peak does not change a lot at different temperatures. We note that the background of CeRu$_2$Al$_{10}$ and CeOs$_2$Al$_{10}$ is different, which is due to the change of Mylar sheet at the window of GM refrigerator.

We evaluated bulk modulus by the Birch equation of state [10]:

$$P = 3/2 B_0 \left[(i/i_0)^{-7} - (i/i_0)^{-5} \right]$$
$$\times \left\{ 1 + 3/4 \left(B_0' - 4 \right) \left[(i/i_0)^{-2} - 1 \right] \right\},$$

where B_0 is the bulk modulus, B_0' is its first pressure derivative, P is the pressure, i ($i = a$, b, c) denotes the lattice parameters, i_0 ($i_0 = a_0$, b_0, c_0) denotes the lattice parameters at ambient pressure. B_0 of a, b, c for
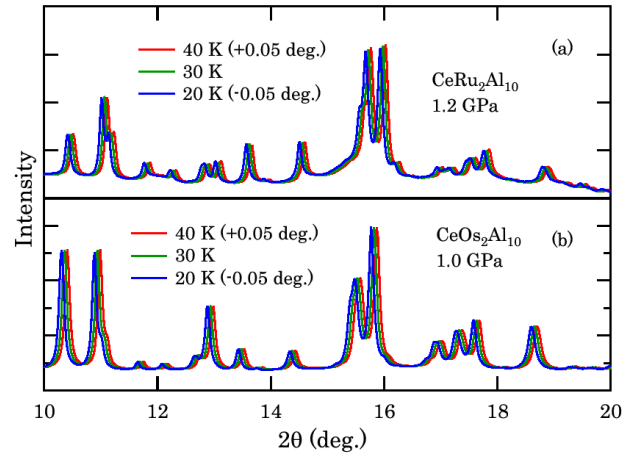

Fig. 2. X-ray diffraction pattern of (a) CeRu$_2$Al$_{10}$ and (b) CeOs$_2$Al$_{10}$ at 20 K (left), 30 K (middle), and 40 K (right). The peaks are shifted for clarity as indicated in the parenthesis.

CeRu$_2$Al$_{10}$ is derived to 101, 128, 97 GPa, respectively. In addition, B_0 of a, b, and c for CeOs$_2$Al$_{10}$ is derived to 106, 144, and 108 GPa, respectively.

The B_0 of V assuming cubic approximation are among these values; 105 GPa for CeRu$_2$Al$_{10}$ and 120 GPa for CeOs$_2$Al$_{10}$ [11]. The large value of b indicates that lattice parameter is insensitive to pressure. The difference of B_0 for b parameter for CeOs$_2$Al$_{10}$ from the other axis is more distinctive than that of CeRu$_2$Al$_{10}$.
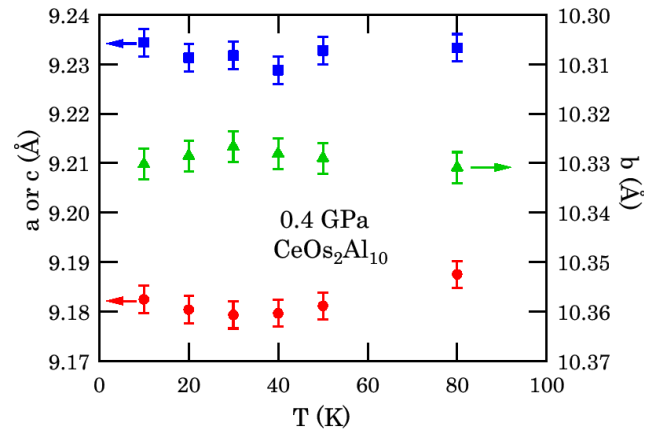

Fig. 3. Lattice parameter a (circle, left axis), b (triangle, right axis), and c (square, left axis) at low temperatures of CeOs$_2$Al$_{10}$ below P_C.

