De Haas–van Alphen study of the spin splitting of the Fermi surface in TbSb

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We have investigated the Fermi surface (FS) and magnetic properties of rare-earth monopnictide TbSb by means of de Haas–van Alphen (dHvA) and high-field magnetization measurements, respectively. The clear dHvA oscillation and spin splitting of the FS were observed. The present result indicates that the determined FS is quite similar to that of LaSb, i.e., TbSb is expected to be a well localized $4f$-electron system. By analyzing the spin splitting of the FS, the exchange interaction between conduction electrons and localized $4f$ ones was estimated quantitatively. It was found that these evaluated values were similar in magnitude to other important ones such as crystalline electric-field effect and exchange and quadrupolar interactions among $4f$ electrons in TbSb. This experimental fact ensures that their interactions are comparable to one another, leading to the fact that the physical properties are sensitive to external variables such as magnetic field in this system.

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I. INTRODUCTION

In rare-earth compounds, it had long been recognized that interesting phenomena such as the Kondo effect, magnetic ordering, heavy fermion system, valence fluctuation system, and so on, are ascribed to strength of the interplay between conduction bands and $4f$-localized electrons.[1,2] Thus, investigating accurately the Fermi surface (FS) and magnetic properties gives us a valuable clue to clarify the enigma in rare-earth compounds. However, high-quality single crystalline samples are required to investigate the Fermi surface. The difficulty to grow high-quality samples had long prevented the progress of investigation of rare-earth compounds. Rare-earth monopnictides with general formula RX_p (R, rare earth; X_p, pnictogen) had this serious problem because of the high melting point and high vapor pressure. However, Suzuki *et al.* succeeded in growing them and they came into the limelight again.[1] In fact, new phenomena and discoveries have been reported in rare-earth monopnictides with high-quality single crystals since then. TbSb is one of the compounds in which much remains to be investigated. The fundamental properties were actually reported, and the $4f$ level scheme under the cubic crystalline electric field (CEF) was established well by means of the magnetic susceptibility, specific heat, and inelastic neutron scattering measurements.[3–6] However, no study of the Fermi surface property has been reported so far. The success in growing high-quality single crystals enables us to observe the de Haas–van alphen (dHvA) signals and to explore the Fermi surface property in this study. According to the previous reports, the ground state of Tb ions with the spin-orbit split $J=6$ splits into Γ_1 (singlet), Γ_2 (singlet), Γ_3 (doublet), Γ_4 (triplet), $\Gamma_5^{(1)}$ (triplet), and $\Gamma_5^{(2)}$ (triplet) with Γ_1 (singlet) as the ground state.[3–6] The interesting feature of this material is that the nonmagnetic Γ_1 (singlet) ground state of Tb ion is realized separated by a small energy gap from the first excited state Γ_4 (triplet). This gives rise to an induced-moment ordering, which involves the so called "singlet-ground-state problem." TbSb shows antiferromagnetic (AF) ordering of type II (MnO type) with the $\langle 111\rangle$ easy axis at $T_N=14.2$ K.[6] The ordered magnetic moment is estimated to be $8.2\mu_B$. This value is almost same as the value of $9\mu_B$ expected from the gJ of Tb^{+3}. Furthermore, the structural phase transition from cubic to trigonal occurs at $T_N=14.2$ K, implying that the orbital angular momentum strongly couples with the spins through the spin-orbit coupling.[7] This fact suggests that a quadrupolar moment also plays an important role in addition to a magnetic moment in this system. Actually, we pointed out the importance of the quadrupolar moment and the mediated interactions in a separate paper.[8]

Here, we review the electric structure of rare-earth monopnictides.[10–12] Most of them are semimetallic compounds with an extremely low carrier concentration. The band calculation indicates that the bottom of the conduction band, originated mainly by $5d$ (R), is at each X point,

