SUCCESSIVE STRUCTURAL PHASE TRANSITIONS OF THE SEMICONDUCTIVE CeRhAs*

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X-ray diffraction experiment has been performed on the semiconductive valence fluctuation compound CeRhAs. Strong superlattice reflections characterized by the wave vector of $q = (0, 1/2, 1/2)$ was observed below $T_1 = 370$ K with intensity anomalies at $T_2 = 235$ K and $T_3 = 165$ K. Below T_2, additional superlattice reflections were seen and some of them disappear below T_3. The observed successive superlattice formation may reflect the electronic gap formation due to the complicated Fermi-surface structure.

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The ternary intermetallic compound CeRhAs was reported to crystallize in the ϵ-TiNiSi type orthorhombic structure which is the same structure as that of a Kondo semimetal CeNiSn [1, 2]. Magnetic susceptibility of this compound exhibits a broad maximum around 500 K. This fact shows that the material is categorized as the valence fluctuation (VF) system at high temperatures. On the other hand, an abrupt decrease of susceptibility is observed at $T_1 = 370$ K with decreasing temperature, indicating that a gap opens at the Fermi level of $4f$ electron state at the temperature [3, 4].

Following this phenomenon, the resistivity, susceptibility, thermo-electric power, thermal conductivity and lattice parameters of CeRhAs exhibit step-like anomalies at the temperatures $T_2 = 235$ K and $T_3 = 165$ K. At the

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temperatures below T_3, the compound behaves as a semiconductor with a rather small energy gap of the order of 200 K [3]. These facts indicate that CeRhAs is classified into a new-type of VF material with a semiconductive ground state after multi-step phase transitions at low temperatures.

In order to investigate the phase transitions in CeRhAs, X-ray diffraction experiments have been performed on this material at various temperatures.

A diffractometer with a Mo rotating-anode X-ray source was used for the experiment. A single crystal sample of CeRhAs ($1.0 \times 1.6 \times 1.1$ mm^3), which was grown by the Bridgman technique [3], was used in the experiment. Sample temperature was controlled between 50 and 400 K by using a closed-cycle refrigerator.

Various superlattice reflections in addition to the fundamental Bragg reflections of the ϵ-TiNiSi type structure were observed at temperatures below T_1 (370 K). Fig. 1 shows the scattering profiles along $[0, \zeta, \zeta]$ direction through $(1, 6, 0)$ reciprocal lattice point at 100 K and 200 K. Fig. 2(a) and (b) show the profiles along $[0, \zeta, \zeta]$ and $[\xi, 0, 0]$ directions, respectively, through $(0, 6, 0)$ reciprocal lattice point at 100 K, 200 K, and 250 K(a) or 300 K(b). Fig. 3 summarizes the temperature dependences of the peak intensities of the satellite peaks seen in Figs. 1 and 2.

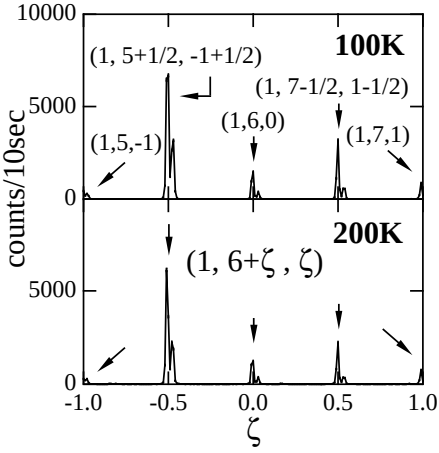

Fig. 1. Scattering profiles along $[0, \zeta, \zeta]$ direction through $(1, 6, 0)$.

Below T_1, strong superlattice reflections were observed at $(h, k, l)\pm$ (0, 1/2, 1/2), where h, k and l are integer, as shown in Fig. 1 and Fig. 3. The peak intensities of the reflections show anomalies at T_2 and T_3. Note that the peak at $(1, 6, 0)$ seen in Fig. 1 is also forbidden in the ϵ-TiNiSi type structure. These superlattice reflections can be characterized by a reduced