Figure 3 shows the lattice parameters of CeOs$_2$Al$_{10}$ at low temperatures below P_C. There is no distinct difference around T_N out of this experimental error attributed to the change of pressure and to the shrink of GM refrigerator by cooling. These results do not contradict to the previous lattice parameters obtained from neutron diffraction with a small anomaly in the case of b parameter at 30 K, because the error bar of neutron diffraction is smaller [12].

3.2. Single crystal analysis

In order to evaluate the effect of cooling on lattice parameters for $CeOs_2Al_{10}$ and for $CeRu_2Al_{10}$, we performed single crystal X-ray structure refinement. The refinement parameters of $CeRu_2Al_{10}$ with $R = 0.028$, $wR = 0.062$, and $S = 1.19$ are compatible to the previous report with $R = 0.043$, $wR = 0.123$, and $S = 1.10$ [13].

Table I shows the lattice parameter of $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$ at 300 K and at 110 K. The a and c parameters of $CeOs_2Al_{10}$ are longer than those of $CeRu_2Al_{10}$, while the b parameter of $CeOs_2Al_{10}$ is almost the same as that of $CeRu_2Al_{10}$. This small b parameter for $CeOs_2Al_{10}$ induces the large difference of B_0 of b from that of a and c. The differences of lattice parameters a, b, and c at 110 K from those at 300 K for $CeRu_2Al_{10}$ are 0.23%, 0.12%, 0.21%, respectively. Those for $CeOs_2Al_{10}$ are 0.18%, 0.09%, 0.21%, respectively.

TABLE I

Lattice parameters and Ce–Ce distance of $CeRu_2Al_{10}$ and that of $CeOs_2Al_{10}$. Estimated standard deviations are given in parentheses.

	$CeRu_2Al_{10}$		$CeOs_2Al_{10}$	
	300 K	110 K	300 K	110 K
a [Å]	9.120(2)	9.099(3)	9.139(2)	9.123(3)
b [Å]	10.268(2)	10.256(4)	10.267(3)	10.258(3)
c [Å]	9.181(2)	9.162(3)	9.187(2)	9.168(3)
Ce-Ce [Å]	5.247	5.237	5.271	5.261

Overall, the lattice parameters of $CeRu_2Al_{10}$ are more sensitive to cooling than those of $CeOs_2Al_{10}$. This is the same tendency as the B_0s of $CeRu_2Al_{10}$ are smaller than those of $CeOs_2Al_{10}$, where B_0 means the hardness against pressure. The lattice parameters of b for $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$ are insensitive to cooling. This tendency is consistent with the results that the lattice parameter of b is insensitive to pressure compared to that of a or c.

Next, we discuss the relation between lattice parameters and physical properties. When $CeRu_2Al_{10}$ is compared to $CeFe_2Al_{10}$, the lattice parameter has an anisotropic contraction. We proposed that the shrinkage of lattice parameters a and c is related to the enhancement of the anisotropic c–f hybridization [11]. When $CeRu_2Al_{10}$ is compared to $CeOs_2Al_{10}$, the effect of c–f hybridization cannot be related to chemical pressure. Although the c–f hybridization of $CeRu_2Al_{10}$ is smaller than that of $CeOs_2Al_{10}$, the volume and the Ce–Ce distance of $CeRu_2Al_{10}$ are smaller than those of $CeOs_2Al_{10}$.

On the other hand, the Ce–Ce distance decreases by 0.19% from 300 K to 110 K for both compounds, which indicates the effect of cooling is the same in these compounds. This study reveals that the comparison of temperature dependence of physical properties on $CeRu_2Al_{10}$ and that on $CeOs_2Al_{10}$ is fruitful because Ce–Ce distance is essential factor for discussing c–f hybridization and magnetic ordering at T_N.

4. Conclusions

We have investigated structure of $CeRu_2Al_{10}$ and $CeOs_2Al_{10}$ at low temperature and at high pressures. Powder X-ray diffraction does not show any hint of structural change or modification at T_N or P_C at room temperature. The structural analysis of the single crystal indicates that the b-axis of this crystal structure is insensitive not only to pressure but also to cooling and that the effect of cooling of Ce–Ce distance for $CeRu_2Al_{10}$ is the same as that for $CeOs_2Al_{10}$.

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