Frustration-Driven Successive Metamagnetic Transitions in TbB$_4$

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Resonant magnetic x-ray diffraction experiments on the Shastry-Sutherland lattice TbB$_4$ were carried out under strong pulsed magnetic fields up to 30 T. TbB$_4$ exhibits a multi-step magnetization process above 16 T when magnetic fields are applied along the c-axis. We examined the intensity of the 010 magnetic reflection as a function of magnetic field and found that the magnetization plateau phases are accompanied by large XY components of magnetic moments, in contrast to normal fractional magnetization plateau phases. The magnetization was calculated using a simple spin model deduced from the above result. Finally we propose that frustration is the key to understanding the observed multi-step magnetization.

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When one applies pressure to a substance, the volume will be reduced at all times depending on its compressibility. In contrast to such natural behavior, several magnetic materials exhibit magnetization plateaus, where the magnetization keeps a constant value at a finite range of magnetic fields even below the saturation field. This “zero compressibility” is simply ascribed to the fact that $S_2$ is a good quantum number, while a variety of mechanisms give rise to plateaus in the magnetization curve.

Let us consider only plateau phases in ordered states here. The easy-axis magnetization of an Ising antiferromagnet is most comprehensible. An example is the one-third magnetization plateau of CoCl$_2$-2H$_2$O [1]. Competing exchange interactions stabilize the $\uparrow\uparrow\downarrow$ structure just below the saturation field. The multi-step magnetization curves of PrCo$_2$Si$_2$ [2] and CeSb [3] are also classified into this category. The plateau phases are described by a complex sequence of up- and down-spins.

Magnetization plateaus are also observed in Heisenberg spins. In geometrically frustrated Heisenberg antiferromagnets, one-third ($\uparrow\uparrow\downarrow$) and one-half ($\uparrow\uparrow\downarrow\downarrow$) plateaus are sometimes observed in triangular- and tetrahedron-based lattices, respectively. Although the field range of the plateau phase is zero for these lattices if only the nearest-neighbor interaction is taken into account, additional mechanisms, such as a four-spin exchange coupling, quantum fluctuations, single-ion anisotropy and magnetoelastic couplings, stabilize the plateau phase in real magnets [4,5,6,7]. A crucial point is that all plateau phases have a collinear magnetic structure. No ordered magnetic moment perpendicular to the magnetic field exists in the plateau phases.

Recently, a multi-step magnetization curve was observed in TbB$_4$. Intriguingly, several experimental evidences indicate that TbB$_4$ resembles none of the abovementioned magnets. In this letter, we report on resonant x-ray diffraction (RXD) experiments on TbB$_4$ up to 30 T. The field dependence of the magnetic intensity provides decisive information on the magnetic structure of the field-induced phases. From this result, we show that TbB$_4$ indeed belongs to a rare class of magnets, characterized by ordered perpendicular components in the plateau phases. We also show that frustration plays a vital role in the multi-step magnetization process on the basis of the calculation of magnetization curves.

The rare-earth tetra-boride RB$_4$ crystallizes into a tetragonal structure (space group: P4/mnbm). The network of the rare-earth ions is equivalent to the frustrated Shastry-Sutherland (SS) lattice [8]. Several pieces of work have thus been carried out from a viewpoint of frustration between rare-earth quadrupole moments [4,10]. Somewhat confusingly, in the strict sense, classical continuous spins on the SS lattice are not frustrated, because the ground state is a unique helical or Néel structure and has no degeneracy [8]. However, for helical structures, none of the antiferromagnetic bonds are antiparallel and thus local pair exchange-energy is not minimized. The spins are not satisfied and still feel “frustration”. We will revisit this point later.

In TbB$_4$, there are two transition points $T_{N1}=44$ K and $T_{N2}=22$ K. The total angular momentum of the Tb ion is large ($J=6$) and hence the Tb spin is approximated by a classical spin. The magnetic structure between $T_{N1}$ and $T_{N2}$ revealed by neutron powder diffraction experiments is shown in Fig. [11]. The magnetic moments are XY-type and are confined in the basal ab-plane. Additional in-plane anisotropy orients the moments parallel to the diagonal line. The nearest-neighbor interaction $J_1$ is antiferromagnetic. The next-nearest-neighbor interaction $J_2$ is probably antiferromagnetic, and $J_1$ and $J_2$ form a frustrated SS lattice. In RB$_4$, the further-neighbor antiferromagnetic interaction $J_3$ is taken into account, which stabilizes the observed magnetic structure. In this structure, the $J_2$ bond is not satisfied. Below $T_{N2}$, the mag-
A single metamagnetic transition is observed. Magnetic field is applied parallel to the [100] and [110] directions, and the one-half magnetization plateau is most prominent. When a magnetic field is applied parallel to the $c$-axis, the number of the steps is reported to be nine, and the one-half magnetization process is shown in Fig. 1(b). The multi-step metamagnetic behavior between 16 and 28 T [13]. The number of the steps is reported to be nine, and the one-half magnetization plateau is most prominent. When a magnetic field is applied parallel to the [100] and [110] directions, a single metamagnetic transition is observed. Magnetization measurements of diluted samples indicated that the multi-step magnetization is inherent to the phase between $T_{N1}$ and $T_{N2}$ [14]. The metamagnetic behavior suggests that the essential nature of the transitions is level-crossing between low-lying multiplets [15]. However, the origin of the multiple successive transitions is not easily understood. Magnetic structures in the high-field plateau phases provide useful information, thus we conducted an x-ray diffraction experiment under strong pulsed magnetic fields, which has been recently developed utilizing brilliant third-generation synchrotron x-rays [16, 17, 18]. Although magnetic x-ray scattering cross-sections are very small, we utilized resonant enhancement of magnetic scattering [19].

