Resonant magnetic x-ray diffraction study on the successive metamagnetic transitions of TbB$_4$ up to 30 T

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Abstract. We report the results of resonant magnetic x-ray diffraction experiments in pulsed high magnetic fields on TbB$_4$, which exhibits successive metamagnetic transitions between 16 and 28 T. The observed field, polarization, and scattering angle dependence of the diffracted intensity indicates that magnetic moments perpendicular to the magnetic field exist in the high-field plateau phases. This result is clearly inconsistent with normal fractional magnetization plateau phases that have magnetic moments only parallel or antiparallel to the field. In order to resolve this discrepancy, we propose magnetic structures consisting of Ising spins and XY spins. A possible mechanism that produces these novel magnetic structures is also discussed.

1. Introduction

Recently, the magnetic properties of rare-earth tetraborides RB$_4$, which crystallize in a tetragonal structure (space group: P4/mmbm), have been intensively investigated. In RB$_4$, the rare-earth ions form a network that is equivalent to a frustrated Shastry-Sutherland (SS) lattice, and thus several pieces of work have been carried out from the viewpoint of frustration, particularly that between rare-earth quadrupole moments [1, 2].

One of the most fascinating experimental results obtained in the study of the RB$_4$ family is the multistep magnetization curve observed for TbB$_4$ [3]. When a magnetic field parallel to the c-axis was applied, TbB$_4$ exhibited 9-fold successive metamagnetic transitions between 16 T and 28 T. The magnetization increased stepwise with increasing magnetic field, and magnetization plateaus were observed between the transition fields, as shown in Fig.1(b). Although similar multiple metamagnetic transitions are sometimes observed in the easy-axis magnetization of Ising magnets such as CeSb and PrCo$_2$Si$_2$ [4, 5], a qualitative difference exists between these magnets and TbB$_4$. The magnetic structures of the Ising magnets comprise a complicated sequence of up and down spins, and, basically, the metamagnetic transitions correspond to a reversal of the spins in some sections in the crystal. A neutron powder diffraction experiment at

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0 T, however, revealed that the magnetic moments of TbB$_4$ are confined to the basal $ab$-plane [6]. Hence, the magnetic moments should simply cant toward the $c$-axis with increasing magnetic field ($\parallel c$), and a simple linear curve is expected for the $c$-axis magnetization of TbB$_4$.

Magnetic structures in the high-field phases provide valuable information on the mechanism that stabilizes a number of magnetization plateaus in TbB$_4$. In the last five years, x-ray diffraction experiments under pulsed high magnetic field have been intensively developed at several places. Field-induced structural changes have been observed for many samples in magnetic fields over 30 T [7, 8, 9]. In order to examine the magnetic structures of TbB$_4$ under high magnetic fields, we utilized this technique with the aid of resonance enhancement to increase the small magnetic x-ray scattering cross section. In this paper, we report the recent results of resonant magnetic x-ray diffraction experiments on TbB$_4$ under pulsed high magnetic fields up to 30 T [10].

Here we briefly summarize the magnetic properties of TbB$_4$. The Tb ion has the large total angular momentum of $J=6$, and thus the Tb spin is approximated by a classical spin. Two transition points $T_{N1}=44$ K and $T_{N2}=24$ K were reported in susceptibility and resistivity measurements [11]. The magnetic structure between $T_{N1}$ and $T_{N2}$ is a non-collinear coplanar structure [6], as shown in Fig. 1(a). The magnetic moments are of XY-type and lie in the $ab$-plane. Additional in-plane anisotropy orients the moments parallel to the [110] and [1 ¯10] directions. The nearest- and next-nearest-neighbor interactions are antiferromagnetic and form a frustrated SS lattice. Below $T_{N2}$, the magnetic moments rotate by 23$^\circ$ about the $c$-axis alternately and the magnetic structure becomes an orthorhombic non-collinear structure.

2. Experimental

The resonant x-ray diffraction (RXD) experiments were carried out at BL22XU in SPring-8. The x-ray energy was tuned to the Tb $L_{III}$ absorption edge ($\approx 7.514$ keV). Magnetic fields up to 30 T were generated using a small pulsed magnet (20 mm in outer diameter and 24 mm in length). The magnet was a split-pair magnet, and the pulse duration was about 0.6 ms.
Figure 2. Field dependence of the peak intensity of magnetic reflections below $T_{N2}$. (a-c) (100) reflection; (a) without polarization analysis, (b) $\pi - \sigma'$ channel and (c) $\pi - \pi'$ channel. (d-f) (500) reflection; (d) without polarization analysis, (e) $\pi - \sigma'$ channel and (f) $\pi - \pi'$ channel. The magnetization curve is also shown in (a) and (d).