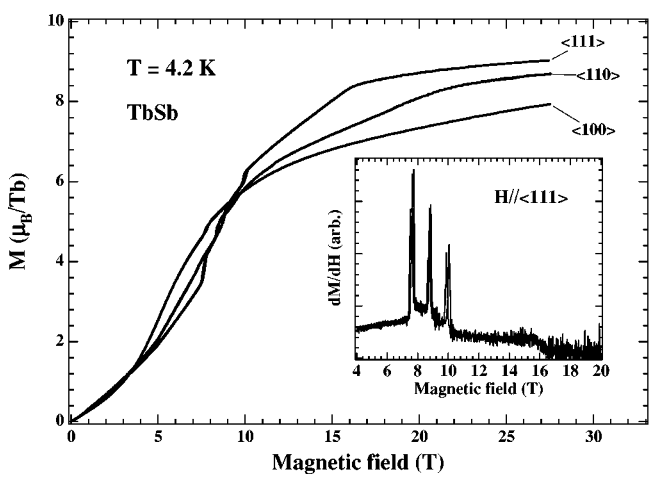

FIG. 1. Magnetization curves of TbSb for $H//\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$. Inset shows the differential magnetization dM/dH for $H//\langle 111\rangle$.

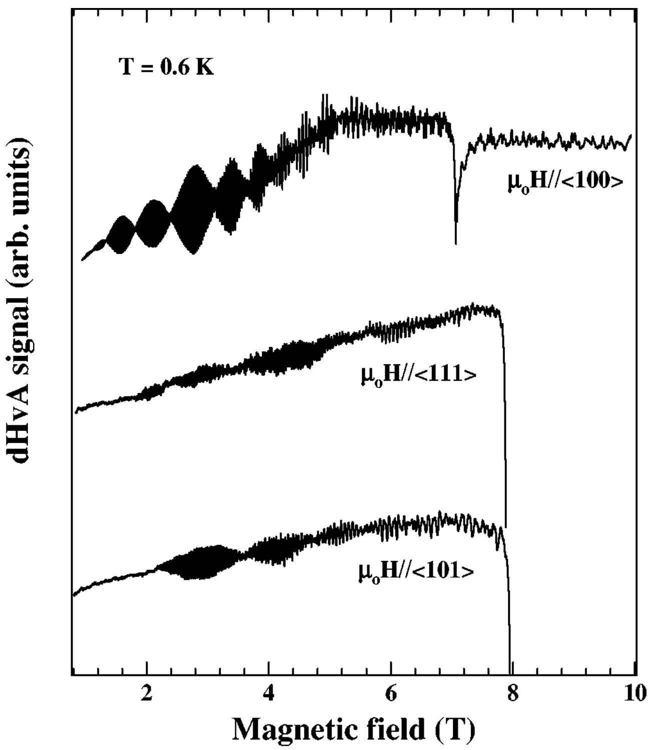

FIG. 2. The dHvA oscillations for $H//\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$.

