Investigation of the Magnetic Model in Multiferroic \( \text{NdFe}_3(\text{BO}_3)_4 \) by Inelastic Neutron Scattering

S. Hayashida\(^1\), M. Soda\(^1\), S. Itoh\(^2\), T. Yokoo\(^2\), K. Ohgushi\(^3\), D. Kawana\(^1\), H. M. Rønnow\(^{1,4}\) and T. Masuda\(^1\)

\(^1\)Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, Tokai, Ibaraki 319-1106, Japan
\(^2\)Neutron Science Division, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan
\(^3\)Department of Physics, Tohoku University, Sendai, Miyagi 980-8581, Japan
\(^4\)Laboratory for Quantum Magnetism, École Polytechnique Fédérale Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(Dated: July 23, 2015)

We performed inelastic neutron scattering measurements on single crystals of \( \text{NdFe}_3(\text{BO}_3)_4 \) to explore the magnetic excitations, to establish the underlying Hamiltonian, and to reveal the detailed nature of hybridization between the \( 4f \) and \( 3d \) magnetism. The observed spectra exhibiting a couple of key features, i.e., anti-crossing of Nd- and Fe-excitations and anisotropy gap at the antiferromagnetic zone center, are explained by the magnetic model including spin interaction in the framework of weakly-coupled \( \text{Fe}^{3+} \) chains, interaction between the \( \text{Fe}^{3+} \) and \( \text{Nd}^{3+} \) moments, and single-ion anisotropy derived from \( \text{Nd}^{3+} \) crystal field. The combination of the measurements and calculations reveals that the hybridization between \( 4f \) and \( 3d \) magnetism propagates the local magnetic anisotropy of the \( \text{Nd}^{3+} \) moment to the \( \text{Fe}^{3+} \) network, leading to the determination of the bulk structure of both electric polarization and magnetic moment in the multiferroics of the spin-dependent metal-ligand hybridization type.

PACS numbers: 75.10.Dg, 75.25.-j, 75.85.+t

I. INTRODUCTION

Coexistence of magnetic order and electric polarization, \textit{multiferroicity}, has become a major topic over the past decade in condensed matter physics. Since multiferroicity was originally discovered in perovskite \( \text{TbMnO}_3 \) various multiferroic compounds have been found, including \( \text{RMnO}_3 \) (\( R = \text{Eu}, \text{Gd}, \text{ Tb}, \text{ and Dy} \))\(^{24}\), \( \text{Ba}_0.5\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_2\text{O}_{22} \)\(^3\), \( \text{Ni}_3\text{V}_2\text{O}_8 \)\(^4\), \( \text{CoCr}_2\text{O}_4 \)\(^5\), \( \text{MnWO}_4 \)\(^6\), \( \text{CuFe}_2\text{O}_2 \)\(^7\), \( \text{LiCu}_2\text{O}_2 \)\(^8\), \( \text{LiCuVO}_4 \)\(^9\), and \( \text{Ba}_2\text{CoGe}_2\text{O}_7 \)\(^10\). Recent theoretical and experimental studies revealed that the electric polarization in these compounds is driven by magnetic long-range order\(^{11–13}\). Since the structure of the order is determined by the exchange pathways and the magnetic anisotropy, experimental identification of the magnetic Hamiltonian is very important for understanding multiferroics.

The rare-earth ferroborates \( \text{RFe}_3(\text{BO}_3)_4 \) (\( R = \text{rare-earth metal} \)) are a series of new multiferroic compounds containing \( \text{R}^{3+} \) (\( 4f^n \)) and \( \text{Fe}^{3+} \) (\( 3d^6 S = 5/2 \)) as magnetic ions. The variety of the anisotropy of the \( \text{R}^{3+} \) moments (\( R = \text{Y}, \text{ Pr}, \text{ Nd}, \text{ Sm}, \text{ Gd} \) and \( \text{Tb} \)) combined with the interaction between the \( \text{Fe}^{3+} \) and \( \text{R}^{3+} \) moments (\( f-d \) coupling) gives rise to diverse magnetoelectric (ME) effects as a function of the \( \text{R}^{3+} \) ions\(^{14–21}\). In these systems the mechanism of magnetoelectricity is explained by the spin-dependent metal-ligand hybridization model\(^{22,23}\).