The magnet was attached to the first stage of a conventional closed-cycle refrigerator, while the sample was attached to the cold head (second stage) of the cryostat. The cryostat was mounted on a conventional diffractometer with a horizontal scattering plane, and we set the $c$-axis normal to the scattering plane. Single crystals of TbB$_4$ were grown by the floating zone method. The sample was a thick plate with dimensions of 1 mm x 1 mm x 0.5 mm with a polished (100) surface. Magnetic fields were applied parallel to the $c$-axis. The peak intensity of the (100) and (500) magnetic reflections was monitored as a function of magnetic field. We also separated diffracted x-rays into $\pi$-polarization (parallel to the scattering plane) and $\sigma$-polarization (normal to the scattering plane) using a PG (006) crystal analyzer and measured their intensities as a function of magnetic field. The polarization of incident x-rays was only $\pi$-polarization. A few tens of field scans were necessary to obtain satisfactory statistics. Details of the experimental setup are also found in Refs. [7] and [10].

3. Results and Discussion

The peak intensity of the (100) and (500) reflections below $T_{N2}$ exhibited a huge enhancement at the Tb $L_{III}$ main edge, indicating that the resonance is ascribed to the electric dipole (E1) transition. The diffraction intensity appeared below $T_{N1}$ and increased with decreasing temperature, indicating a magnetic origin of the diffraction intensity [10].

The field dependence of the peak intensity of the (100) and (500) reflections below $T_{N2}$ is shown in Fig. 2. The photon energy was tuned to the peak energy of the energy spectra. The intensity of the (100) reflection without polarization analysis (Fig. 2(a)) is constant up to 16 T and gradually decreases above 16 T as the field is increased. Consistency of the up-sweep and down-sweep data suggests that induction heating of the metallic TbB$_4$ is negligible. The data of the (500) reflection (Fig. 2(d)) also show a similar tendency, although an abrupt jump is observed at 16 T. This is probably due to the high sensitivity of such large-2$\theta$ reflections to the small structural change expected at 16 T.

An important finding in these data is that a considerable amount of intensity remains in the
magnetization plateau phases above 16 T. Furthermore, polarization analysis clearly indicated that the diffraction intensity of the (100) reflection is dominated by the \( \pi - \sigma' \) channel, as shown in Figs. 2(b) and 2(c). For the (500) reflection, although the data above 25 T are not available due to low intensity, we can reach the same conclusion for the diffraction intensity below 25 T.

The resonant x-ray scattering amplitude of rare-earth ions at the E1 transition is given by [12]

\[
f_{\text{res}} \propto \alpha_0(\omega) \hat{\epsilon}_i \cdot \hat{\epsilon}_i - i \alpha_1(\omega) (\hat{\epsilon}_i \times \hat{\epsilon}_i) \cdot \vec{m} + \alpha_2(\omega) \hat{\epsilon}_i \cdot O \hat{\epsilon}_i,
\]

where \( \vec{m} \) is the magnetic moment and \( \hat{\epsilon}_i \) and \( \hat{\epsilon}_i' \) are the polarization vectors of the incident and scattered x-rays, respectively. The symmetrical second-rank tensor \( O \) describes the anisotropy of the Tb 5d orbital caused by an anisotropic crystal environment or a quadrupole order and is represented by a linear combination of the five elements \( O_{xy}, O_{yz}, O_{zx}, O_{22}, \) and \( O_{20} \). The first term in Eq. (1) is the conventional anomalous scattering, which does not contribute to the forbidden reflection in this case, and the second term is the magnetic scattering. The last term corresponds to the anisotropy of the tensor of susceptibility (ATS) scattering.

The scattering amplitudes of magnetic and ATS components are listed in Table 1 for the geometry of the current experiments (c-axis \( \perp \) scattering plane), where \( \theta \) is the Bragg angle. The Bragg angles of the (100) and (500) reflections are 6.6° and 35.2°, respectively. The absence of the \( \pi - \pi' \) process for both high and low scattering-angle reflections signifies that \( m_z, O_{22} \), and \( O_{20} \) do not contribute to the \( (h00) \) reflections \( (h: \text{odd integer}) \). In addition, a RXD experiment on TbB\(_4\), which has a magnetic structure identical to that of TbB\(_4\) at 0 T, revealed that resonant intensity at \( (h00) \) reflections \( (h: \text{odd integer}) \) arises only from the magnetic moment \( m_y \) \((\propto \cos \theta)\) for this geometry[13, 14]. The similarity of the field dependence of the (100) and (500) reflections suggests that the \( \theta \) dependence of the diffraction intensities in the high-field phases and in the low-field phase is the same. We can thus conclude that \( m_y \) and/or \( O_{zx} \) give rise to the resonant intensity in the high-field phases. Quite recently, a neutron diffraction experiment on TbB\(_4\) under pulsed high magnetic fields succeeded and reported similar field dependence of the magnetic diffraction intensity of the (100) reflection [15]. Hence the pure \( O_{zx} \) order is excluded, and we can conclude that the major order parameter in the high-field phases is \( m_y \), that is, the magnetic moment perpendicular to the applied magnetic field.