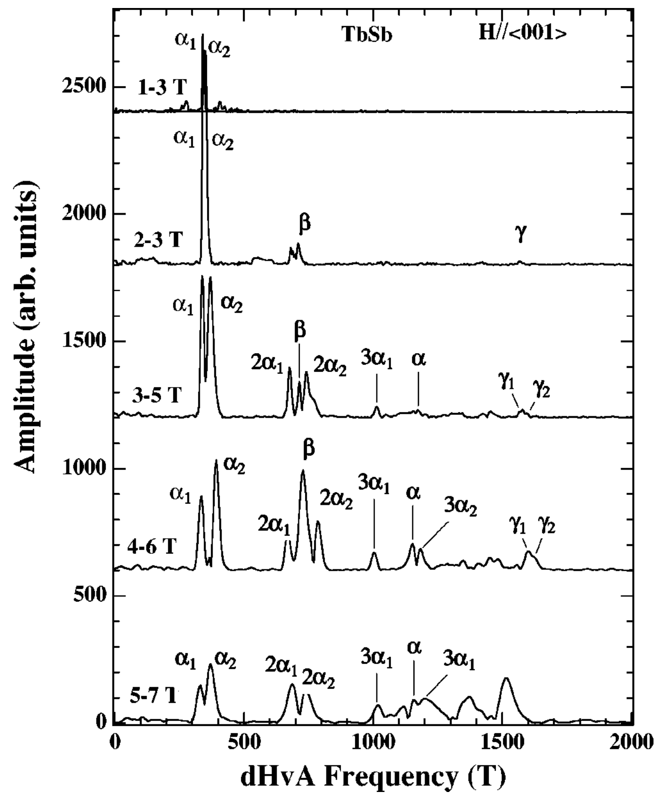

FIG. 3. The field dependence of the corresponding FFT spectrum for $H//\langle 100\rangle$ below H_m.

slightly overlapping with the top of the valence band originated mainly by np (X_p), where n denotes an integer.[12] The FS of reference material LaSb has been investigated deeply and intensively so far. The FS of LaSb consists of twofold ellipsoidal electron FS's α at the X points and twofold spherical hole FS's β and twofold octahedral hole FS's γ at the Γ point. Here every twofold FS is degenerate for up and down spins. In a ferromagnetic metal the spin-up and spin-down FS's are separated in energy by the exchange splitting between localized $4f$ electrons and conduction ones.[13] This indicates that the spin splitting of FS can be observed in high magnetic field where all magnetic spins are aligned by applied magnetic fields. By analyzing the spin splitting of FS and induced magnetization, we can estimate the interaction energy of the exchange if spin splitting FS can be observed in the field induced ferromagnetic phase, as will be described in detail later. The dHvA effect is a powerful tool to study the conduction electrons. It provides a very useful and important piece of information to understand the FS property. On the other hand, the magnetization measurement provides information about the magnetic property, mainly originated from $4f$-electron state of Tb ions. The purpose of this study is to investigate the interplay between localized $4f$ electrons and conduction ones based on the results of both the measurements. As mentioned above, the interplay plays a crucial role in this system. However, it is difficult and exceptional to obtain a clear spin splitting and its quantitative analysis accurately because both the high-quality single crystals and experimental conditions, i.e., at low temperatures and in high magnetic fields, are inevitably essential. Furthermore, the shape of the magnetization curve is important as well to observe the spin splitting as mentioned in the main text.

In this paper, we will report the FS's and magnetic properties of TbSb by means of the dHvA and high-field magnetization measurements, respectively. We will demonstrate clear dHvA signals and spin splitting of FS in TbSb, and also give quantitative discussion of the exchange energy between localized $4f$ electrons and conduction ones. The preliminary report has been published in Ref. 14.

II. EXPERIMENT

The single crystalline TbSb sample was prepared by Bridgeman method in a closed tungsten crucible. The Magnetization (M) measurements were performed with a standard pick-up coil system up to 30 T by using the pulsed magnetic field. The samples were shaped into thin plates to avoid the eddy current effect due to the pulsed magnetic field. The detailed magnetization in low fields was measured by a commercial superconducting quantum interference device magnetometer (Cryomagnetics). The dHvA measurements were performed by a standard field modulation technique using a ^{3}He cryostat at temperatures down to 0.5 K and a superconducting magnet in fields up to 8 T and a hybrid magnet in fields up to 23 T at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

III. EXPERIMENTAL RESULTS

Figure 1 shows the magnetization curve M-H of TbSb for $H//\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ at 4.2 K. The low-field region

