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Crystal structure and magnetic properties of new ternary uranium compound U_3TiBi_9

Gaku Motoyama[a*], Yoshinori Haga[b], Akira Yamaguchi[c], Ikuto Kawasaki[c],
Akihiko Sumiyama[c] and Tomoo Yamamura[d]

[a]*Graduate School of Material Science, Shimane University, 1060 Nishikawatsu, Matsue, Shimane, 690-8504, Japan;* [b]*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Naka-gun, Ibaraki, 319-1195, Japan;* [c]*Graduate School of Material Science, University of Hyogo, Kouto, Ako-gun, Hyogo, 672-8504, Japan;* [d]*Institute for Materials Research, Tohoku University, Aoba-ku, Sendai, Miyagi, 980-8577, Japan*

The crystal structure of the newly discovered compound U_3TiBi_9 was determined from single-crystal X-ray diffraction data. The space group is $P6_3/m$ with the lattice parameters a = 11.691 Å, c = 6.331 Å. U_3TiBi_9 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; U_3TiBi_9

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 Ce_3TiSb_5, $CeTi_3Sb_4$ and U_3TiSb_5 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 Ce_3TiBi_5 and $CeTi_3Bi_4$, 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 Ce_3TiSb_5 ($P6_3/mcm$) and $CeTi_3Sb_4$ ($Fmmm$). It is found that Ce_3TiBi_5 and $CeTi_3Bi_4$ 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.

*Corresponding author. Email: motoyama@riko.shimane-u.ac.jp

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 U_3TiBi_9 are shown in **Figure 1**. The crystal was easily damaged in air, and collapses during the first several hours after leaving it in air.
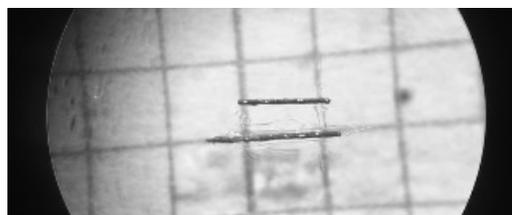
Figure 1. Single crystals of U_3TiBi_9. The needle axis corresponds to the crystallographic c axis. A grid of the cross-section is equal to 1 × 1 mm². The weight of the largest crystal, which was obtained in this work, is 0.07(3) mg.

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 oxidization 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 ($P6_3/m$) 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 Ce_3TiBi_5 gave only a poor agreement between the calculated and observed intensities. The space-group $P6_3/m$ of the obtained needle-shape crystals is different from that of Ce_3TiBi_5, although the crystal shape is very similar between the obtained crystal and Ce_3TiBi_5. And then a is larger than that of Ce_3TiBi_5, 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 $TiBi_6$ 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 U_3TiBi_5 but U_3TiBi_9. Moreover the change additionally results in a slight octahedron's rotation about the c-axis. The crystallographic parameters of U_3TiBi_9 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.
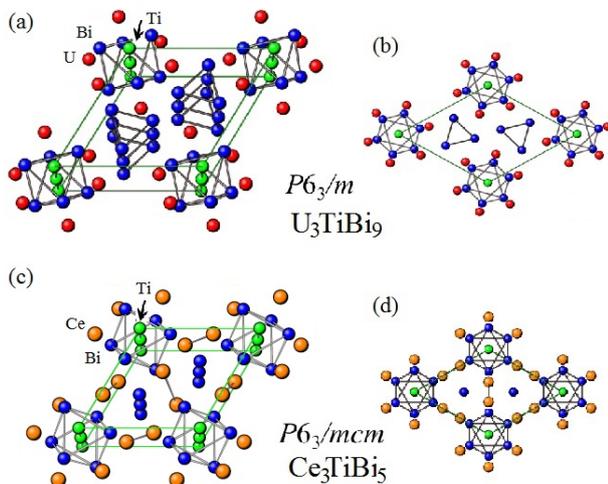
In the crystal structure of Ce_3TiBi_5, the Ce atoms are located in the face of ac-plane and form zig-zag chains along parallel to the c-axis. However, because of the slight rotation of the octahedron, the U atoms in the crystal structure of U_3TiBi_9 are off from the face of the ac-plane. The distance 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.