This result is obviously inconsistent with ordinary magnetization plateau phases, in which the magnetic moments are parallel or antiparallel to the magnetic field. Usually, the coexistence of antiferromagnetic perpendicular components and ferromagnetic parallel components is indicative of a canted antiferromagnetic (CAF) structure. However, the direction of the moments in CAF structures is parallel to the vector sum of the internal and external fields. Hence, a slight increase of the external field always results in a small increase of the parallel component, and magnetization plateaus cannot be observed in CAF structures. Therefore, the perpendicular components and parallel components of the magnetic moments must spatially separate at different sites. We propose magnetic structures that consist of very hard XY-type magnetic moments and Ising-like magnetic moments for the plateau phases in TbB\(_4\). An example of the magnetic structure in the one-third plateau phase is depicted in Fig. 3(b).

### Table 1. Scattering amplitude of magnetic and ATS scattering components for the \( \pi\pi' \) and \( \pi\sigma' \) channels.

| \( m_x \) | \( m_y \) | \( m_z \) | \( O_{xy} \) | \( O_{yz} \) | \( O_{zx} \) | \( O_{22} \) | \( O_{20} \) |
|---|---|---|---|---|---|---|---|
| \( \pi\pi' \) | 0 | 0 | \( i \sin 2\theta \) | 0 | 0 | 0 | \(-1 \cos 2\theta / \sqrt{3} \) |
| \( \pi\sigma' \) | \( i \sin \theta \) | \(-i \cos \theta \) | 0 | 0 | \(-\sin \theta \cos \theta \) | 0 | 0 |
A possible interpretation for these novel magnetic structures is energy level crossing between low-lying multiplets. In Tb ions, the $J = 6$ ground-state is split into several multiplets owing to crystalline electric fields (CEF). If the expected value of $J_z$ in upper levels is larger than that in the lowest levels, level crossing happens at some magnetic field $H_c(\parallel z)$ (Fig. 3(a)). Such level crossing and accompanying metamagnetic transitions are observed in a number of rare-earth compounds [16, 17]. Recently, Tanaka pointed out that the fourth-order Stevens operator equivalent $O_4^0$ in the CEF Hamiltonian plays an important role in the magnetic properties of $RB_4$ compounds [18]. He interpreted major features of the susceptibility and the magnetization of $RB_4$ ($R$=Tb, Dy, Ho, Er) by introducing $O_4^0$ to the spin Hamiltonian. The effect of the usual single-ion type anisotropy $O_2^0 = 3J_z^2 - J(J+1)$ is established. Replacing $J_z$ by $J \cos \Theta$, where $\Theta$ is the polar angle, we find that the $B_0^4O_4^0$ has a minimum at $\Theta = 0$ and favors Ising spins when the coefficient $B_0^4$ is negative. If the $B_0^4$ is positive, the lowest energy is obtained at $\Theta = \pi/2$ and XY spins are selected. On the other hand, the effect of $O_4^0 = 35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1)^2 + 3J^2(J+1)^2$ is in marked contrast to that of $O_2^0$. The $B_4^0O_4^0$ has two minima at $\Theta = 0$ and $\pi/2$ when the coefficient $B_4^0$ is negative, while a single minimum exists at an intermediate angle when $B_4^0$ is positive. Hence, the negative $B_4^0$ prefers both XY and Ising spins, and spins with intermediate angles have high energy. In TbB$_4$, it is most likely that XY-type ground states and Ising-type first excited states are selected by negative $B_4^0$. It is considered that the level scheme shown in Fig. 3(a) is highly probable.

Normally, level crossing occurs simultaneously at all sites. However, if there are interactions between the excited states, the interactions can split the single metamagnetic transition into successive metamagnetic transitions by stabilizing several particular arrangements of excited Ising states. RKKY-type long-range interactions are expected in metallic TbB$_4$ and may cause the successive transitions.

4. Summary
We have investigated the high-field magnetization plateau phases of TbB$_4$ using RXD. The magnetic intensity observed at the (100) and (500) reflections in the plateau phases indicated that large magnetic moments normal to the magnetic field coexist with forced ferromagnetic moments parallel to the magnetic field. We proposed magnetic structures that consist of XY spins and Ising spins for the plateau phases, and also inferred that the origin of the novel magnetic structures and the successive metamagnetic transitions of TbB$_4$ is energy level crossing between the low-lying multiplets of the Tb ions.
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