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^{11}B Nuclear Magnetic Resonance Study of Spin Structures in Terbium Tetraboride

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Abstract : ^{11}B nuclear magnetic resonance (NMR) measurements were performed on the single crystals of TbB_4 to investigate local electronic structure and *4f* spin dynamics. ^{11}B NMR spectrum, Knight shift, spin-lattice and spin-spin relaxation rates were measured down to 4 K at 8 T. ^{11}B NMR shift and linewidth are huge and strongly temperature dependent due to the *4f* moments. In addition, both are proportional to magnetic susceptibility, indicating that the hyperfine field at the boron site originates from the *4f* spins of Tb. Below T_N, the single broad resonance peak of ^{11}B NMR splits into several peaks reflecting the local magnetic fields due to antiferromagnetic spin arrangements. The longitudinal and the transverse relaxation rates, $1/T_1$ and $1/T_2$, independent of temperature above T_N, decreases tremendously confirming huge suppression of spin fluctuation below T_N.
Key words : TbB_4, ^{11}B NMR, antiferromagnetism, rare-earth tetraborides

Recently, the binary boride compounds have been extensively studied since these systems show a variety of fascinating and intriguing properties ranging from various magnetic phase transitions, heavy fermion behavior, mixed-valence phenomena to superconductivity.[1] Those compounds include MgB_2, hexaborides and tetraborides. Rare-earth tetraborides RB_4 have been investigated thoroughly over a few decades by using single crystals.[2] Most RB_4 (R = Nd, Sm,

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Gd, Tb, Dy, Ho, Er, Yb) exhibits antiferromagnetism [3] in the range of T_N = 7 - 57 K. The exceptional compounds are PrB4 with a ferromagnetic order [3] at T_C = 25 K, and CeB_4 and YbB_4 with no order. The magnetic interaction is known to be invoked by Rutherman-Kittel-Kasuya-Yoshida (RKKY) interaction.

TbB_4 is known as a metallic antiferromagnetic compound with T_N = 43 K [4-6] and the effective magnetic moment μ_{eff} = 9.8 μ_B. The tetragonal to orthorhombic distortion occurs at 80 K [4] much above T_N. However, the distortion and relative volume change is reported to be small for TbB_4.[4] According to neutron diffraction studies, magnetic structure is antiferromagnetic collinear with the moments perpendicular to the tetragonal c-aixs. [5,6] Below T_N another magnetic phase transition around 22 K shows up, as for DyB_4, HoB_4 and TmB_4.[7] Since nuclear magnetic resonance (NMR) measurements sensitively probe local magnetic field and electronic spin dynamics using nuclear spins, we have adopted ^{11}B NMR measurements to probe the spin configurations as well as local electronic structures and *4f* spin dynamics in TbB_4.

Pure single crystals of TbB_4 were synthesized by the solution growth method using Al flux, which is similar to the growth of rare-earth hexaborides.[8] Magnetization and magnetoresistance measurements were carried out to characterize these crystals. Pulsed NMR measurements were carried out with our home-made pulsed spectrometers. The broad spectra were scanned by the point-by-point method changing the spectrometer frequency. The phase-alternating pulse sequences were employed to significantly reduce the electromechanical vibration (ringdown) after pulses. Relaxation rates, $1/T_1$ and $1/T_2$, were measured by the solid-echo pulse sequence. ^{11}B NMR spectrum, shift, $1/T_1$ and $1/T_2$ were measured in the range of 4.0 - 295 K at 8.0 T.

Fig. 1 shows the ^{11}B NMR spectrum at 295 K (a) and 10 K (b). The spectrum at 295 K, above T_N = 43 K, shows a single broad peak with the negative shift of K = -0.0040% and the large linewidth of $\Delta\nu$= 0.93 MHz. The spectrum at 50 K shows a single peak with a much larger shift and a larger linewidth; K = -0.024% and $\Delta\nu$= 3.6 MHz, as shown in Fig. 2. The negative shift of ^{11}B NMR indicates that the shift at the boron sites is dominated by core-polarization field. Fig. 2 confirms that the ^{11}B NMR shift as well as linewidth is strongly

