Large Softening of Longitudinal Elastic Modulus in TbB₄

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Abstract. Rare earth tetraborides have a tetragonal crystalline structure with the space group P4/mmbm. The rare earth ions form the Shastry-Sutherland lattice in the c plane in these compounds, which evokes us an interesting electronic property due to the geometric frustration of spins and orbitals. TbB₄ undergoes two phase transitions at \( T_{N1} = 42.1 \) K and \( T_{N2} = 21.7 \) K, respectively. Because of the clear cusp-type anomaly in the temperature dependence of magnetic susceptibility, the transition at \( T_{N1} \) should be an antiferromagnetic one. The origin of the transition at \( T_{N2} \) is unclear at present. To investigate the possibility of multipolar ordering, we measured temperature dependencies of elastic moduli using the ultrasonic phase comparison method. The longitudinal elastic modulus \( C_{11} \) shows large softening with more than 17\% reduction of the stiffness at \( T_{N2} \) in contrast to no anomaly at \( T_{N1} \). This result suggests ferro-type ordering of the quadrupole \( O_{Γ3} \) at \( T_{N2} \). The macroscopic spontaneous strain in the c plane emerging due to the ferroquadrupolar ordering may lift the geometric frustration.

1. Introduction

Rare earth tetraborides have attracted much attention in recent years because of their unique crystalline structure. These compounds crystallize in a tetragonal symmetry with the space group P4/mmbm. The network of rare earth ions is equivalent to the so-called Shastry-Sutherland lattice [1]. Not only the geometric frustration of spin but also a geometric quadrupolar frustration was proposed for DyB₄ [2]. TbB₄ undergoes two phase transitions around \( T_{N1} = 44 \) K and \( T_{N2} = 24 \) K [3]. Magnetic susceptibilities both for the magnetic field directions along \( a \) and \( c \) show a cusp at \( T_{N1} \), followed by a weak kink at \( T_{N2} \). The clear cusp suggests that the transition at \( T_{N1} \) should be an antiferromagnetic one. However, the origin of the transition at \( T_{N2} \) is unclear at present. Recent neutron powder diffraction experiment revealed the magnetic structure of the antiferromagnetic intermediate phase (\( T_{N1} > T > T_{N2} \)) and also revealed that the magnetic structure below \( T_{N2} \) was compatible with the orthorhombic distortion with emphasizing an importance of ferroquadrupolar interaction in this compound [4]. In order to investigate the possibility of multipolar ordering, we measured temperature dependence of elastic moduli which are extremely sensitive to a quadrupolar transition [5].

2. Experimental

High-quality single crystal TbB₄ was grown under Ar flow by a floating-zone method using an image furnace with four xenon lamps [6]. Temperature \( T \) dependence of elastic modulus was measured between 4.2 and 300 K using the phase comparison-type pulse echo method. The elastic modulus \( C \) was calculated using the relation \( C = \rho v^2 \) with the room-temperature value of mass density \( \rho = \)
6.326 g/cm$^3$, where $v$ is a sound velocity in sample. The ultrasonic frequencies of 30 MHz and 90 MHz were used for $C_{11}$ and $C_{33}$ measurements, respectively. The specific heat measurement revealed that the phase transition points $T_{N1}$ and $T_{N2}$ of our sample were 42.1 and 21.7 K, respectively [7]. The electronic entropy reached Rln5 at $T_{N1}$, where R is the gas constant, indicating that there are at least five 4$f$-electronic levels below an energy scale of ~50 K.

3. Results and Discussion

Figure 1 shows temperature dependence of longitudinal elastic stiffness $C_{33}$ in TbB$_4$. $C_{33}$ increases monotonically with decreasing temperature. There is a shallow dent around 75 K, which may be due to a crystal electric field effect. No anomaly can be seen at both transition points, indicating no coupling between the total symmetric strain and order parameters.

