Magnetic Properties of Single-Crystal TmNi

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Single-Crystal TmNi samples were grown by use of a metallic crucible. The temperature dependence of specific heat was measured in the temperature range from 1.4 to 80 K by the adiabatic method and two transitions were observed at 2.7 and 3.8 K. In addition, the Schottky-type specific heat was observed and it was discussed on the basis of energy level splitting due to crystalline electronic field effect. The magnetization curves were measured in a field up to 5 T at various temperatures for principal axes. We proposed the magnetic structure in the lower temperature region. The magnetic susceptibilities were measured in the temperature range from 5.0 to 300 K for principal axes, and the average value of the effective magnetic moment for principal axes was estimated at $8.9 \times 10^{-29} \text{ Wb} \cdot \text{m} / \text{Tm}^{3+}$, which is in good agreement with the Tm^{3+} free ion value.

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I. Introduction

It has been reported that the intermetallic compounds between heavy rare-earth and nickel $R\text{Ni}$ crystallize into the orthorhombic FeB-type structure (space group Pnma), where R corresponds to heavy rare-earth from Dy to Lu and Y. The magnetic structures of these $R\text{Ni}$ (R : heavy rare-earth) series were reported as the canted ferromagnetic type in an ordered state except for Yb, Lu and Y; YbNi has canted antiferromagnetic moments. LuNi and YNi are nonmagnetic.⁽¹⁾⁻⁽³⁾

TmNi is one of the $R\text{Ni}$ series and has the orthorhombic FeB-type crystal structure and the canted ferromagnetic moment as mentioned above. Walline and Wallece reported that TmNi is ferromagnet with the Curie temperature 8 K.⁽¹⁾ They also reported the derivation from the Curie Weiss law below 80 K for the magnetic susceptibility, which suggests that the crystalline electric field (CEF) effect plays an important role in this material. Abrahams *et al.* reported that TmNi orders ferromagnetic below 4 K (T_C).⁽²⁾ Gignoux *et al.* studied the magnetic structure in TmNi by means of the neutron diffraction measurement for powder samples. They proposed the model that the ferromagnetic component is parallel to c -axis and the antiferromagnetic component is parallel to a -axis, and the canted net moments lie in ac -plane. Also the observed Curie temperature was 7 K and the canted angle was 52 degrees from the principal axes. They also calculated the energy scheme of Tm^{3+} in TmNi by the CEF effect using the point charge model.⁽³⁾

According to these reports with the different magnetic transition temperatures, it is expected that there are plural phase transitions for TmNi. In order to make it clear, we studied the thermomagnetic properties for TmNi using single crystals and specific heat using poly-

crystals. In this paper, we will report the results of these experiments. Furthermore, we will report the comparison our results with the energy scheme by Gignoux *et al.*⁽³⁾ and propose the magnetic structure corresponding two transitions for TmNi.

II. Experimental

Polycrystalline samples of TmNi were prepared by arc melting under a high purity argon gas atmosphere. The purity of thulium and nickel elements are 99.9% and 99.99%, respectively. The mother crystals were examined by means of X-ray powder method and confirmed to be single phase of orthorhombic FeB-type structure (space group Pnma) as shown in Fig. 1.⁽⁴⁾ According to our X-ray diffraction experiments. We determined the lattice parameters for the a , b and c -axes to be $6.96 \times 10^{-1} \text{ nm}$, $4.10 \times 10^{-1} \text{ nm}$, $5.40 \times 10^{-1} \text{ nm}$, respectively. This structure can be built from trigonal prisms where the corners are occupied by rare-earth atoms and the center by the

Fig. 1 Crystal structure of TmNi compound. It is the orthorhombic FeB-type (space group Pnma). The Tm site is shown by the black circle, and the Ni site is white circle.

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nickel atom. Single crystals were grown by the Bridgman method with a molybdenum crucible. The molybdenum crucible was filled with about 1.3×10^4 Pa high purity argon gas. Crystallographic directions were determined by the back Laue camera method. The samples were cut along each principal axis.