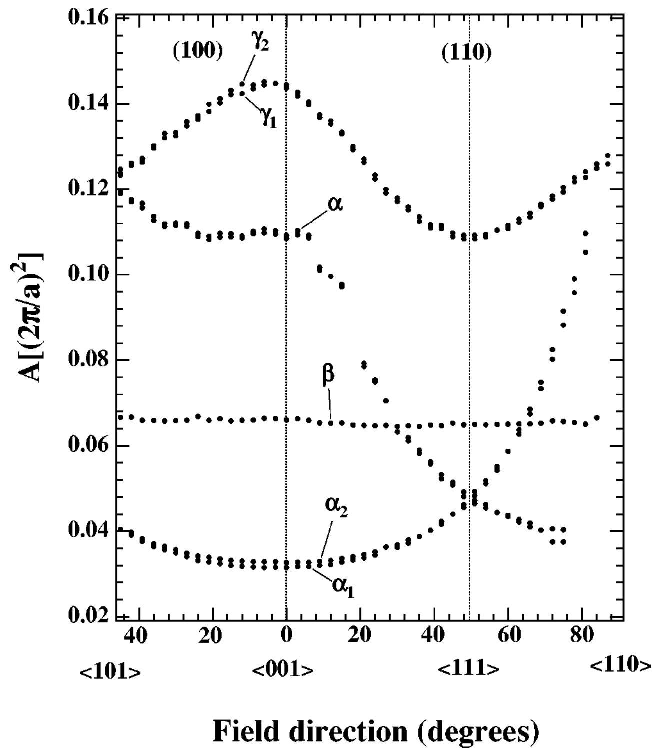

FIG. 4. The angular dependence of the extremal cross-section area of FS in the AF phase.

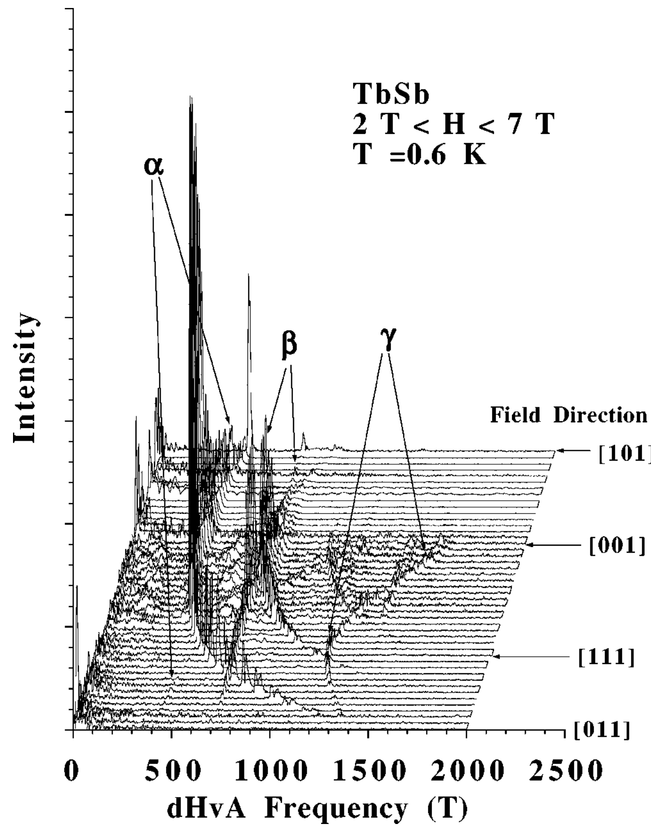

FIG. 5. The FFT spectrum for the obtained dHvA oscillations in the AF phase.

below 4 T, M-H curve shows a small magnetic anisotropy. A sharp one-step metamagnetic transition is found below T_N for $H//\langle 100\rangle$, $\langle 110\rangle$. This result is in good agreement with the previous result.[15,16]

The sharp three-step metamagnetic transition for $H//\langle 111\rangle$ at 8, 9, 10 T is also reported here. It is noted that only a one-step transition was observed in the previous measurement.[15,16] The inset of Fig. 1 shows the differential magnetization dM/dH for $H//\langle 111\rangle$. A three-step transition for $H//\langle 111\rangle$ is recognized distinctly. All metamagnetic transitions are accompanied by a slight hysteresis indicating the first-order nature. In the low-field region, a slight convex M-H curvature is observed, whereas in the high-field region a slight concave one is observed for three principal axes. The magnetization is almost saturated in high magnetic fields of 30 T with a value of $9.0\mu_B$/Tb. This value is very close to the Tb^{+3} free-ion one, i.e., $gJ=9.0\mu_B$/Tb. The observed anisotropy of magnetization in high magnetic fields is in order of $M^{\langle 111\rangle}>M^{\langle 011\rangle}>M^{\langle 001\rangle}$ reflecting the ground-state split by CEF effect, that is, $\Gamma_1-\Gamma_4$ states as already pointed out by Cooper *et al.*[15]

