Crystal structure and magnetic properties of new ternary uranium compound U₃TiBi₉

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The crystal structure of the newly discovered compound U₃TiBi₉ was determined from single-crystal X-ray diffraction data. The space group is P6₃/m with the lattice parameters a = 11.691 Å, c = 6.331 Å. U₃TiBi₉ shows an antiferromagnetic ordering at T_N = 31.5 K. A clear anomaly was observed at T_N on the temperature dependences of magnetic susceptibility and electrical resistivity.

Keywords: uranium intermetallic; inversion symmetry; antiferromagnetic ordering; U₃TiBi₉

1. Introduction

The uranium compounds exhibit a variety of superconductivities and magnetic behaviors including Pauli itinerant, heavy fermion and local moment ordering, where the 5f electrons play principal roles [1-3]. The heavy fermion originates from the hybridization effect between the conduction electrons and the f electrons. The 5f electrons have an intermediate character between the localized 4f electrons of rare-earth compounds and the itinerant 3d electrons of transition metals. This characteristic of the 5f electrons leads to the variety of physical properties of the U compounds.

The crystallographical studies of the ternary Ce-Ti-Sb and U-Ti-Sb systems have already been carried out by S. H. D. Moore et al. [4] and A. Mar et al. [5], respectively. The existence of some ternary compounds including Ce₃TiSb₅, Ce₃TiSb₄ and U₃TiSb₅ was already confirmed. However there has been no report of the ternary compound in the Ce-Ti-Bi and U-Ti-Bi systems. As the results of our investigation in the Ce-Ti-Bi system, we found two new compounds Ce₃TiBi₅ and Ce₃TiBi₄, which are obtained by a Bi self-flux method, and their single crystals form needles and plates, respectively [6]. Each of the two new compounds is isostructural with the antimonides Ce₃TiSb₅ (P6₃/mcm) and Ce₃TiSb₄ (Fmmm). It is found that Ce₃TiBi₅ and Ce₃TiBi₄ exhibit an antiferromagnetic ordering at 3.5 K and 5.0 K, respectively. In this paper, we report the discovery of the first U-Ti-Bi intermetallic compound and its magnetic properties.

2. Experimental

The single crystal samples were prepared by the Bi self-flux method. The purities of the materials of U, Ti and Bi are 99.9, 99.9 and 99.99 %, respectively. The starting materials were placed in the ratio U : Ti : Bi = 3 : 1 : 40 into an alumina crucible and sealed under high vacuum in a quartz tube. The sealed ampoule was heated up to 1000 °C, kept for 11 h, followed by a slow cool at 2 °C/h to 500 °C. The excess bismuth flux was removed from the crystals by using a centrifuge, then the needle-shaped single crystals were obtained. The prepared single crystals of the habit of U₃TiBi₉ are shown in Figure 1. The crystal was easily damaged in air, and collapses during the first several hours after leaving it in air.

Figure 1. Single crystals of U₃TiBi₉. The needle axis corresponds to the crystallographic c axis. A grid of the cross-section is equal to 1 x 1 mm². The weight of the largest crystal, which was obtained in this work, is 0.07(3) mg.

Crystal structure investigation was done by single-crystal X-ray diffraction experiments. Diffraction data were collected using an imaging plate detector with Mo Kα radiation. The single crystal sample for the
X-ray diffraction was coated by vacuum grease to avoid oxidation and no apparent change in the diffraction intensities has been observed during the measurement. Structural solution by the direct method and refinements of the structural parameters were performed using the SHELX software [7].

Electrical resistivity was measured by a standard four-terminal method, and magnetic susceptibility and magnetization were measured using a commercial SQUID magnetometer (Quantum Design MPMS). To prevent the sample from oxidizing, the resistivity measurement was carried out in the pressure cell filled with Daphne7373 as pressure transmedium. The applied pressure was almost ambient pressure.

3. Crystal structure

The crystal structure has been successfully solved by the single crystal X-ray diffraction. 7757 Bragg reflections were successfully indexed for the hexagonal structure (P63/m) with lattice parameters \( a = 11.691(1) \) Å and \( c = 6.331(1) \) Å, where 791 were unique. The first attempt by reference to the structure of the Ce3TiBi5 gave only a poor agreement between the calculated and observed intensities. The space-group P63/m of the obtained needle-shape crystals is different from that of Ce3TiBi5, although the crystal shape is very similar between the obtained crystal and Ce3TiBi5. And then \( a \) is larger than that of Ce3TiBi5, although \( c \) is smaller [6]. Lattice parameters of a U-compound usually shrink in comparison with the isostructural Ce-compound. This unexpected results derive from a change from the single Bi-chain to triangle prism of Bi which lies between the three TiBi6 octahedron, as shown in Figure 2. The octahedral structure is common structure between the both compounds. As the result, the chemical composition of the obtained crystal is not U3TiBi9 but U3TiBi9. Moreover the change additionally results in a slight octahedron’s rotation about the c-axis. The crystallographic parameters of U3TiBi9 as well as the refinement details are shown in Table 1. The good agreement between the observed and calculated structure factors assures validity of the structural model.

