Single crystal growth and fermi surface properties in ThSb\textsubscript{2} and ThBi\textsubscript{2}

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We grew high-quality single crystals of ThSb\textsubscript{2} and ThBi\textsubscript{2} and carried out the de Haas-van Alphen (dHvA) measurement and the full-potential LAPW band calculation. Detected main dHvA branches named $\alpha$ and $\alpha'$ correspond to an electron Fermi surface, while branch $\beta$ corresponds to a main hole Fermi surface. Each Fermi surface shows approximately the same cross-sectional areas for ThSb\textsubscript{2} and ThBi\textsubscript{2}. On the other hand, the corresponding cyclotron effective masses of ThBi\textsubscript{2} are larger than those of ThSb\textsubscript{2}, which is approximately consistent with a ratio of an electronic specific heat coefficient $\gamma$ of ThBi\textsubscript{2} to that of ThSb\textsubscript{2}, $\gamma_{\text{ThBi}2}/\gamma_{\text{ThSb}2} = 1.4$. This might be due to a small band width of ThBi\textsubscript{2}, compared with the one of ThSb\textsubscript{2}, reflecting large lattice constants of ThBi\textsubscript{2}, compared with those of ThSb\textsubscript{2}.

Keywords: ThSb\textsubscript{2}; ThBi\textsubscript{2}; dHvA; Fermi surface; energy band calculation

1. Introduction

The 5\textit{f}-electrons in a magnetic uranium compound possess dual nature: localized and itinerant features. Namely, the 5\textit{f} electrons contribute to the volume of the Fermi surface and also to a magnetic moment at the uranium sites \cite{1}. A non-5\textit{f} thorium compound does not become a reference compound for the corresponding uranium compound because valence electrons of the Th atom, 6\textit{d}\textsuperscript{2}7\textit{s}\textsuperscript{2}, are different from 5\textit{f}\textsuperscript{3}6\textit{d}\textsuperscript{1}7\textit{s}\textsuperscript{2} or 5\textit{f}\textsuperscript{2}6\textit{d}\textsuperscript{2}7\textit{s}\textsuperscript{2} of the U atom. The number of valence electrons in the thorium compound is, however, the same as that of a 4\textit{f}-itinerant cerium compound. The topology of the Fermi surface in ThRhIn\textsubscript{5} \cite{2} is approximately the same as in 4\textit{f}-itinerant CeCoIn\textsubscript{5} \cite{3}, for example. The cyclotron effective masses are, however, significantly different between ThRhIn\textsubscript{5} and CeCoIn\textsubscript{5}. Large cyclotron masses in CeCoIn\textsubscript{5} are due to the many-body Kondo effect.

In the present study, we grew single crystals of ThSb\textsubscript{2} and ThBi\textsubscript{2} with the tetragonal structure by the self-flux method and studied the Fermi surface properties. The experimental purpose of the present study is to clarify the electronic properties of Sb-5\textit{p} and Bi-6\textit{p} electrons and also a small contribution of Th-5\textit{f} electrons to conduction electrons.

2. Experimental procedure

Single crystals of ThSb\textsubscript{2} and ThBi\textsubscript{2} with the anti-Cu\textsubscript{2}Sb\textsubscript{2}type tetragonal structure (No. 129, $D\textsubscript{4h}$, $P4/nmm$), were grown by Sb and Bi self-flux method, respectively. Starting materials of 2N(99% pure)-Th, 6N-Sb, and 4N-Bi, with concentration of Th:Sb(Bi)=1:9, were inserted in an alumina crucible. The crucible was encapsulated in a quartz ampoule, heated to 1100 °C, slowly cooled to 300 °C, taking 12 days, and finally cooled to room temperature. The size of an obtained plate-like single crystal was about $1 \times 2 \times 0.3 \text{ mm}^3$ in ThSb\textsubscript{2}, revealing a flat tetragonal (001) plane, as shown in Figure 1\textsuperscript{(a)}. ThBi\textsubscript{2} is also obtained as a thin plate with a much large size, as shown in Figure 1\textsuperscript{(b)}. To confirm the sample quality, we measured the electrical resistivity. The residual resistivity $\rho_0$ is 0.3 $\mu\Omega\cdot\text{cm}$ and the residual resistivity ratio RRR ($= \rho_{\text{RT}}/\rho_0$, $\rho_{\text{RT}}$: resistivity at room temperature) is 85 for ThSb\textsubscript{2}, and $\rho_0 = 0.7 \mu\Omega\cdot\text{cm}$ and RRR = 37 for ThBi\textsubscript{2}, indicating high-quality samples.

