Crystal field excitations on NdFe$_3$(BO$_3$)$_4$ investigated by inelastic neutron scattering

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Abstract. We performed inelastic neutron scattering experiments on a multiferroic material NdFe$_3$(BO$_3$)$_4$ to explore the crystal field excitations, where the magnetic anisotropy of the Nd$^{3+}$ crystal field was responsible for the multiferroicity. Flat modes were observed at 8.5 meV and 17.4 meV in the neutron spectrum. The analysis revealed that these excitations were the transitions from the ground state to the first and second excited states of the Nd$^{3+}$ crystal field.

1. Introduction
Multiferroic compounds, which exhibit both magnetic and dielectric orders, have attracted great attention since the discovery of a huge magnetoelectric (ME) effect in TbMnO$_3$ [1]. Among them, the rare-earth ferborates $R$Fe$_3$(BO$_3$)$_4$ ($R = Y$ and rare-earth metal) are a series of new multiferroic compounds containing $R^{3+} (4f^n)$ and Fe$^{3+} (3d^5 S = 5/2)$ as magnetic ions. They show diverse ME effects as a function of the $R^{3+}$ ions ($R = Y, Pr, Nd, Sm, Gd$ and Tb) [2, 3, 4, 5, 6, 7] because of the variety of magnetic anisotropies and of strong coupling to the Fe$^{3+}$ moments. Recent studies revealed that the mechanism of the magnetoelectricity in these compounds was explained by the spin-dependent metal-ligand hybridization model [8, 9].

We focus on NdFe$_3$(BO$_3$)$_4$, where the Nd$^{3+}$ ions ($4f^3$) carry a magnetic moment with $J = 9/2$. The crystal structure of NdFe$_3$(BO$_3$)$_4$ is trigonal with space group $R32$. The point symmetry of the NdO$_6$ octahedra is $D_3$; a threefold symmetry along the crystallographic $c$ - axis and three twofold axes in the $ab$ - plane as shown in Fig. 1(a). Studies on the heat capacity, magnetic susceptibility [10], and ME effect [3, 6] revealed that an easy-plane type antiferromagnetic (AF) order and a spontaneous electric polarization simultaneously appeared at $T_N = 30$ K and a huge electric polarization was induced by a magnetic field. An optical spectroscopy study exhibited five Kramers doublets by the Nd$^{3+}$ crystal field [11]. A neutron diffraction study exhibited the easy-plane type AF order at $T \leq T_N$; the Fe$^{3+}$ and Nd$^{3+}$ magnetic moments aligned ferromagnetically along the $c$ - axis and aligned antiferromagnetically along the $a$ - axis with the propagation vector $k = \{0, 0, 3/2\}$ [12, 13].

In the present study we explored the crystal field excitations of the Nd$^{3+}$ ion in NdFe$_3$(BO$_3$)$_4$ by means of an inelastic neutron scattering (INS) technique. Very recently it
was revealed that the magnetic anisotropy of the Nd$^{3+}$ crystal field drove the multiferroicity in NdFe$_3$(BO$_3$)$_4$ [14]. It is significant to investigate the Nd$^{3+}$ crystal field for the further understanding of the ME effect in the rare-earth ferroborates.

2. Experimental details
Single crystals of NdFe$_3$(BO$_3$)$_4$ were grown by a flux method [15]. Details of the growing method are described in Ref. [14]. Plate-shaped crystals having the crystallographic $a^*\cdot c^*$ plane as shown in Fig. 1(b) were obtained. 22 pieces of the single crystals were coaligned so that the $a^*-c^*$ plane was horizontal. The crystal alignment was performed by a transmission Laue method using a high energy X-ray CCD camera. We placed the crystals on an aluminum holder. The average mass of the crystals was 0.1 g. The total mass of the sample was 2.1 g.

We performed the INS experiment at the High Resolution Chopper Spectrometer (HRC) installed in the Material and Life Science Experimental Facility of J-PARC [16, 17, 18]. White neutrons are monochromatized by a Fermi chopper synchronized with the production timing of the pulsed neutrons at the HRC. The energy transfer $\hbar \omega$ was determined from the time of flight (TOF) of scattered neutrons detected at position sensitive detectors (PSDs). The $T_0$ chopper was set at 50 Hz, a collimator of 1.5° was installed in front of the sample, and the “$S$” Fermi chopper with 200 Hz was used to obtain high neutron flux. We used a GM-type closed cycle cryostat to achieve 40 K and 15 K. The energy of the incident neutron beam was $E_i = 51.04$ meV yielding an energy resolution of $\Delta E = 2.5$ meV at the elastic position. We set the incident neutron beam with $k_i//a^*$.