In the crystal structure of Ce3TiBi5, the Ce atoms are located in the face of ac-plane and form zig-zag chains along parallel to the c-axis. However, because of the slight rotation of the octahedron, the U atoms in the crystal structure of U3TiBi9 are off from the face of the ac-plane. The distance between the U atoms get longer and the U atoms no longer form a zig-zag chain, unfortunately. The nearest U-U distance is 4.774 Å, which is decided from the distance between the two U atoms surrounded the same Bi octahedron.

| Atom | Site | sym. | \( x \)  | \( y \)  | \( z \) |
|------|------|------|---------|---------|------|
| Bi1  | 12i  | 1    | 0.1460  | 0.5282  | 0.0009|
| Bi2  | 6h   | m    | 0.1766  | 0.2407  | 1/4  |
| U    | 6h   | m    | 0.3410  | 0.0917  | 1/4  |
| Ti   | 2b   | -3   | 0       | 0       | 0    |

Table 1. Crystallographic parameters for U3TiBi9 (space group: P63/m; lattice parameters \( a = 11.691(1) \) Å, \( c = 6.331(1) \) Å). The data were corrected for Lorentz and polarization effects. The overall agreement factor \( R_1 = \sum|F_o|-|F_c|/\sum|F_o| = 0.0591 \), where \( F_o \) and \( F_c \) are observed and calculated structure factors, where anisotropic atomic displacement parameters have been refined.

4. Magnetic properties

4.1. Magnetic susceptibility

Figures 3(a) and 3(b) shows the temperature \( T \) dependence of the magnetic susceptibility \( \chi(T) \) and magnetization curve \( M(H) \) of U3TiBi9 for magnetic field \( (H) \) parallel and perpendicular to the c-axis. \( \chi(T) \) follows roughly as the Curie-Weiss law above 100 K to 300 K as shown in the inset of the Figure 3(a). The paramagnetic effective moment 3.5 \( \mu_B \) corresponds to the free uranium ion value, but there is 50 % ambiguity because of the measurement using a very small single crystal. \( \chi(T) \) shows large anisotropy, \( \chi(T) \) perpendicular to the c-axis is several times larger than that of the c axis. It is suggested that the easy axis of magnetization is perpendicular to the c axis.

\( \chi(T) \) of the both axes show a peak at 31.5 K and decrease with decreasing temperature, especially the distinct decrease was observed on \( \chi(T) \) of the easy axis. This anomaly does not show a hysteresis behavior within the measurement accuracy. It is considered that this anomaly is attributed to the antiferromagnetic ordering. The magnetization curves of the whole data exhibit linear \( H \) dependence up to 10 kOe. We cannot observed any metamagnetic behavior at least until 10 kOe.

Figure 2. Comparison between crystal structures of U3TiBi9 (a, b) and Ce3TiBi5 (c, d).
4.2. Electrical resistivity

The $T$ dependences of electrical resistivity $\rho(T)$ and $T$ derivative of the electrical resistivity $\partial\rho/\partial T(T)$ on $U_3TiBi_9$ are shown in Figures 4(a) and 4(b), respectively. With decreasing temperature from 300 K to 80 K, $\rho(T)$ gradually increases and then it rapidly decreases below 40 K after showing the flat $T$ dependence. The antiferromagnetic phase transition is observed as a small but clear kink at 31.5 K. At low temperature, $\rho(T)$ finally approaches to a constant value.

The electrical resistivity as a function of $T^2$ as shown in the inset of the Figure 4(a) shows the linear dependence below 8 K. A least square fit of the data to the expression $\rho(T) = \rho_0 + A T^2$ gave $\rho_0 = 8.9 \mu\Omega\cdot\text{cm}$ and $A = 0.224 \mu\Omega\cdot\text{cm/K}^2$. The residual resistivity ratio $\rho_{300K}/\rho_0$ is 29, indicating a good quality sample. The large $A$ coefficient 0.224 $\mu\Omega\cdot\text{cm/K}^2$ indicates a strong electron correlation, which is consistent with the Sommerfeld coefficient $\gamma = 150 \text{mJ/(K}^2\cdot\text{mol})$ according to the Kadowaki-Woods relation. For an accurate estimate of the $\gamma$ value, we should measure a specific heat of the $U_3TiBi_9$. It may be noted that a broad anomaly was observed around 16.5 K on the $\partial\rho/\partial T(T)$, where is lower than the magnetic transition temperature, although we do not have enough data about the broad anomaly to discuss it at present.

The antiferromagnetic transition temperature on $\rho(T)$ agrees with that on $\chi(T)$. The electrical resistivity of $U_3TiBi_9$ increases approximately as log $T$ with decreasing $T$, this behavior well appears on the typical antiferromagnetic heavy fermion U-compounds such as UPd$_2$Al$_3$. The cause of the log $T$ dependence and the small anomaly at $T_N$ on $\rho(T)$ is considered to be a competition between Kondo effect and RKKY exchange interaction in this system. However, the distinct decrease on $\chi(T)$ at $T_N$ was observed, in spite of the small kink at $T_N$ on $\rho(T)$. We need more future studies to discuss the ground state of this system.

5. Conclusion

We have found the U-Ti-Bi intermetallic compound $U_3TiBi_9$ and clarified that it crystallizes in the $P6_3/m$ hexagonal structure. The magnetic susceptibility of $U_3TiBi_9$ seems to follow the Curie-Weiss law at high temperature. This new uranium compound shows the antiferromagnetic ordering at 31.5 K and the Kondo behavior at least on the temperature dependence of the electrical resistivity.

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