The crystal structure has the trigonal space group \( \text{R}3\text{c} \), which belongs to the structural type of the mineral huntite \( \text{CaMg}_3(\text{CO}_3)_4 \)\(^{24}\). As shown in Fig. (a) the main feature is that distorted \( \text{FeO}_6 \) octahedra form spiral chains with threefold screw-axis symmetry along the crystallographic \( c \)-axis. Each chain includes three \( \text{Fe}^{3+} \) ions in the unit cell. The chains are separated by the \( \text{R}^{3+} \) and \( \text{B}^{13+} \) ions.

In \( \text{NdFe}_3(\text{BO}_3)_4 \) the \( \text{Nd}^{3+} \) ions (\( 4f^3 \)) carry magnetic moment with \( J = 9/2 \). The magnetic susceptibility showed anisotropic decrease below 29 K, and the heat capacity showed well-defined \( \lambda \) type anomaly at the same temperature, implying a phase transition to an antiferromagnetic (AF) ordered state with Néel temperature of \( T_N = 29 \text{ K} \). At \( T \geq T_N \) the susceptibility is concave downward, indicating the short-range AF order because of the low dimensionality of the magnetic system. Spontaneous electric polarization simultaneously appears in the AF ordered phase\(^{20}\). The electric polarization significantly increases upon applying a magnetic field parallel to the \( a \)-axis. The magnitude of the electric polarization reaches \( P_a \sim 300 \mu \text{C/m}^2 \) at 1.3 T and 4.2 K\(^{17,18}\), which means that the magnetization along the \( a \)-axis induces the large electric polarization along the \( a \)-axis. A neutron diffraction study exhibited an easy-plane type AF order at \( T \leq T_N \); the \( \text{Fe}^{3+} \) and \( \text{Nd}^{3+} \) magnetic moments align ferromagnetically along the \( a \)-axis and propagate antiferromagnetically along the \( c \)-axis with the propagation vector \( \textbf{k} = (0, 0, 3/2) \) in Fig. (a)\(^{26,27}\). Both of \( \text{Fe}^{3+} \) and \( \text{Nd}^{3+} \) moments are simultaneously ordered at the \( T_N \), indicating non-negligible \( f-d \) coupling. Further decreasing the temperature at \( T \leq T_{IC} = 13.5 \text{ K} \), the commensurate (C) magnetic peak splits into a pair of incommensurate (IC) peaks where the magnetic moments are in the \( ab \)-plane and the AF helix propagates along the \( c \)-axis.

Magnetic dynamics have been investigated by spectroscopic methods using electromagnetic waves. ESR mea-
FIG. 1: (Color online) (a) The crystal structure and magnetic structure of NdFe₃(BO₃)₄ (hexagonal, space-group R32). (b) Laue image of a crystal with the c∗-axis parallel to the incident X-ray beam. Crystals of NdFe₃(BO₃)₄ on the aluminia holder viewed from above (c) and from the side (d). (e) Reciprocal space in the a∗-c∗ plane. The square at (h, k, l) = (−1, 0, −1) is a nuclear Bragg reflection. The circle at (0, 0, −1.5) is a magnetic Bragg reflection. Red curves indicate spectra measured with k//a∗ for ℏω = 0, 1 and 3 meV. The blue shaded area indicates the range of the observed scattering plane for k//a∗ = 2.352 Å⁻¹ and ℏω = 0 meV when sample is rotated.

Measurement detected an energy gap suggesting a uniaxial magnetic anisotropy in the ab-plane. It also detected lifting of the Kramers doublet of the Nd³⁺ ion due to the molecular field from the neighboring Fe³⁺ ions. Optical spectroscopy provided the energy levels of the crystal field of the Nd³⁺ ion and determined the parameters of the crystal field Hamiltonian. In NdFe₃(BO₃)₄ exhibiting the strong f-d coupling, the investigation of excitation spectra including Fe³⁺ spin wave and Nd³⁺ crystal field in a wide wave-vector energy space is crucial in order to identify the magnetic Hamiltonian and to unravel the detailed nature of hybridization between 3d and 4f magnetism. Furthermore in constructing the Hamiltonian, careful consideration of magnetic anisotropy is important in the multiferroics of the spin-dependent metal-ligand hybridization mechanism type, in which the magnetic anisotropy directly determines the polarization structure.