The specific heat of TmNi was measured in the temperature range from 1.4 to 80 K by the adiabatic method. The same experiment was done for LuNi to estimate the phonon and the electronic contributions and to derive the magnetic part. The LuNi is nonmagnetic and crystallizes in the orthorhombic FeB type, which is the same with TmNi.

The magnetization curves were measured by means of the SQUID magnetometer at various temperatures in the range from 2.0 to 20 K in a magnetic field up to 5 T. The AC magnetic susceptibility measurements were also performed with frequency 220 Hz in the temperature range from 1.9 to 8.0 K and the DC magnetic susceptibilities at field 0.1 T from 5.0 to 300 K.

III. Results

Figure 2 shows the temperature dependence of specific heat in the temperature range from 1.4 to 80 K for polycrystalline TmNi and LuNi samples. For TmNi, we observed two anomalies at 2.7 and 3.8 K. It is considered that the λ type anomaly at 3.8 K corresponds to Curie temperature T_C . The lower anomaly at 2.7 K will be discussed later. For LuNi, we obtained the electronic specific heat coefficient γ and Debye temperature Θ_D to be 2.3×10^{-3} J/mol·K⁻² and 207 K, respectively. We use the result of specific heat measurement for LuNi to estimate the contribution by phonon in ferromagnet TmNi, as discussed in the next chapter. Furthermore, we note that there is a large magnetic contribution above T_C in TmNi.

Figure 3 shows the temperature dependence of C/T in the temperature range from 1.4 to 5.0 K to make the phase transition clear. The transition at 3.8 K cor-

Fig. 2 Temperature dependence of the specific heat of TmNi and LuNi in the temperature range from 1.4 to 80 K. A transition corresponding to T_C was observed at 3.8 K for TmNi. The large magnetic contribution is seen above T_C .

Fig. 3 Temperature dependence of specific heat/temperature, C/T for polycrystalline TmNi. T_C was observed at 3.8 K and another anomaly T_R at 2.7 K.

Fig. 4 Temperature dependence of the reciprocal susceptibilities for a TmNi single crystal in magnetic field 0.1 T in the temperature range from 5.0 K to 300 K. Deduced effective moments for the principal axes are 8.7×10^{-29} , 8.9×10^{-29} and 8.9×10^{-29} Wb·m, respectively.

responds to the Curie temperature as mentioned above, and there is the another transition T_R at 2.7 K.

Figure 4 shows the temperature dependence of reciprocal susceptibilities along the principal axes in the temperature range from 5.0 to 300 K. We note that these are not parallel and not linear each other below 200 K in this figure. About the a -axis, the slope of the reciprocal susceptibility $1/\chi$ below 200 K is larger than that above 200 K. We consider that the CEF effect is a cause for the change of the slope. The reciprocal susceptibilities are in good agreement with the Curie-Weiss law above 200 K. The deduced effective moments for the a , b and c -axes are 8.7×10^{-29} Wb·m, 8.9×10^{-29} Wb·m and 8.9×10^{-29} Wb·m, respectively, which are in good agreement with the Tm^{3+} free ion value 8.81×10^{-29} Wb·m. These results indicate that the Ni atoms in the TmNi compound have no magnetic moment as described in the previous reports and Tm-ions are in the trivalent state.⁽¹⁾⁻⁽³⁾ These slopes in the high temperature region define the paramagnetic Curie temperatures for the a , b and c -axes to be -18 , -6.1 and 8.3 K, respectively.

Fig. 5 Temperature dependence of AC magnetic susceptibilities for c -axis of a single-crystalline TmNi in the temperature range from 1.8 to 8.0 K. Two transitions were observed. The transition at 3.8 K corresponds with T_C . Another anomaly at 2.7 K was also observed in the specific heat measurement.

Fig. 6 Initial magnetization curves of a TmNi single crystal along the principal axes at 2.0 K in the field up to 5.0 T. The solid line is the guide for eyes.