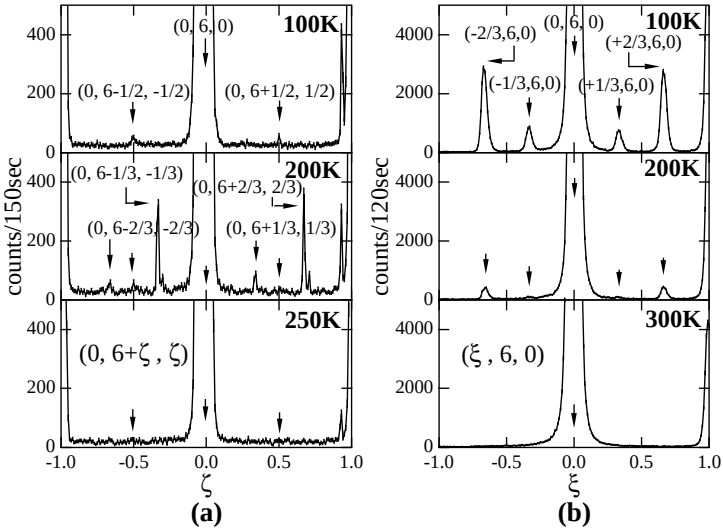

Fig. 2. Scattering profiles along (a) $[0, \zeta, \zeta]$ and (b) $[\xi, 0, 0]$ through $(0, 6, 0)$.

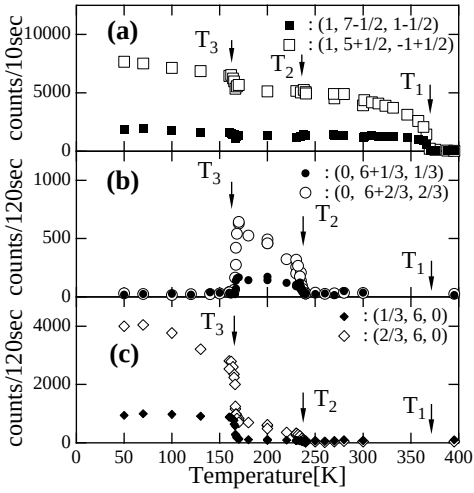

Fig. 3. Temperature dependences of peak-intensities of superlattice reflections.

wave vector $\boldsymbol{q}_1 = (0,\ 1/2,\ 1/2)$. It is remarkable that the intensities of the superlattice reflections of $\boldsymbol{q}_1$ is comparable to or even stronger than those of fundamental Bragg peaks at low temperatures: for example, the peak intensity of the superlattice peak $(1, 5, \text{-}1) + (0, 1/2, 1/2)$ is about 7000/10 sec at 100 K as shown in Fig. 1, whereas those of the fundamental peaks $(0, 6, 0)$ and $(0, 7, 1)$ are about 8000 and 4000/10 sec, respectively, at the same temperature. These facts indicate that the atomic displacement relevant to the

phase transition at T_1 is extremely large, and that the basic period of the crystal becomes twice the ϵ-TiNiSi type unit cell along the b- and c- directions.

Between T_2 and T_3, additional superlattice reflections characterized by the wave vectors $\boldsymbol{q}_2 = (0,\ 1/3,\ 1/3)$ and $\boldsymbol{q}_3 = (1/3,\ 0,\ 0)$ are seen. Moreover, although not shown here, reflections of $\boldsymbol{q}_4 = (0,\ 1/6,\ 1/6)$ and $\boldsymbol{q}_5 = (1/3,\ 1/3,\ 1/3)$ were also observed in the same temperature range. Below T_3, the reflections of $\boldsymbol{q}_2$, $\boldsymbol{q}_4$, $\boldsymbol{q}_5$ disappear, while those of $\boldsymbol{q}_1$ and $\boldsymbol{q}_3$ are suddenly enhanced.

Since above results indicate that the basic crystal structure of CeRhAs below T_1 is different from the ϵ-TiNiSi type one, we also carried out a powder diffraction experiment on this material at room temperature. Samples were prepared by powdering the same batch single crystals as that used in the single crystal diffraction experiments. As a result of the experiment, no clear superlattice reflection of $\boldsymbol{q}_1$ was observed. It suggests that the structure of CeRhAs at room temperature is changed to the structure close to the ϵ-TiNiSi type one by powdering process.

The present work indicates that CeRhAs undergoes successive structural phase transitions at the temperatures T_1, T_2, and T_3. The X-ray diffraction results together with the result of susceptibility measurement strongly suggest that the phase transition at T_1 is a kind of Peierls transition which gives rise to the structural transformation with a huge atomic displacement. Investigation of the Fermi-surface structure and comparison with the present X-ray diffraction data is necessary. Detailed analysis of the superlattice structure in each phase is in progress to understand the interesting properties of this material.

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