Synchrotron x-ray diffraction experiments were carried out at undulator beamline BL22XU at SPring-8. The x-ray energy was tuned to the Tb $L_{III}$ absorption edge (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 pulse duration was about 0.6 ms. The magnet was a split-pair, and two windows were prepared for incoming and outgoing x-rays. The magnet and a sample were attached to the 100 K and 10 K stages of a conventional closed cycle refrigerator, respectively. Details of experimental setup are described in Ref. [16]. Single crystals of TbB$_4$ were grown by the floating zone method. The sample was a thick plate of dimensions 1 mm $\times$ 1 mm $\times$ 0.5 mm with a polished (010) surface. The FWHM of the $\omega$ profile of the 020 reflection was about 0.06$^\circ$.

The scattering plane was horizontal. The $b^*$ axis lay in the scattering plane and the $c$-axis was perpendicular to the scattering plane. We observed the forbidden 010 reflection, which is a magnetic Bragg point as demonstrated in the neutron experiment [11]. The azimuthal angle $\Psi$, which is the rotation about the scattering vector, is a key parameter in RXD. We define $\Psi=0$ when the $c$-axis is perpendicular to the scattering plane. $\Psi$ was kept close to zero throughout this experiment. Magnetic fields were applied parallel to the $c$-axis. We used a high-counting-rate detector and measured diffraction intensity as a function of time with a typical resolution of 10 $\mu$s. The field strength was also monitored as a function of time, and we obtained the field dependence of the diffraction intensity from these two series of data.

Polarization measurements were carried out at the peak energy below $T_{N2}$ and above $T_{N1}$. The fluorescence spectrum is also shown. The intensity of the 010 reflection exhibits huge enhancement at the $L_3$ main edge, implying that the resonance is ascribed to electric dipole (E1) transition. Subsequent measurements were carried out at the peak energy (7.512 keV). The temperature dependence of the integrated intensity of the 010 reflection is shown in Fig. 2(b). The intensity appears below $T_{N1}$ and is constant below $T_{N2}$. The effect of beam heating is estimated to be at most 2 K from the differences between the reported and observed transition temperatures.

Here we briefly mention the resonant x-ray scattering amplitude [21] of the Tb ion, which is proportional to

$$f_{\text{res}} \propto iC_1(e_i^* \times e_i) \cdot m + C_2 \epsilon_i^* O \epsilon_i,$$  \hspace{0.5cm} \text{(1)}

where $m$ is the magnetic moment and $e_i$ and $\epsilon_i$ are the polarization vectors of the incident and scattered x-rays, respectively. The symmetric second-rank tensor $O$ describes anisotropy of the Tb 5d orbital caused by anisotropic crystal environment or quadrupole order and is represented by a linear combination of the five elements $O_{xy}, O_{yz}, O_{zx}, O_{xx},$ and $O_{yy}$. The first term in eq. (1) is magnetic scattering and the last term causes anisotropy of the tensor of susceptibility (ATS) scattering. Through measurements on temperature and azimuthal angle dependence with polarization analysis were performed by TM [20]. The results were consistent with the magnetic
The field dependence of the peak intensity of the 010 reflection in high-field phases. In addition, recent neutron diffraction experiments of TbB₄ under pulsed magnetic fields have shown that the field dependence of the 010 reflection in neutron diffraction is also similar to that of x-ray diffraction [22]. Neutrons observe mₓ, mᵧ, and m₂. Hence pure Oᵧz+O₂zz order is inconsistent with the neutron result. mₓ or mᵧ must exists. Actually all data are well interpreted by assuming that the major order parameter in the high-field phases is mₓ, magnetic moments perpendicular to magnetic fields.

This is a rather surprising result, because all magnetic moments in plateau phases are parallel or antiparallel to the magnetic field as mentioned in the introduction. A canting magnetic structure, usually derived from the coexistence of parallel and perpendicular components, results in a continuous magnetization curve unlike the observed step-like magnetization process. Accordingly, we submit an idea that in TbB₄ the magnetic structures in the plateau phases consist of very hard XY-type magnetic moments and Ising-like magnetic moments.