Figure 5 shows the temperature dependence of AC magnetic susceptibility for the c -axis. Also two transitions were observed at 2.7 and 3.8 K. Along the a and b -axes, two transitions were observed at the temperatures corresponding to those of the c -axis. These transition temperatures correspond to T_R (2.7 K) and T_C (3.8 K). The result supports that of specific heat measurement.

Figure 6 shows the initial magnetization curves of TmNi along the principal axes at 2.0 K in the magnetic field up to 5.0 T. The magnetization curve along the a -axis shows the spin flop at 0.11 T as shown by the solid line in the figure. A small ferromagnetic component was observed along the b -axis. Along the c -axis, the ferromagnetic magnetization curve was observed.

Figure 7(a) shows the temperature dependence of the detailed magnetization curves along the a -axis at various temperature in the field up to 1.0 T. The spin flop was observed; in brief, there is an antiferromagnetic component below T_C .

Identically, Figs. 7(b) and (c) show along the b -axis up to 0.20 T and the c -axis up to 5.0 T at various tempera-

Fig. 7 (a) Initial magnetization curves of a TmNi single crystal along a -axis at 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, 3.50, 3.75 and 4.00 K in the field up to 1.0 T. Around 0.1 T, a spin flop was observed below 2.7 K. (b) Initial magnetization curves along b -axis at 2.00, 2.40, 2.80, 3.20, 3.60 and 4.00 K in field range 0.20 T. A small amount of ferromagnetic component was observed below 2.8 K. (c) Initial magnetization curves along c -axis at 2.00, 2.40, 2.80, 3.20, 3.60, 4.00 K, 10.0 and 20.0 K. Ferromagnetic component was observed below T_C .

tures, respectively. Along the b -axis, a small ferromagnetic component was observed below 2.8 K, and the magnetization curves show the paramagnetic behavior above 2.8 K. Along the c -axis, the magnetization curves indicate a simple ferromagnetic one.

IV. Discussion

1. Temperature dependence of magnetic structure in TmNi

We discuss the magnetization curves and propose the magnetic structure for intermetallic compound TmNi.

Figures 7(a) and (c) show the magnetization curves for the a and c -axes in the temperature range from 2.0 to 20 K. Below Curie temperature 3.8 K, antiferromagnetic component appears along a -axis, and ferromagnetic component along c -axis. Furthermore, below 2.7 K, the magnetization curve along the b -axis shows a small amount of ferromagnetic component as shown in Fig. 7(b). The ferromagnetic component vanishes above 2.7 K. These results indicate the existence of two magnetic phases. Two transitions at 2.7 and 3.8 K were also observed in the specific heat and AC magnetic susceptibilities measurements. The vanishing of the ferromagnetic component along b -axis indicates that the canted moment lies in the ac -plane and the resultant ferromagnetic moment is along the c -axis in temperature range from 2.7 to 3.8 K as shown in Fig. 8(a). We will discuss the ferromagnetic

component which appears below 2.7 K along the b -axis.

Isikawa *et al.* studied the magnetic properties of the HoNi compound.⁽⁵⁾ They reported that its magnetic structure is the canted ferromagnetic type and it has two magnetic transitions $T^*=13$ K and $T_C=35$ K. Furthermore they reported that an antiferromagnetic component appears along the c -axis and a ferromagnetic component along the a -axis below T_C , and along the b -axis a small amount of ferromagnetic component appears below T^* . It indicates that the canted moment rotates around the c -axis with keeping a canted angle, also the paramagnetic component appears between T^* and T_C . Between T^* and T_C , the canted ferromagnetic moment lies in the ac -plane and resultant ferromagnetic moment along the a -axis. According to the comparison of magnetization curves for TmNi and HoNi, it is concluded that the magnetic moments for TmNi rotate around the a -axis while keeping a canted angle 2θ below 2.7 K as shown in Fig. 8(b).