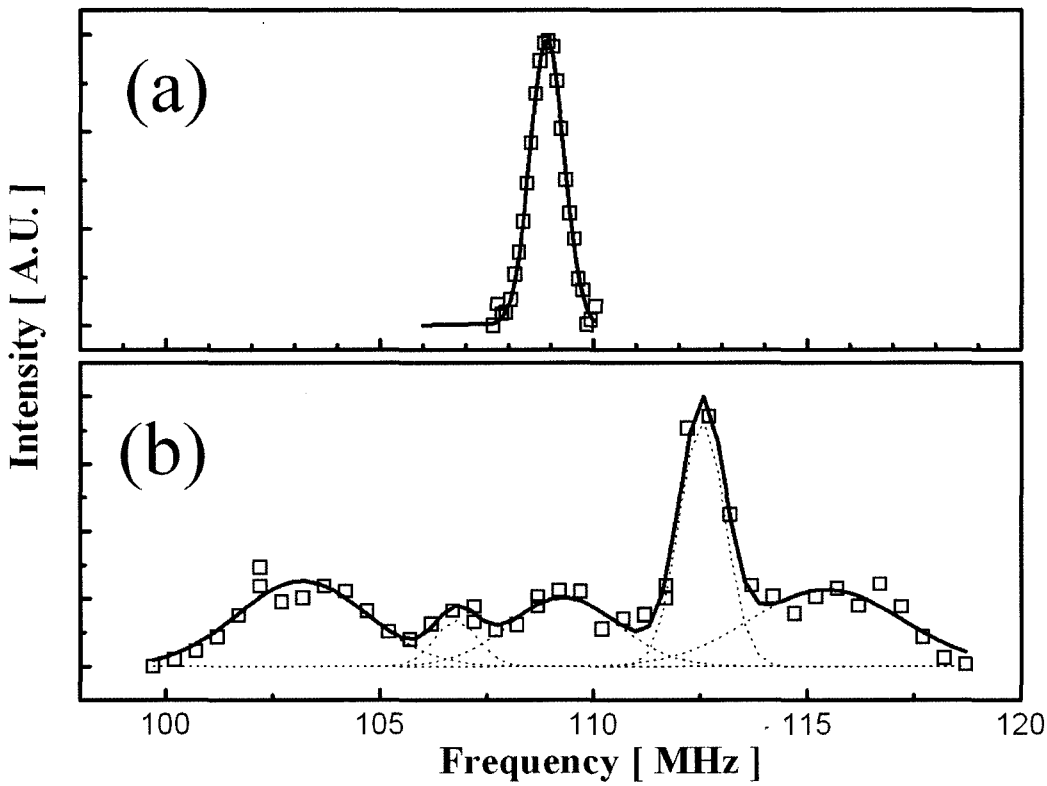

Fig. 1. ^{11}B NMR spectrum at 8 T; (a) At 295 K above T_N (b) At 10 K below T_N. The lines represent a Gaussian fit to respective resonance peaks.

