11B-NMR study on Shastry-Sutherland system TbB₄

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Abstract. ¹¹B-NMR experiments were performed in high magnetic fields applied along $a$-axis up to 17.5T to investigate the field-induced magnetic phase transitions and the magnetic structure in high magnetic fields microscopically for the single crystalline TbB₄, Shastry-Sutherland-type frustrated antiferromagnet. It was found that the field-swept $¹¹$B-NMR spectra observed at low magnetic field changes drastically at $H_C = 15.9$ T, where the magnetization jump occurs. Based on a simple model of four-spin cluster and the classical dipole-dipole interaction, we have calculated NMR spectra, which qualitatively reproduced the observation below $H_C$ but the one above $H_C$ showed discrepancy.

1. Introduction
The rare-earth tetraboride RB₄ crystallizes in the tetragonal structure ($P4/mmbm$, No.127). The arrangement of magnetic R ions in the $c$-plane is topologically equivalent to the two dimensional Shastry-Sutherland lattice [1], in which it is expected that the geometrical magnetic frustration plays an important role for the magnetic properties. Recently, the extensive studies of $S = 1/2$ orthogonal dimer system SrCu₂(BO₃)₂, in which the 3$d$ moments of Cu ions form the Shastry-Sutherland lattice, were carried out experimentally and theoretically [2, 3] because this system shows the characteristic magnetization plateaus caused by the geometrical magnetic frustration. While, the title compound TbB₄ shows the metallic behaviour and the magnetic interaction between 4$f$ moments of Tb ions is expected to be Ruderman-Kittel-Kasuya-Yoshida (RKKY)-type which is three dimensional and long-ranged so that the geometrical magnetic frustration of TbB₄ may not be so important for the magnetism, compared with that of SrCu₂(BO₃)₂. However, because there are electric multipole interactions in TbB₄, we expect that appearance of the novel magnetism caused by the interplay between the geometrical magnetic frustration in the Shastry-Sutherland lattice and electric multipole interactions.

The successive magnetic phase transitions were observed in TbB₄ at $T_{N1} = 44$ K and $T_{N2} = 24$ K in the magnetic susceptibility measurements [4], indicating the existence of the magnetic frustration. From the measurements of the magnetic susceptibility in the magnetic field applied along various directions, it was expected that there is the easy-plane type magnetic anisotropy in the $c$-plane. The magnetic structures of TbB₄ at zero magnetic field both in the low-temperature phase below $T_{N2}$ and in the intermediate phase between $T_{N1}$ and $T_{N2}$ have been determined by means of the neutron powder diffraction experiments [5]. The magnetic structure in the low-temperature phase is shown in Fig. 1 (a), in which four magnetic moments at Tb sites in a unit cell form the non-collinear magnetic structure...
and make angles with $\phi = 23^\circ$ lying within the $c$-plane, and stacks ferromagnetically along the $c$-axis. Also, the magnitude of the magnetic moment at $T = 3$ K was estimated as $8.2 \mu_B$ which is 91% of the full moment $9 \mu_B$ of the Tb$^{3+}$ ion. It was expected that the intermediate angle $\phi = 23$ is due to the subtle orthorhombic distortion by the structural phase transition at $T = 80$ K [6].

The most striking feature of magnetism of TbB$_4$ is the nine-step field-induced jumps and several plateaus observed between $H = 16$ and 28 T in the magnetization process at $T = 4.2$ K for $H//c$-axis [7]. Because it was already found that the ordered moments of TbB$_4$ lie in the $c$-plane below $T_{N2}$, this behaviour is quite unusual and is expected to be due to the interplay between the geometrical magnetic frustration in the Shastry-Sutherland lattice and electric quadruple interactions. For the applied magnetic field in the $c$-plane on which we focus attention, one large magnetization jump was observed [8] at $H_C = 15.9$ T for $H//[100]$ and at 12 T for $H//[110]$, and this large magnetization jump, as well as the details of the magnetization curve and the change in the spin structure around the jump is not fully understand yet.

By means of NMR technique, so far, an experiment in magnetic fields parallel with the (110) axis has been only reported in the single crystalline TbB$_4$ so far [8]. In this experiment, the splitting of $^{11}$B-NMR spectra due to the antiferromagnetic ordering was demonstrated. However, microscopic investigation on the magnetic structure in high magnetic fields for $H//a$-axis is still untouched. In this article, we report our preliminary results of $^{11}$B-NMR experiments in high magnetic fields along the $a$-axis for the single crystalline TbB$_4$.

![Figure 1](image_url)

**Figure 1.** (a) Schematic crystal structure projected onto $ab$ plane, and the dominant interactions $J_1$ and $J_2$. (b) The spin structure determined by powder neutron diffraction at zero field [5].

2. Experimental
The single crystal of TbB$_4$ was grown by the floating-zone method. A single crystal with the size of $3 \times 3 \times 0.5$ mm$^3$ was used in the present NMR experiments. The field-swept spectra of $^{11}$B-NMR were measured at $T = 4$ K in magnetic fields along the $a$-axis up to $H = 17.5$ T using the 20 T superconducting magnet in the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

In $P4/mmb$ structure, there are three Wyckoff positions for B sites, 8j, 4e and 4h. Reflecting rather a low local symmetry at the $^{11}$B ($l = 3/2$) site, NMR signal from each position splits into three peaks by the eqq-effect. We first show the spectrum for comparison measured at a low field around 13 T and $H//c$-axis in Fig. 2 (a). By utilizing the fact that all the boron sites in each Wyckoff position have the
same eqq-splitting when $H$ is parallel with $c$-axis, we adjusted the sample direction to be $H//c$ with the precision of $\pm 0.1$ degree, and then rotated the sample by 90 degree so that $H$ is parallel precisely with $a$-axis. Note that the electric quadruple frequency $v_0/\gamma$ of each boron site is below 0.05 T, where $\gamma$ is the gyromagnetic ration of $^{11}$B.