![Figure 1. Temperature dependence of elastic modulus $C_{33}$ in TbB$_4$. The ultrasonic frequency was 90MHz.](image)

Figure 2 shows temperature dependence of longitudinal elastic stiffness $C_{11}$ in TbB$_4$. $C_{11}$ initially increases with decreasing temperature. At $T_{N1}$, there is a tiny kink which is, however, invisible in this scale. We observed significant softening of $C_{11}$ with more than 17% reduction of the stiffness around $T_{N2}$. With further decreasing temperature, $C_{11}$ is restored to almost the background stiffness. $C_{11}$ is not a pure symmetric elastic mode. It is the response to both the total symmetric strain and the shear strain $\varepsilon_{\alpha\beta} = \varepsilon_{xx} - \varepsilon_{yy}$. Because $C_{33}$ shows no anomaly at $T_{N2}$, we do not expect the coupling between the total symmetric strain and order parameters. The softening of $C_{11}$ should originate from huge softening of transverse $(C_{11} - C_{12})/2$ which is the response to the $\varepsilon_{T3}$ strain. To prove this anticipation, $(C_{11} - C_{12})/2$ measurement is underway. The $\varepsilon_{T3}$ strain directly couples to the quadrupole $O_{T3}$, which should be the order parameter of the phase transition at $T_{N2}$. We believe that the data shown in Fig. 2 demonstrates that quadrupolar fluctuations survive in the magnetically ordered phase below $T_{N1}$. If ferroic ordering of $O_{T3}$ occurs, the macroscopic spontaneous strain $\varepsilon_{T3}^S$ must emerge. This is consistent with the neutron experiment result that the magnetic structure below $T_{N2}$ was compatible with the orthorhombic distortion [4]. To confirm that the transition at $T_{N2}$ is ferroquadrupolar, we utilize the expression of elastic modulus [8]:

\[ \varepsilon_{T3} = C_{11} \varepsilon_{xx} - 2C_{12} \varepsilon_{yy} + C_{13} \varepsilon_{zz} \]
where $C_t^0$, $g$ and $K$ are background stiffness, strain-quadrupole coupling constant and quadrupole-quadrupole coupling constant, respectively. Here we assume a two-ion interaction expressed by the effective Hamiltonian:

$$H = C_t^0 \frac{\varepsilon_{ij}^2}{2} + g \sum_i O_{O_i} + K \sum_{i,j} O_{O_i} O_{O_j}.$$

Hence, if $K$ has a positive value, the transition is ferroquadrupolar. We tried to reproduce the softening of $C_{11}$ by Eq. 1 with assuming that the background stiffness has linear $T$ dependency as $C_t^0 = a + bT$. The solid curve shown in Fig. 2 represents the best fit with fitting parameters: $a = +427.98$ GPa, $b = -0.0387$ GPa/K, $K + g^2 / C_t^0 = +21.59$ K and $K = +21.47$ K, respectively. This result strongly suggests that the ferroic ordering of $O_{T3}$ undergoes at $T_{N2}$.

By emergence of the macroscopic spontaneous strain $\varepsilon_{ij}^S$, lattice parameters $a$ and $b$ become nonequivalent and thus the geometric frustrations may lift by the phase transition at $T_{N2}$. Matsumura et al. also pointed out that the orthorhombic strain probably causes the magnetic energy gain below $T_{N2}$ [4]. The reason why the quadrupolar fluctuations survive in the magnetically ordered phase is open question at present. Further ultrasonic experiments are in progress.

4. Conclusion
We have measured temperature dependencies of longitudinal elastic moduli of TbB$_4$ in the temperature range between 4.2 and 300 K. We found large softening of $C_{11}$ around $T_{N2} = 21.7$ K. We obtained the positive value of the quadrupole-quadrupole coupling constant from the data fitting to the strain susceptibility. The origin for the phase transition at $T_{N2}$ is plausibly the ferroquadrupolar
ordering of $O_{\Gamma_3}$. The appearance of orthorhombic strain in the $c$ plane by the ferroquadrupolar ordering may diminish the geometric frustration in TbB$_4$.

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