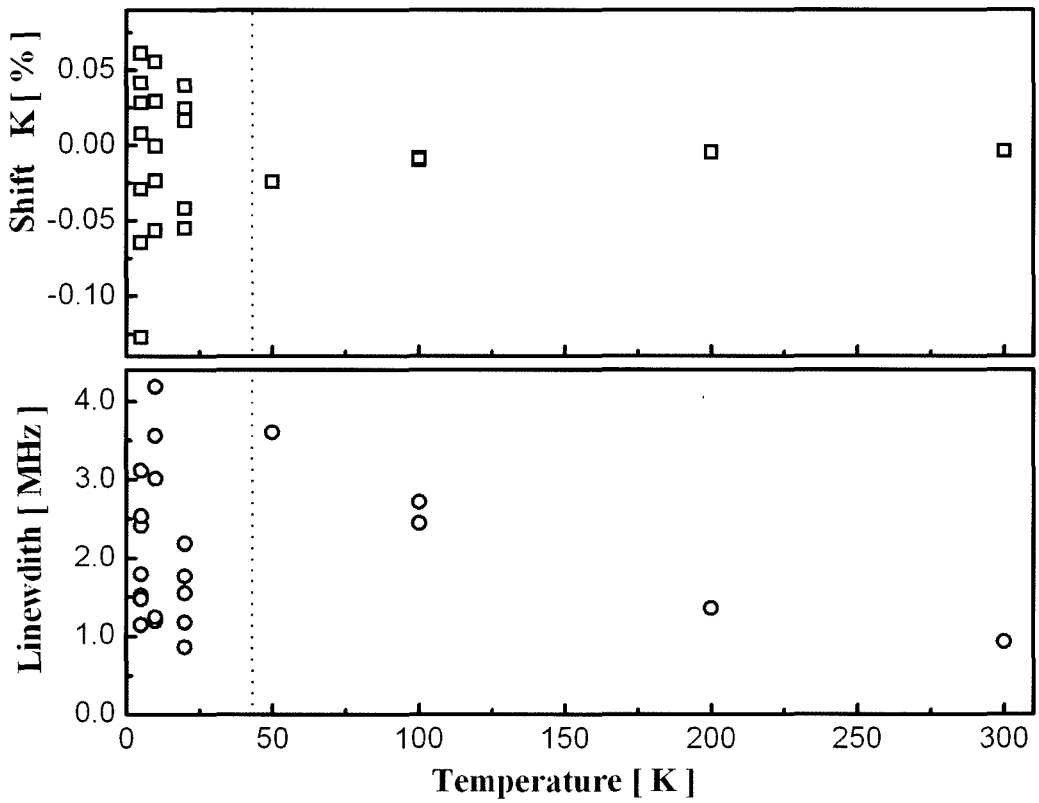

Fig. 2. Shift and linewidth of ^{11}B NMR at 8 T. The dotted line stands for T_N.

temperature dependent increasing in proportion to the susceptibility down to T_N. This confirms that the shift and the linewidth of ^{11}B NMR are dominated by the hyperfine field from the Tb *4f* spins.

Fig. 1(b) shows the ^{11}B NMR spectrum at 10 K below $T_N = 43$ K. This contrasts with Fig. 1(a) above T_N. The *single* broad peak at 295 K in Fig. 1(a) splits into *six* even broader resonance peaks in the antiferromagnetic state. Since a magnetic order of electron spins generates local magnetic field in addition to the static external magnetic field for NMR measurements, the splitting of NMR peaks are often a clear signature of magnetic order. Furthermore, the local field, obtained from the respective peak frequency, at the respective nuclear position is utilized to find out spin configurations in the ordered state. In particular, the antiferromagnetic order is often evidenced by doubling up the number of resonance peaks due to the two alternating spin orientations, as shown below T_N in Fig. 2.

At this point, it should be pointed out that RB_4 has a tetragonal crystal structure with *P4/mbm* point symmetry at room temperature. Thus the R ions are at the *4g* symmetry positions and the boron sublattice forms up chains of B_6 octahedra parallel to the c-axis, which are connected by pairs of boron atoms. Therefore, there are three different boron sites, which are magnetically nonequivalent. The difference is direction and distance to the Tb *4f* moments. The temperature evolution of four resonance peaks is crucial to determine spin orientations. However, the detailed analysis using computer simulation is required to pin down correct spin configuration. Far above T_N, relaxation rates $1/T_1$ and $1/T_2$ are very large, respectively, $\sim 10^4$ and $\sim 10^5$ s^{-1} and temperature-independent suggesting that the spin correlation between Tb *4f* spins is weak and the spin fluctuation is independent. Below T_N, not only $1/T_1$ but also $1/T_2$ is significantly reduced to, respectively, $\sim 10^{-1}$ and $\sim 10^4$ s^{-1} at 5 K, indicating that the spins are ordered and the spin dynamics are suppressed dramatically.

In summary, we have performed ^{11}B NMR measurements on the single crystals of TbB_4 to investigate local electronic structures and *4f* spin dynamics. ^{11}B NMR shift and linewidth are huge and strongly temperature dependent due to the *4f* moments. In addition, both are proportional to the magnetic susceptibility, indicating that the hyperfine field at the boron site

originates from the *4f* spins of Tb. Below T_N, the single broad resonance peak of ^{11}B NMR splits into several peaks reflecting the local magnetic fields due to antiferromagnetic spin arrangements. $1/T_1$ and $1/T_2$, independent of temperature above T_N, decrease dramatically below T_N confirming huge suppression of spin fluctuation.

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