Figure 2 shows the typical dHvA oscillations of TbSb measured at 0.6 K for the field along $\langle 100\rangle$, $\langle 101\rangle$, and $\langle 111\rangle$. The beats are observed in the dHvA oscillations, which comes from spin-splitting of the FS. Figure 3 shows the field dependence of the corresponding fast Fourier transform (FFT) spectrum for $H//\langle 001\rangle$ below H_m. The angular dependence of the extremal cross-section areas of the FS A_{ext} in the AF phase is shown in Fig. 4. Here we use the unit of $(2\pi/a)^2$ for the area A_{ext}. Most of the obtained dHvA branches are similar to those of the reference material LaSb. We determined all observed branches as indicated by greek labels in Fig. 4, referring to the well-established FS of LaSb; twofold ellipsoidal electron FS's α at the X point and twofold spherical hole FS's β and twofold octahedral hole FS's γ at the Γ point.[9,11,12] It is noted that a distinct spin splitting of FS was observed in α, γ branches. Figure 5 shows the FFT spectrum for the obtained dHvA oscillations in the AF phase. Here the FFT procedure has been performed in the field range from 2 T to 7 T. Figure 6 shows the field dependence of the FFT spectrum along the $\langle 100\rangle$ axis at 1.5 K. It is noted that a distinct spin splitting of FS was observed also in β branch, especially in the fields above the metamagnetic transition. The width of spin-splitting observed in α and β branches increases with increasing the field. The cyclotron mass m_c^* of each branch along the $\langle 100\rangle$ axis was determined by using the conventional method, i.e., by fitting the observed temperature dependence of the amplitude to the Lifshitz-Kosevich formula.[17] The determined results are summarized in Table I. The masses in the range from $0.180m_0$ to $0.365m_0$ are almost same as those of LaSb.[11,12,18] There is no remarkable mass enhancement in any of the obtained FS's in TbSb. Figure 7 shows the field dependence of the dHvA frequency F of α and β branches along the $\langle 100\rangle$ axis at 1.5 K. It is noted that a distinct spin-splitting of FS was observed also in γ branch, especially in the fields above the metamagnetic transition. The mean of the spin-up F and spin-down one exhibits a pronounced field dependence, indicated by dotted lines in Fig. 7. Furthermore, the behaviors