We estimated the hyperfine field at each boron site for the case of $H//c$-axis, based on the spin structure reported at zero field [5], and by assuming the uniform canting of the 4$f$ moments from the $c$-plane and the classical dipole-dipole interaction between the 4$f$ moments and $^{11}$B nuclear spins. When the field is applied along $c$-axis, all the 8j and 4h peaks degenerate, because all the 4$f$ moments rise up from $ab$-plane uniformly at low fields below the multiple steps[7,9]. Only the 4e peaks split into the two sub groups with the different hyperfine fields. The calculated hyperfine fields qualitatively reproduce the observed spectrum, and we can assign all the observed peaks to the crystallographic sites as shown in Fig. 2 (a).

Figure 2. (a) Profiles of $^{11}$B-NMR field-swept spectra measured at 4.2 K with $H//c$-axis. The solid lines show the site assignment for the eqq-split peak positions of $^{11}$B-NMR signal of each Wyckoff position. (b) Profile of spectra of $H//a$-axis taken at various magnetic fields 13 to 17 T. The original point of abscissa is set to the zero-shift position $v_0/\gamma$. The arrows show the position of observed seven peaks. The dashed line show the constant field of $H_C=15.9$ T. (c) $M$-$H$ curve near $H_C=15.9$ T. Dashed lines show the field region of NMR measurements.

3. Results and Discussion

Figure 2 (b) shows the representative field-swept spectra of $^{11}$B-NMR in TbB$_4$ at various frequencies for $H//a$-axis at $T = 4$ K. At low fields $H<H_C$, there observed the seven peaks, shown by arrows in Fig. 2 (b). Each peak contains the three eqq-split lines inside, and corresponds to each crystallographically or magnetically inequivalent boron sites. As increasing the field, the peaks in higher field side #5-$#7$ shifted to higher field appreciably, while those in the lower field side #1, #2 and at the zero-shift region #3-$#4$ did not move. A drastic change comes at the field of magnetization jump $H_C=15.9$ T, where the peaks of #1-$#3$ suddenly disappear. Note that in Fig. 2 (b), the constant-field line is shown by a dashed steep line, and that only the spectra above the line belong the field region $H>H_C=15.9$ T. The disappearance of #1-$#3$ clearly demonstrates a drastic change in the hyperfine field brought by the magnetization jump at $H_C=15.9$ T.

In order to explain the observed spectra we have estimated the transferred hyperfine field at the each boron sites, assuming the classical dipole-dipole interaction between 4$f$ moments and $^{11}$B nuclei.
First, the direction of each $4f$ moments was calculated based on a simple four-spin model [7] with appropriate exchange interactions $J_1, J_2$ and anisotropy up to quadrature terms, which well reproduce the observed magnetization curve. Next, we added up the contribution from Tb$^{3+}$ ions within $9 \times 9 \times 9$ unit cells to obtain the hyperfine field at each sixteen boron sites in the centered unit cell. A histogram of thus obtained sixteen values of the field should give the schematic $^{11}$B-NMR spectrum. Since the width of observed peaks in the field direction $H_{\perp a}$ is very large, eqq-splitting is considered to be submerged within each peak.

In Fig. 3, the calculated spectra are shown with the schematic view of spin directions under various field up to 20 T. Correspondence between the observed spectra and the calculation holds qualitatively within the measured field region, that is, observed seven peaks #1-#7 are considered to correspond to $\frac{1}{2}$-$4h$, $\frac{1}{4}$-$8j$, $\frac{1}{4}$-$8j$, $4e$, $\frac{1}{4}$-$8j$, $\frac{1}{4}$-$8j$, $\frac{1}{2}$-$4h$ respectively. However, the value of the shift for each peak and its field-dependence does not agree with each other. The calculation of the hyperfine fields including RKKY interaction is considered to be necessary.

**Figure 3.** Schematic view of calculated spectra of $^{11}$B-NMR based on the calculation of the four-spin model[7]. The Wyckoff letters show the position of each sixteen B atom in a unit cell. Open, grey and black bars correspond to $4h$, $8j$ and $4e$ respectively.

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**References**

[1] Shastry B S and Sutherland B 1981 *Physica* B+C108 1069.
[2] Kageyama H, Yoshimura K, Stern R, Mushnikov N V, Onizuka K, Kato M, Kosuge K, Slichter C P, Goto T and Ueda Y 1999 *Phys. Rev. Lett.* 82 3168.
[3] Miyahara S and Ueda K 2003 *J. Phys. Condens. Matter* 15 R327 and references therein.
[4] Fisk Z, Maple M B, Johnston D C and Woolf L D 1981 *Solid State Commun.* 39 1189.
[5] Matsumura T, Okuyama D and Murakami Y 2007 *J. Phys. Soc. Jpn.* 76 015001.
[6] Heiba Z, Schafer W, Jansen E and Will G 1986 *J. Phys. Chem. Solids* 47 651.
[7] Yoshii S, Yamamoto T, Hagiwara M, Takeuchi T, Shigekawa A, Michimura S, Iga F, Takabatake T and Kindo K 2007 *J. Mag. Mag. Mater.* 310 1282; Yoshii S, Yamamoto T, Hagiwara M, Michimura S, Shigekawa A, Iga F, Takabatake T, and Kindo K; 2008 *Phys. Rev. Lett.* 101 087202.
[8] Mean B J, Kang K H, Kim J H, Hyun I N, Lee M, and Cho B K 2006 *Physica* B 378-380 600.
[9] Kobayashi K, Yoshii S, Iga F, Goto T *in preparation*. 