High-field magnetization of TmB$_4$

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Abstract. The magnetization $M$ of single crystalline TmB$_4$ has been investigated in high magnetic fields up to 54 T and shows considerably anisotropic behavior. In the ordered antiferromagnetic state, the $M$ for $B \parallel [001]$ reaches the saturation magnetization $M_s$ at about 4 T accompanying with plateaux at $1/8 M_s$ and $1/2 M_s$. On the other hand, for $B \parallel [100]$ and [110], the $1/2 M_s$ state and the saturation of $M$ were observed at much higher field above 30 T. The results are discussed in relation to the effects of magnetic frustration and the crystalline electric field.

1. Introduction

Rare-earth tetraboride RB$_4$ crystallizes in the tetragonal structure ($P4/mmb$). The network of magnetic R ions in the $c$ plane is characterized by orthogonal dimers that is equivalent to the Shastry-Sutherland lattice (SSL) [1] (figure 1(a)). In RB$_4$, the bond length between the nearest-neighbor R atoms, $d_{NN}$, is very close to that of the 2nd-neighbor, $d_{NNN}$, it can intuitively be expected that the corresponding magnetic interactions $J_1$ and $J_2$ are also close to each other. Then, there should be strong magnetic frustration, if $J_1$ is antiferromagnetic. Owing to this geometric feature, novel phenomena originating from the frustrated interaction between the R moments are expected. Indeed multiple phase transitions have been found in many of RB$_4$ compounds [2]. In ErB$_4$ [3], the magnetization process shows a plateau region at a half of the saturation magnetization $M_s$, where the competition of the Zeeman effect with a frustrating magnetic interaction was discussed as an origin of the $1/2 M_s$ state. Recent studies also revealed an important role of the geometrical quadrupolar frustration, as discussed for DyB$_4$ [4].

In TmB$_4$, successive antiferromagnetic transitions occur at 11.7 K ($T_{N1}$) and 10 K ($T_{N2}$) [2]. The magnetic susceptibility $\chi$ shows a strong anisotropy between $B \parallel c$ and $B \perp c$ in the paramagnetic temperature region, and $\chi_{cc}$ has a broad maximum. This behavior is quite similar to that of ErB$_4$. In order to have further insight into the magnetic properties of TmB$_4$ and to investigate how the magnetic anisotropy plays a role in the occurrence of the magnetization plateau, we have studied the magnetization process of a single crystalline sample at various temperatures in high magnetic fields up to 54 T.

2. Experimental

The single crystal of TmB$_4$ was grown by the floating-zone method. The high-field magnetization measurement was carried out by using a non-destructive pulse magnet. The magnetization was
3. Results and Discussion

Figure 2 shows representative results of magnetization $M$ curves along the three principal directions in the antiferromagnetic state. Considerably anisotropic behavior of $M$ is observed. The $M$ for $B \parallel [001]$ shows steep jumps at 1.9 T and 3.6 T, and reaches the saturation magnetization $M_s$ of 6.8 $\mu_B$/f.u. at about 4 T, where the obtained $M_s$ is close to the magnetic moment (7 $\mu_B$) of free Tm$^{3+}$ ions. The noticeable characteristic is that the $M$ exhibits plateaux at $1/2 M_s$ and also at $1/8 M_s$ only in the descending field process. This behavior well agrees with the result obtained in a steady field [5]. The magnetization in the (001) plane, on the other hand, is very hard and the saturation field is very high compared with that along the [001] axis. The $M$ along the [100] axis shows a steep increase above 30 T and reaches the saturation at around 42 T. The differential magnetization $dM/dB$ reveals an appearance of three characteristic increase of $M$, i.e., two sharp peaks at $B_{c1} = 32$ T and $B_{c2} = 33.2$ T and one broad peak at $B_{c3} = 38.5$ T, as shown by arrows in the lower panel of figure 2. The three-step increases of $M$ are also observed along the [110] direction with $B_{c1} = 34$ T, $B_{c2} = 35.5$ T and $B_{c3} = 52.2$ T. It should be noting that a stepwise behavior also appears at around $1/2 M_s$ along both [100] and [110] directions. One feature to be emphasized is that the $1/2 M_s$ state along the [110] direction is much stable than that along the [100] direction. This fact suggests an existence of anisotropy in the (001) plane.

The magnetization curves have also been investigated at higher temperatures. As for the [001] direction, the plateaux at $1/2 M_s$ and $1/8 M_s$ disappear above 8 K. Details of the magnetization behavior for $B \parallel [001]$ investigated in a steady field will be reported in a separate paper. Here, we present results on the high-field measurement along the [100] and [110] axes (figure 3). The stepwise behavior at $1/2 M_s$ becomes obscure with increasing temperature, and it is hard to recognize the $1/2 M_s$ state above $T_{N1}$ along both [100] and [110] directions. On the other hand, the steep increase above 30 T still survives even in the paramagnetic temperature range. A
Figure 3. Magnetization curves along the [100] and [110] axes at designated temperatures.

close look at the dM/dB reveals that, for both B || [100] and B || [110], the anomaly at Bc1 disappears above TN1, whereas the peak of dM/dB at Bc2 scarcely changes its position up to 20 K, although it broadens with increasing temperature. As for the peak at Bc3, a tiny trace also remains at 15 K along the [100] direction at almost same field position with that at 1.3 K.