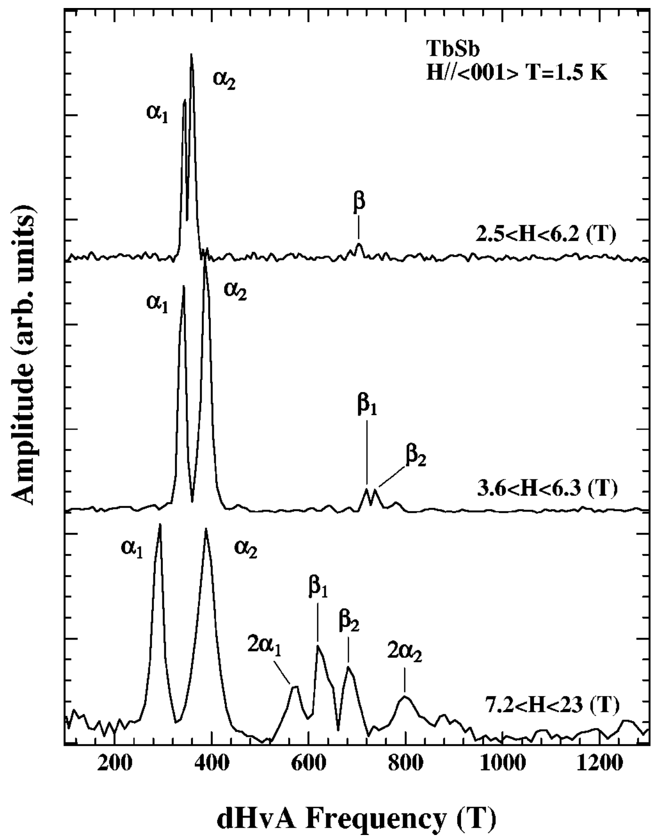

FIG. 6. The field dependence of the corresponding FFT spectrum for $H//\langle 100\rangle$ across H_m.

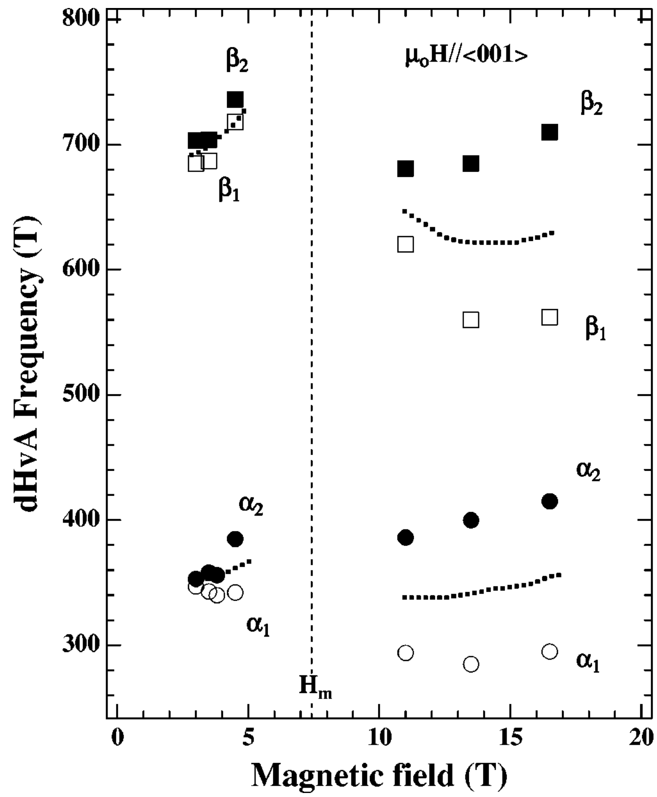

FIG. 7. The field dependence of the dHvA frequency F of α and β branches along the $\langle 100\rangle$ axis.

change across the metamagnetic transition. We will discuss this below.

IV. DISCUSSIONS

As a beginning we would like to discuss the magnetic property, especially CEF effect in TbSb. The $4f$-level scheme of Tb^{3+} split by CEF effect in TbSb was proposed by previous reports such as the magnetic susceptibility, specific heat, inelastic neutron scattering, and ultrasonic measurements as shown in Fig. 8.[3–6,8] It is noted that an energy splitting Δ between the ground-state Γ_1 singlet and Γ_4 triplet is rather small compared to other singlet-ground-state compounds such as PrSb, 73 K,[19] and TmSb, 25 K.[20] It indicates that the excited state can mix into the ground state easily by external magnetic fields in TbSb. By utilizing this $4f$-level scheme some important physical parameters such as Tb-Tb effective exchange interaction and quadrupolar interactions were estimated. These values will be discussed in detail later.

Next we will discuss briefly the M-H curves of TbSb. The high-field M-H curve, especially for $H//\langle 111\rangle$ exhibits the unexpected three-step metamagnetic transition. We would

TABLE I. The effective mass of each branch along principal axes in TbSb.