Table 1. Crystallographic parameters for U_3TiBi_9 (space group: $P6_3/m$; lattice parameters $a = 11.691(1)$, $c = 6.331(1)$ 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.

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

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 U_3TiBi_9 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 μ_B/U 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 U_3TiBi_9 (a, b) and Ce_3TiBi_5 (c, d).
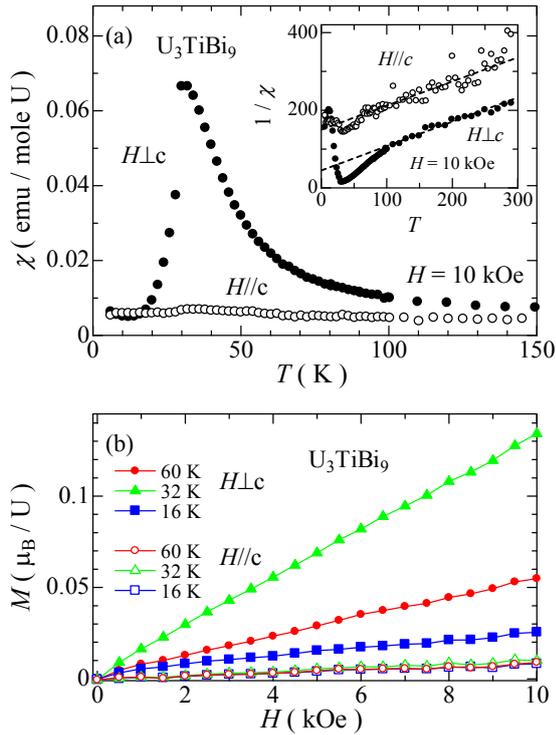
Figure 3. Temperature dependence of the magnetic susceptibility (a) and magnetization curve (b) of U_3TiBi_9. A static magnetic field were applied parallel and perpendicular to the c-axis. The inset of the (a) shows the $1/\chi$ vs. T plot.

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 $\rho_0 = 8.9\ \mu\Omega\cdot$ cm and $A = 0.224\ \mu\Omega\cdot$ cm/K^2. The residual resistivity ratio ρ_{300K}/ρ_0 is 29, indicating a good quality sample. The large A coefficient 0.224 $\mu\Omega\cdot$ cm/K^2 indicates a strong electron correlation, which is consistent with the Sommerfeld coefficient $\gamma = 150$ mJ/(K$^2\cdot$ mol) according to the Kadowaki-Woods relation. For an accurate estimate of the γ 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
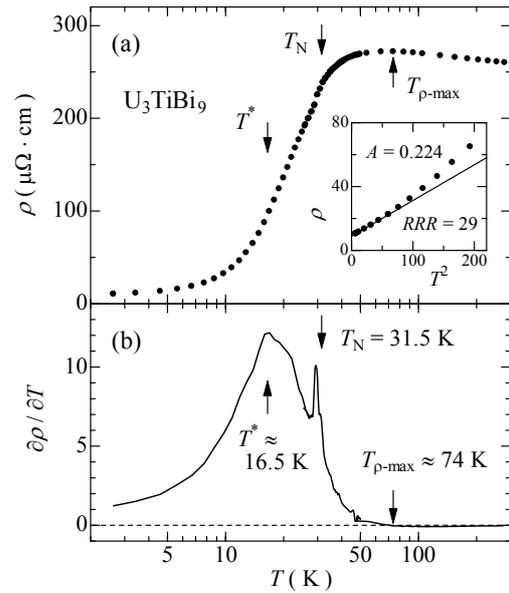

Figure 4. Temperature dependences of the electrical resistivity (a) and temperature derivative of the electrical resistivity (b) of U_3TiBi_9. The inset shows the electrical resistivity as a function of T square. The current was applied along the c-axis.

decreasing T, this behavior well appears on the typical antiferromagnetic heavy fermion U-compounds such as UPd_2Al_3[2]. 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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