In RB₄ series, the magnetic property of TmB₄ is qualitatively very similar to that of antiferromagnetic ErB₄ (TN = 15.4 K). In both compounds, the magnetic susceptibility shows a large anisotropy in the paramagnetic region: χ∥c is much larger than χ⊥c at low temperature, and χ⊥c has a broad maximum at around 30 K (ErB₄) and 80 K (TmB₄). Such behavior of χ is usually explained by a CEF effect. Magnetization of ErB₄ also exhibits a plateau at 1/2 Ms below TN for field applied both parallel and perpendicular to the [001] axis, where the transition field along the [100] axis is several times as large as that along the [001] axis. From the analysis of the magnetic susceptibility and the specific heat [3], in ErB₄, the doublet of |Jz⟩ = |±15/2⟩ has been suggested as the CEF ground state for the Kramers Er³⁺ ion (4f¹¹, J = 15/2) with the first and second excited doublet states which locate at about 20 K and 40 K above the ground state, respectively. In addition, the antiferromagnetic collinear structure has been reported for ErB₄ by the neutron scattering study with moments aligned parallel to the [001] direction [6]. These facts suggest that the moment in ErB₄ has a strong Ising type single-ion anisotropy at low temperature with the easy axis parallel to the [001] direction. In TmB₄, at present, we don’t have any knowledge on the magnetic structure in the ordered antiferromagnetic state. However, the very similar characteristics of the magnetic properties to that of ErB₄ strongly indicate that the Tm moment also has a strong Ising type single-ion anisotropy, leading to a collinear structure along the [001] axis. The preliminary study of the specific heat indicates that the magnetic entropy reaches Rln2 at TN1, which suggests a doublet state as the CEF ground state though it is a non-Kramers doublet for Tm³⁺ ion (4f¹², J = 6).

Supposing an antiferromagnetic collinear structure below TN2, one intuitive scenario may be proposed that the 1/2 Ms state observed for B || [001] has a ferrimagnetic structure with three of four moments pointing the field direction (↑↑↑↓), as illustrated in figure 1(b). Here, we assume that the direction of Tm moments is restricted along the [001] axis due to a strong single-ion anisotropy. In the model, the magnetic unit in zero field consists of two orthogonal dimers in the (001) plane, where the nearest-neighbor moments couple antiparallel to each other due to a
dominant antiferromagnetic interaction $J_1$. By applying field along the [001] direction, a \( \uparrow\uparrow\uparrow\downarrow \) arrangement should be stable before saturation arrangement \( \uparrow\uparrow\uparrow\uparrow \) due to a competition of the Zeeman effect with a magnetic interaction, if $J_2$ is also antiferromagnetic. However, as one can see, this simple model does not explain an appearance of the 1/8 $M_s$ state, which must have a long period modulation. This may suggest a significant role of a magnetic frustration attributed to the SSL formed by Tm$^{3+}$ ions in the (001) plane. A neutron scattering study is desired to further discuss the origin of the magnetization plateaux.

As for the magnetization process in the (001) plane, the situation seems to be rather complicated. Based on the CEF picture, the very small initial slope of $M$ is mainly because the ground state doublet has almost zero component in this direction. Then, the recovery of the magnetization at high field is attributed to a crossing or a reconstruction of CEF levels. A large CEF splitting in TmB$_4$ manifests existence of the steep increase of $M$ in the (001) plane even at 20 K, as shown in figure 2. The appearance of the three step feature of $M$ in the ordered state may be originated from a combined effect of the CEF and magnetic frustration. Besides this, as mentioned before, the anisotropic behavior is also clarified in the (001) plane as the large difference of $B_{c3}$ value between $B \parallel [100]$ and $B \parallel [110]$. Since the local symmetry of Tm site is characterized by a uniaxial twofold axis directed to the equivalent [110] axis, it is reasonably expected that the Tm moments feel such a perturbative field as an origin of the anisotropy in the (001) plane.

In summary, we have presented the magnetization process of TmB$_4$ in very high fields in the ordered state. By comparing the results with that of ErB$_4$, we have described the several features which must be characteristics of RB$_4$ compounds that possess a strong Ising type single-ion anisotropy along the [001] direction.

- Magnetization exhibits a plateau at the half of the saturation magnetization for both $B \parallel [001]$ and $B \perp [001]$.
- The transition field for $B \perp [001]$ is much larger than that for $B \parallel [001]$.
- In the (001) plane, the 1/2 $M_s$ state along the [110] direction is much stable compared with that along the [100] direction.

Besides these, other extra features have been found in the Tm compound: The 1/8 $M_s$ state along the [001] direction and the transition at $B_{c1}$ along the (001) plane. In order to give a quantitative description, we need further knowledge on several parameters, such as exchange constants and CEF coefficients and so on, which is left for the future subject.

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