2. Schottky type specific heat and energy level

We assume that the specific heat of magnetic compound TmNi can be divided into three parts, that is, electronic contribution $C_{el.}$, phonon contribution $C_{phon.}$ and magnetic contribution $C_{mag.}$ as follows:

$$C = C_{el.} + C_{phon.} + C_{mag.} \quad (1)$$

Using the measurement results of specific heat for LuNi and well-known relation (2)⁽⁶⁾, we estimate the non-magnetic part of specific heat for TmNi, as shown in Fig. 9. Electronic contribution for specific heat is negligibly small in the figure. Phonon contribution for specific heat is derived in reference to the observed specific heat for nonmagnetic LuNi having the same structure as TmNi using eq. (2). Therefore, we can refer LuNi for the phonon contribution of specific heat for TmNi.

$$\Theta_D^{TmNi} = \sqrt{M^{LuNi}/M^{TmNi}} \cdot \Theta_D^{LuNi}, \quad (2)$$

where Θ_D^{TmNi} and Θ_D^{LuNi} are the Debye temperatures of TmNi and LuNi, respectively. M^{TmNi} and M^{LuNi} are the masses of TmNi and LuNi, respectively. Figure 9 shows the magnetic contribution for the specific heat derived from our estimations. The Schottky type specific heat due to energy level splitting could be observed above Curie temperature T_C . This fact indicates that the CEF effect plays an important role in TmNi.

Figure 10 shows the temperature dependence of magnetic entropy, which is $R \ln 2$ at T_C . The ground state of Tm^{3+} in TmNi is a doublet. The Schottky type specific heat is expressed by following eq. (3) for multi energy levels.⁽⁷⁾

$$C_{Sch.} = Nk_B \frac{\sum (\Delta_r/T)^2 (g_r/g_0) \exp(\Delta_r/T)}{\{1 + \sum (g_r/g_0) \exp(\Delta_r/T)\}^2}, \quad (3)$$

where N is the Avogadro's constant, k_B the Boltzmann constant, g_r the number of degeneracy in excited state, g_0 the number of degeneracy in ground state and Δ_r the energy gap between the ground and r -th excited one in Kelvin unit. Total angular momentum quantum number

Fig. 8 (a) Magnetic structure of TmNi between 2.7 K (T_R) and 3.8 K (T_C). The canted net, $\{1/2(m_1 + m_2)\}$, moment lies in ac -plane. (b) Magnetic structure of TmNi below 2.7 K (T_R). It is determined by the magnetization curves for the principal axes. Deduced canted angle from the principal axis θ is 49 degrees.

Fig. 9 Temperature dependence of specific heat for TmNi, phonon contribution and magnetic contribution in the temperature range from 1.4 to 80 K.

Fig. 10 Temperature dependence of magnetic entropy in the temperature range from 1.4 to 80 K. At T_R , the value of entropy is $R \ln 2$, indicating that the ground state is a doublet.

J of Tm^{3+} is 6, the entropy should release $R \ln(13)$ originally. Figure 10 shows that 90% of $R \ln 13$ is released at 80 K.

Figure 11 shows the energy level scheme of Tm^{3+} in TmNi by Gignoux *et al.* The splitting width is about 250 K. The ground state is doublet. The solid line indicates the calculated Schottky-type specific heat using eq. (3) with the energy level scheme of Gignoux *et al.* in Fig. 12. This is in good agreement with our observation results in the figure.

We conclude that between T_R and T_C , the canted ferromagnetic moment lies in the ac -plane and the resultant ferromagnetic moment is along the c -axis and below $T_R = 2.7$ K, the magnetic moments for TmNi rotate around the a -axis while keeping the canted angle at 2.7 K, the magnetic moments for TmNi rotate around the a -axis while keeping a canted angle 2θ . The magnetic

Fig. 11 Energy scheme of Tm^{3+} in TmNi crystal. It was calculated by Gignoux *et al.* The ground state is a doublet and the width is about 250 K.

Fig. 12 Temperature dependence of specific heat of magnetic contribution for TmNi. The solid line indicates the Schottky type specific heat from the calculated energy scheme by Gignoux *et al.*

specific heat is explained by the Schottky-type one.

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