The orientation of the single crystal sample of ThSb\textsubscript{2} and ThBi\textsubscript{2} were determined by the X-ray Laue method. We also determined the lattice parameters and atomic positions of ThSb\textsubscript{2} at room temperature. The small

[Figure 1. Single crystal ingots of (a) ThSb\textsubscript{2} and (b) ThBi\textsubscript{2}.]
single crystal sample was mounted on a glass fiber. The measurements were performed on a CCD detector with graphite monochromated Mo-Kα radiation. We summarize in Table 1 the crystal structure data in ThSb₂. These values are in good agreement with the previous data of \( a = 4.344 \text{ Å} \), \( c = 9.154 \text{ Å} \), and \( z = 0.27 \) for Th (2c) and 0.63 for Sb₂ (2c) [4]. We cannot, however, determine the crystal structure data in ThBi₂ because of intensive oxidation of the sample. It is reported that \( a = 4.492 \text{ Å} \), \( c = 9.298 \text{ Å} \), and \( z = 0.28 \) for Th (2c) and 0.63 for Bi₂ (2c) for ThBi₂ [5].

3. Experimental results and analyses

We measured the specific heat \( C \) by the thermal relaxation method down to 0.4 K, as shown in Figure 2. The specific heat decreases steeply with decreasing temperature. The solid line in Figure 2 is a fitting curve based on an electronic specific heat \( \gamma T \), the phonon contribution \( \beta T^3 \), and the nuclear contribution of Sb and Bi based on the electric quadrupole term \( A/T^2 \), namely \( C = \gamma T + \beta T^3 + A/T^2 \). We obtained the electronic specific heat coefficient \( \gamma \), the Debye temperature \( \Theta_D \), and the coefficient \( A \) as 2.6 mJ/\((K^2\cdot\text{mol})\), 151 K, and 0.050 mJ/K/mol for ThSb₂ and 3.3 mJ/\((K^2\cdot\text{mol})\), 151 K, and 0.18 mJ/K/mol for ThBi₂.

We carried out the dHvA experiment by the field-modulation method with a frequency of 55.8 Hz and a modulation field of 83 Oe. Figure 3(a) shows the typical dHvA oscillations for the magnetic field along \( H \parallel [001] \) in ThSb₂. The corresponding FFT spectrum is shown in Figure 3(b).

The detected dHvA branches \( \alpha \), \( \alpha' \), \( \beta \), \( \beta' \), \( \gamma \), and the others are observed, with the dHvA frequencies ranging from \( F = 1.88 \times 10^4 \text{ to } 9.74 \times 10^5 \text{ Oe} \), as shown in Figure 3(b). Here, the dHvA frequency \( F = (\pi \beta S_F/2 e) \) is proportional to the maximum or minimum cross-sectional area \( S_F \) of the Fermi surface, which is shown as a unit of magnetic field. We rotated the sample against the magnetic field, and obtained the angular dependences of the dHvA frequencies, as shown in Figure 4(a). Solid lines are guides connecting the data. The detected dHvA branches \( \alpha \) and \( \alpha' \) are due to cylindrical parts of Fermi surfaces. Branch \( \gamma \) is due to a closed small Fermi surface.

Table 1. Lattice parameters and atomic positions at room temperature in ThSb₂, where \( R \) and \( wR \) are the reliability factors, and \( B \) is the equivalent isotropic atomic displacement parameter.

| Space group | Lattice parameter (Å) | Atom Position | \( B \) |
|-------------|-----------------------|--------------|-------|
| \( P4/mmm (D_{4h}^5) \) | \( a=4.3512, c=9.1853 \) | Th (2c) 0, 1/2, 0.2741 | 0.41 |
| No. 129 | (\( R=6.45, wR=17.41 \)) | Sb (2a) 0, 0, 0 | 0.59 |
| | | Sb (2c) 1/2, 0, 0.6297 | 0.54 |

Table 2. dHvA frequencies \( F \) and the cyclotron masses \( m_c \) for \( H \parallel [001] \) in ThSb₂, together with the theoretical dHvA frequencies \( F_0 \) and the band masses \( m_0 \). See the text for the details of calculations.