Branch	Effective mass (m_0) $\langle 100\rangle$	$\langle 110\rangle$	$\langle 111\rangle$
α_1	0.224	0.243	0.295
α_2	0.213		0.247
β_1	0.207	0.180	0.202
β_2			
γ_1	0.317		0.393
γ_2	0.257		0.365

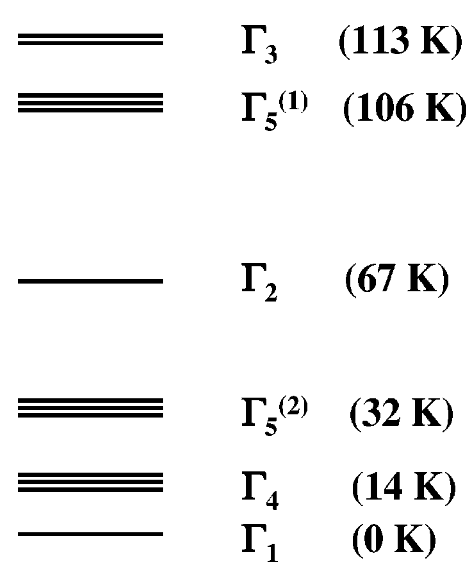

FIG. 8. The $4f$-level scheme model of Tb^{3+} in TbSb deduced from the previous reports (Refs. 3–5).

TABLE II. The estimated exchange interaction between $4f$ electrons and conduction electrons in TbSb, combined with that in TmSb, Pr. The magnetic, quadrupolar interactions and CEF splitting between the ground state and first excited state are also listed.

	$I_{d\text{-}f}$ (meV)	$I_{p\text{-}f}$ (meV)	J_1 (meV)	J_2 (meV)	$g_{\Gamma 3}$ (mK)	$g_{\Gamma 5}$ (mK)	Δ (K)
TbSb	34	10	4[a]	92[a]	33[a]	30[a]	14[b]
TmSb	55[c]	84[c]					25[d]
Pr	95[e]						95[e]

[a]Reference 8.
[b]References 3–6.
[c]Reference 25.
[d]Reference 20.
[e]Reference 23.

like to put special emphasis on this observation. The magnetization value reaches $4.5\mu_B$/Tb at the first transition field, then $5.0\mu_B$/Tb at the second one and $6.0\mu_B$/Tb at the third one, for $H//\langle 111\rangle$, e.g., easy axis at 4.2 K. At the first transition field the magnetization value is precisely 1/2 of the saturation value (M_0), probably indicating that HoP-type intermediate ferrimagnetic spin structure is realized in magnetic fields. The ratio of the magnetic moment parallel and perpendicular to the $\langle 111\rangle$ axis is 1:1.[22] This intermediate ferromagnetic phase is expected to appear when the quadrupolar interactions are dominant in the system as seen in HoP and DySb[21,22] because the direction of the magnetic moments is restricted by the orbital state of rare-earth ions. For the more detailed discussions and possible magnetic structure in magnetic field, refer to our separate paper.[8]

Next we will discuss the FS property of TbSb. The obtained angular dependence of the dHvA frequencies indicates that the topology of FS is almost same as that of LaSb's, compared to LaSb except for the spin splitting of FS's in α and β branches.[9–12,18] This fact reveals that the $4f$ electrons of Tb are well localized in TbSb. In α and β branches, a clear spin splitting of FS's was observed in the field dependence of the dHvA frequencies. The spin splitting of these branches is ascribed to the exchange interaction between $4f$ electrons of Tb and conduction electrons. The exchange energy may be expressed by the Heisenberg Hamiltonian as follows:[23,24]

$$\mathcal{H}_{ex}=-(g-1)I_{ex}\sum_{R}\ \sigma(\mathbf{R})\cdot J(\mathbf{R}), \tag{1}$$

where $\sigma(\mathbf{R})$ is the itinerant spin density at $\mathbf{R}$ and $J(\mathbf{R})$ is the angular momentum of the $4f$ electrons at $\mathbf{R}$. g is Lande's g factor. The central parameter I_{ex} is an effective exchange integral (interaction) between the conduction (s, p, d) electrons and the $4f$ electrons. In the induced ferromagnetic state, the energy of Bloch electrons with spins antiparallel to the localized spin magnetization is raised by the molecular field. The calculation for the perturbation of a cross-sectional area of FS (A_{ext}) caused by the exchange splitting yields the following formula:

$$\Delta F=|F_{up}(H)-F_{down}(H)|$$
$$=-\frac{g-1}{g\mu_B}\frac{m_c^*}{m_0}I_{ex}A_{ext}\left(M-\frac{\partial M}{\partial B}B\right), \tag{2}$$

where the Onsager relation

$$F=\frac{\hbar c}{2\pi e}A_{ext} \tag{3}$$

was used. m_0 denotes the bare cyclotron mass. The induced change of a dHvA frequency is thus proportional to the product of the cyclotron mass ratio (m_c^*/m_0), the effective exchange interaction I_{ex}, and the magnetization $(M-\partial M/\partial BB)$. As one can see, if a magnetization curve exhibits the almost linear dependence with respect to the external field, neither the spin splitting nor field dependence of FS are not observed. Based on the above discussion by Wulff *et al.*,[23] we can estimate the exchange interaction energy I_{ex}. For the simplicity, the same cyclotron effective mass for different spin states is assumed here. The obtained values are summarized in Table II, combined with those of the other compound TmSb and Pr.[25,25] The I_{ex} determined by α branch involves onsite d-f exchange interactions, whereas that of the β branch involves the intersite p-f exchange interactions. Since a clear spin splitting of the FS in γ branch was not observed above H_m, E_{ex} for γ branch was not estimated in the present study. The other important physical values in TbSb are also summarized in Table II, determined by other groups and our preceding report.[3,4,6,8,19,22–24] It should be noted that they are similar in magnitude to one another. In other words, several competing interactions and physical values in energy are present at low temperatures in this system. This potentially leads to the situation that external variables such as pressure and magnetic field can cause a wide variety of physical phenomena. In fact, it seems that the observed three-step metamagnetic transition in the present M-H curve for $H/\langle 111\rangle$ reflects the complicated spin structure induced by magnetic fields.

Finally, we will comment on the field dependence of obtained dHvA frequency. Unfortunately the dHvA effect does not provide us the true frequency $F(B)$ in a magnetic system with a strongly field dependent Fermi surface. The obtained momentary frequency F_m corresponds to the quantity

$(H/B)^2(dB/dH)[F(B)-B\partial F/\partial B]$.[26,27] We are not concerned here with the field dependence of dHvA Frequency F. However, it is apparent that the mean of the up-spin F and down-spin one is changed largely across the metamagnetic transition point. At present it is difficult to conclude the origin. We suggest it to be ascribed to a change of the spin structure across the transition, i.e., a change of the magnetic Brillouin zone from the following two reasons.

(1) The magnetization almost saturates above the metamagnetic transition.

(2) TbSb can be classified into the well-localized $4f$-electron system above the metamagnetic transition.

This picture of field dependence of dHvA frequency is seen in $NdIn_3$ reported by Umehara *et al.*[28–30] The determination of the spin structure of TbSb in magnetic field and determination of the topology of FS above H_m provide us valuable and important information to clarify a change of FS across the H_m.

V. CONCLUDING REMARKS

In this paper, we have performed the dHvA and high-field magnetization measurements on rare-earth monopnictide TbSb. We observed the clear dHvA oscillation and determined the topology of the FS. The shape of FS is quite similar to that of LaSb, indicating that TbSb is a well-localized $4f$-electron system. The cyclotron mass is in the range from $0.180m_0$ to $0.365m_0$, which is almost same as that of LaSb. That is to say, no mass enhancement occurs. We estimated the exchange energy between the localized $4f$ electrons and conduction ones from the observed spin splitting of FS's in TbSb. This value is comparable to the other important values such as magnetic exchange interaction, quadrupolar one, and the first excited energy of CEF. The close degrees of them in energy are considered to cause fascinating and exotic physical phenomena in rare-earth monopnictides in external physical variables.

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