3. Experimental results and discussions
An INS spectrum at 15 K is shown in Fig. 2(a). A well-defined flat excitation is observed at 17 meV and a weak flat one is observed at about 8 meV. Strong intensities at $\hbar \omega \lesssim 6$ meV in the wide $Q$ range are from dispersive Fe-centered spin waves [14]. A weak flat intensity at about 20 meV is from an instrumental artifact [14]. Dispersive spectra in the range of $|Q| > 2$ Å$^{-1}$ are from the aluminum that is used for the sample can and sample holder.

One-dimensional energy cuts obtained by integrating the intensities in the range of 1.5 Å$^{-1}$ $\leq |Q| \leq 1.9$ Å$^{-1}$ are shown in Fig. 2(b). The red triangles and blue circles indicate the data measured at 40 K and 15 K, respectively. The data at 15 K are fitted by the sum of five Gaussian
functions; the solid black curve is for an incoherent elastic scattering, the dashed curve is for the Fe-centered spin-wave excitation, the solid green curve is for a couple of intrinsic excitations, and dotted curve is for the instrumental artifact. The peak energies of the green curve are estimated to be 8.5 meV and 17.4 meV, and they agree with the energy of the first and second excited states of the Nd$^{3+}$ crystal field reported in the optical spectroscopy [11]. This suggests that these excitations are the transitions from the ground state to the first and second excited states. A quite small temperature dependence is observed between the data at 40 K and that at 15 K.

We simulated neutron intensities of the Nd$^{3+}$ crystal field. At the Nd$^{3+}$ site with the $D_3$ symmetry, the crystal field Hamiltonian is defined as follow:

$$\mathcal{H}_{CF}(D_3) = B_2^6 C_6^0 + B_4^6 C_4^0 + iB_4^4 (C_4^4 + C_{-4}^4)$$

$$+ B_6^6 C_6^0 + iB_3^6 (C_6^6 + C_{-6}^6) + B_6^6 (C_6^6 + C_{-6}^6). \quad (1)$$

The $B_p^q$ are the crystal field parameters and the $C_p^q$ are the spherical tensor operators. We used the values of the parameters $B_p^q$ reported in Ref. [11].

Then, the neutron intensity is expressed by

$$\frac{d\sigma}{d\Omega dE} \propto \sum_{n,n'} p_n \left[ \langle n' | J_+ | n \rangle \right]^2 + \left[ \langle n' | J_- | n \rangle \right]^2 \delta (\hbar \omega + E_n - E_{n'}). \quad (2)$$

Here $J_+$ and $J_-$ are, respectively, the raising and lowering operators of the total angular momentum $J$, and $p_n$ is the product of the probability that $|n\rangle$ state is occupied. $E_n$ and $E_{n'}$ are the energies of the $|n\rangle$ and $|n'\rangle$ levels, respectively. We calculated the excitation energies and the neutron intensities of the transferred states from the ground state to the first and second excited states using McPhase software suit [19]. A ratio of the calculated intensities $(I_{1st}/I_{2nd})_{cal}$ is 0.71, and that of the experimental intensities $(I_{1st}/I_{2nd})_{exp}$ is 0.49. The experimental results are semi-quantitatively consistent with the calculations. Furthermore, we obtained the temperature dependence of the intensity as $(I_{40K}/I_{15K})_{cal} = 0.93$ by calculating $p_n$s at 40 K and 15 K by assuming that the initial state was the ground state. The small temperature dependence is
consistent with the data in Fig. 2(b). The observed excitations are, thus, interpreted as the first and second excited states of the Nd$^{3+}$ crystal field.

It is noted that the peak at 8.5 meV is broader than the peak at 17.4 meV in Fig 2(b). This broadening was also reported in the optical spectroscopy [11]. It is known that a spectrum of the crystal field excitation is broadened by coupling of phonon [20] and dynamic Jahn-Teller effect [21, 22]. This broadening of the peak is ascribed to an interaction between the Nd$^{3+}$ moment and lattice vibration since the magnetoelastic coupling was observed in NdFe$_3$(BO$_3$)$_4$ [3].

4. Conclusion
The INS measurements were performed on the single crystals NdFe$_3$(BO$_3$)$_4$ to explore the Nd$^{3+}$ crystal field excitations. In addition to the Fe-centered spin waves previously reported, dispersionless excitations are observed at 8.5 meV and 17.4 meV. Our analysis reveals that they are the transitions from the ground state to the first and second excited states of the Nd$^{3+}$ ion in the crystal field.

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