| Experiment | Theory (LDA) | Theory (LDA+5f) |
|------------|--------------|-----------------|
| \( F(\text{Oe}) \) | \( m_c(\text{m}) \) | \( F_0(\text{Oe}) \) | \( m_0(\text{m}) \) | \( F(\text{Oe}) \) | \( m_c(\text{m}) \) | \( F_0(\text{Oe}) \) | \( m_0(\text{m}) \) |
| \( \alpha \) | 9.739 | 0.78 | 9.817 | 0.834 | 9.587 | 0.702 |
| \( \alpha' \) | 6.304 | 1.02 | 6.297 | 0.874 | 6.154 | 0.745 |
| \( \beta \) | 5.054 | 0.57 | 5.254 | 0.470 | 5.062 | 0.441 |
| \( \beta' \) | 0.514 | 0.29 | 0.361 | 0.351 | 0.442 | 0.280 |
| \( \gamma \) | 0.188 | 0.11 | 0.217 | 0.088 | 0.210 | 0.078 |
calculated the energy band structure for ThSb$_2$ by using the full-potential linearized augmented plane wave (FLAPW) method with the local density approximation (LDA) for the exchange correlation potential. We have also tried to shift 5f level in Th to reproduce the γ value, properly. In the present band calculation, the scalar relativistic effect was taken into account for all the electrons, and then the spin-orbit coupling was included self-consistently for all the valence electrons as in a second variational procedure. 6s$^2$6p$^6$6d$^2$7s$^2$ electrons for Th and 4d$^5$5s$^2$5p$^3$ electrons for Sb are treated as valence electrons in the calculation. The space group and lattice parameter are adopted from Table 1. Figures 4(b) and (c) show the theoretical angular dependences of dHvA frequencies $F_b$, and the corresponding Fermi surfaces, respectively. Here, we have used an upward shifted potential by 0.2 Ry, for the 5f electrons in Th. A reason of this correction is described later. The detected dHvA branches are identified as follows:

1) Branches α and α’ are due to outer and inner orbits of the band 43-electron Fermi surface, respectively.
2) Branches β and β’ are due to a belly orbit of a flat closed band 42-hole Fermi surface and a small neck Fermi surface, respectively.
3) Branch γ is due to a small band 44-electron Fermi surface.

Here, we note why we introduced the extra potential for the 5f electrons in Th. If we simply calculate the band calculation on the basis of LDA, we obtained the theoretical γ value of $\gamma_b = 2.83 \text{ mJ/(K}^2\cdot\text{mol)}$. This value is larger than the experimental value of $\gamma = 2.6(\pm0.03) \text{ mJ/(K}^2\cdot\text{mol)}$. This value of 2.83 mJ/(K$^2$·mol) is usually much enhanced by the electron-phonon interaction, most likely reaching 3.0 mJ/(K$^2$·mol) in reality. The theoretical γ value should be smaller than the experimental one. The obtained larger γ value is mainly due to a tail of the partial density of states of Th-5f electrons, which are mainly unoccupied above the Fermi energy $E_F$. We therefore shifted the 5f level upward by 0.2 Ry to reduce the effect of 5f bands in Th. The corresponding theoretical γ value is $\gamma_b = 2.33 \text{ mJ/(K}^2\cdot\text{mol)}$, which is consistent with the experimental value of $\gamma = 2.6 \text{ mJ/(K}^2\cdot\text{mol)}$. This treatment has been once introduced to the energy band calculation of ThIn$_3$ [6]. Then, the Fermi surfaces are reproduced properly.

We also show in Figure 5 the total and partial density of states, which was calculated on the basis of LDA+5f 0.2Ry. The Fermi surfaces are mainly composed from Sb-5p electrons, together with a small contribution of Th-6d and -5f electrons.

Similarly, we measured the dHvA oscillations in ThBi$_2$. We show in Figure 6 the angular dependences of the dHvA frequencies in ThBi$_2$, which are almost the same as those of ThSb$_2$. The dHvA frequencies in ThBi$_2$
are, however, slightly smaller than those in ThSb₂. The cyclotron masses in ThBi₂ are found to be larger than those of ThSb₂, as shown in Figure 7. The electronic specific heat coefficient $\gamma$ in ThBi₂ is also larger than the one in ThSb₂, $\gamma_{\text{ThBi}2}/\gamma_{\text{ThSb}2} = 1.4$, as shown in Figure 2. This is a characteristic feature. We will discuss this point.

Bi-6$p$ electrons and Sb-5$p$ electrons become main conduction electrons in ThBi₂ and ThSb₂, respectively. The lattice constants of ThBi₂ are larger than those of ThSb₂, as mentioned in Sec. 2. This brings about a small band width in ThBi₂, compared with the one in ThSb₂, although the wave function of 6$p$ in Bi is extended more than that of 5$p$ in Sb. This is a main reason why the band mass or the cyclotron mass in ThBi₂ is larger than the one in ThSb₂.

4. Concluding remark

We grew single crystal of ThSb₂ and ThBi₂ and studied the Fermi surface properties. The cyclotron masses are in the range from 0.11 to 1.02 $m_0$ ($m_0$: rest mass of an electron) in ThSb₂ and from 0.13 to 1.87 $m_0$ in ThBi₂, respectively. The cyclotron masses of ThBi₂ are large compared with those of ThSb₂. This might be due to a small band width of ThBi₂, compared with the one of ThSb₂, reflecting large lattice constants of ThBi₂, compared with those of ThSb₂. In the present band calculation, we introduced an extra potential for the 5$f$ electrons in Th to shift the 5$f$ level upward in energy. It is important to determine experimentally the correct energy position of the Th-5$f$ electrons in the energy dispersion, which is left to the future study.

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