In order to interpret this novel magnetic structure, we propose the following spin model. The low-lying multiplets are approximated by the ground-state XY-spin S with the in-plane anisotropy E and the excited-state Ising spin S with the energy gap G. The spin Hamiltonian is

$$H = \sum_{m=1,2,3} J_m \left( \sum_{i,j} (S_i^x S_j^x + S_i^y S_j^y) + \sum_{k,l} s_k^z s_l^z \right)$$

$$- E \sum_i (|S_i^y|^2 - \frac{1}{2}) + G \sum_k (s_k^2)^2 - g_s \mu_B H_s \sum_k s_k^z,$$

where the spins are unit vectors; i and j sites are occupied by XY spins and k and l sites are occupied by Ising spins.

Magnetization curves were calculated for finite-size cells with periodic boundary conditions. We consider 4 spins in the crystallographic unit cell (1 x 1 cell). For simplicity, we initially consider a four-clock model by

| \(\pi\sigma\) | \(m_x\) | \(m_y\) | \(m_z\) | \(O_{xy}\) | \(O_{yz}\) | \(O_{zx}\) | \(O_{zz}\) | \(O_{yy}\) |
|---|---|---|---|---|---|---|---|---|
| \(\pi\pi\) | 0 | 0 | 0 | 0 | 0 | 0 | -1 | \(-\cos 2\theta\) |
| \(\pi\sigma'\) | \(i \sin \theta\) | 0 | 0 | \(\cos \theta\) | \(\sin \theta\) | 0 | 0 | 0 |

TABLE I: Scattering amplitude of each component of magnetic and ATS scattering at \(\Psi=0\) for \(\pi\pi'\) and \(\pi\sigma'\) channels.
taking the limit $E \to \infty$. For example (see Fig. 3(a)),
allowed states for spins 1 and 3 are $\mathcal{E} (−\sqrt{2},−\sqrt{2},0)$,
$\mathcal{E} (\sqrt{2},\sqrt{2},0)$, $\mathcal{O} (0,0,1)$ and $\mathcal{O} (0,0,−1)$. In this case, we
calculated energies of all $4^4=256$ states and found ground
states. For rather wide parameter sets, this model has
the same ground state as observed. A calculated magnetization
curve for $J_1 = 2, J_2 = 1, J_3 = 2$ and $G = 1$ is
shown in Fig. 3(a). The one-half magnetization plateau
is clearly reproduced and the corresponding magnetic
structure is shown in the inset. Similar results were ob-
tained with other sets of parameters and different cell
sizes ($2 \times 2$ and $1 \times 3$ cells).

It is interesting to note that a number of states that
have various magnetizations are degenerate at the criti-
cal fields $H_{c1/2}$ and $H_{c1}$. This is in fact an ordinary phe-
nomenon observed in metamagnetic transitions. How-
ever, if this degeneracy is lifted, the multi-step magneti-
zation curve of TbB$_4$ can be reproduced. Three me-
chanisms can lift the degeneracy: (i) difference in magni-
tization between $S$ and $s$, (ii) interactions beyond $J_3$, and
(iii) frustration. While the first two mechanisms cause
symmetric splits at $H_{c1/2}$ and $H_{c1}$, the observed mag-
etization curve is asymmetric. For instance, the one-
third plateau is clearly visible, whereas the two-third
plateau is indistinguishable, as seen in Fig. 3(b). It is
evident that the last mechanism, frustration, plays an essen-
tial role. A possible magnetic structure of the one-
third plateau phase is shown in Fig. 3(b). Here we set
the in-plane anisotropy $E$ finite so that the moments can
rotate in the $ab$-plane. The Ising sites behave like de-
cects. In frustrated magnets, as pointed out in the in-
troduction, the local pair exchange-energy is not mini-
imized. Hence, when a defect is introduced, the magnetic
structure around the defect relaxes and gains exchange
energy. This does not happen in magnetic lattices with-
out frustration, because all exchange energies have been
minimized.

For magnetic systems with short-range interactions, it
is expected that small commensurate unit cells are more
stable than large or incommensurate cells. Thus it is
plausible that a finite number of selected magnetization
steps appear in the magnetization curve through the frus-
tration mechanism. This mechanism is active only when
the density of the Ising sites is less than half (up to $J_3$).
Therefore the degeneracy is lifted only at $H_{c1/2}$. The
diffraction intensity of magnetic structures based on the
model shown in Fig. 3(a) is one-quarter of the intensity
at 0 T. The observed intensity is, however, about 40% of
that at 0 T, implying presence of other order parameters,
such as $O_{20}$ and $O_{yz}$.

In conclusion, we have investigated the multi-step mag-
etization process of TbB$_4$ using RXD. The magnetic
intensity observed in the plateau phases illustrates that
large XY-components of the magnetic moments coexist
with aligned Z-components. A simple spin model repro-
duces the one-half magnetization plateau, and it is found
that the frustrated nature of the SS lattice lifts the de-
generacy at the critical fields and creates the observed
multi-step metamagnetic behavior. Paradoxically, frus-
tration is not only an origin of degenerate states, but also
breaks degeneracy.

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FIG. 3: (a) Calculated magnetization curve for $E \to \infty$. The
magnetic structure of the one-half plateau phase is shown in
the inset. $\odot$ denotes a spin parallel to the $z$-axis. (b) Possible
magnetic structure of the one-third plateau phases.