In the present paper we study inelastic neutron scattering (INS) spectra on NdFe₃(BO₃)₄ to explore the magnetic excitations and to establish the underlying Hamiltonian. Following to the introduction we describe the experimental details about the sample preparation and the setup of INS measurements in Sec. II. Subsequently in Sec. III the INS spectra of NdFe₃(BO₃)₄ are demonstrated. We observed spin waves of the Fe³⁺ moment below 6 meV and transition between the lifted states of Kramers doublet of the Nd³⁺ ion at 1 meV. A couple of characteristic features are an anti-crossing of the Fe- and Nd-excitations, and a small anisotropy gap at the antiferromagnetic zone center. In Sec. IV the magnetic model including an in-plane anisotropy derived from the crystal field excitation of the Nd³⁺ moment and the non-negligible f-d coupling is constructed. The observed spectra are successfully analyzed by the linear spin wave theory based on the model. The origin of the in-plane anisotropy is revealed to be the crystal field of the Nd³⁺ ion. In Sec. V possibility of magnetic anisotropy of the
Fe$^{3+}$ moment is discussed. It is turned out that the anisotropy is very small, and, instead, the Fe$^{3+}$ moment inherits an in-plane anisotropy through hybridization with the Nd$^{3+}$ moment. The conclusions are given in Sec. VI. The magnetic Hamiltonian in NdFe$_3$(11BO$_3$)$_4$ is established in the present study. Combination of the measurement and the detailed calculation revealed that the hybridization between $4f$ and $3d$ magnetism propagates the local magnetic anisotropy of the Nd$^{3+}$ ion to the Fe$^{3+}$ network, resulting in the bulk structure of multiferroics. The local symmetry of the rare-earth ion is a driving force for the non-local multiferroicity in NdFe$_3$(11BO$_3$)$_4$.

II. EXPERIMENTAL DETAILS

Single crystals of NdFe$_3$(11BO$_3$)$_4$ were grown by a flux method. We first synthesized polycrystalline samples from the starting materials, Nd$_2$O$_3$, Fe$_2$O$_3$, and $^{11}$B$_2$O$_3$. The stoichiometric amounts of the starting materials with a total mass of about 16 g were mixed, ground, and put into an alumina crucible. The crucible was heated at 980 °C for 72 h. The flux is Bi$_2$MoO$_6$ $+$ 3 $^{11}$B$_2$O$_3$ $+$ 3/5 Nd$_2$O$_3$; Bi$_2$MoO$_6$ was synthesized by the solid state reaction from Bi$_2$O$_3$ and MoO$_3$ inside an alumina crucible at 600 °C for 24 h. A mixture of about 60 g of NdFe$_3$(11BO$_3$)$_4$ and the flux with the mass ratio of 1 : 3 was put into a platinum crucible inside the alumina crucible. The crucible was heated to 1000 °C for 4 h, kept at this temperature for 1 h, cooled to 962 °C for 1 h, and slowly cooled down to 870 °C for 120 h; then the furnace was shut down to the room temperature. The flux was removed by decanting at 900 °C, and washing the crystals with HCl solutions.

We coaligned 22 pieces of single crystals so that the crystallographic $a^*$ - $c^*$ plane is horizontal. Alignment was performed by transmission Laue method using a high energy X-ray Laue camera. The X-ray source was YXLON MG452 and the maximum energy of the white X-ray beam was 310 keV. We recorded Laue patterns using a high-speed CCD camera, with imaging size 10 cm x 10 cm (1024 x 1024 pixel). Figure (b) shows a Laue image of a crystal in the $c^*$ - plane. This pattern exhibits the threefold symmetry along the $c^*$ - axis. We placed the crystals on an alumina holder as shown in Figs. (c) and (d). The average mass of the crystals was 0.1 g. The total mass of the sample was 2.1 g.

The INS experiment was performed at the High Resolution Chopper Spectrometer (HRC) installed in the Material and Life Science Experimental Facility of J-PARC. At the HRC white neutrons are monochromatized by a Fermi chopper synchronized with the production timing of the pulsed neutrons. The energy transfer
$h\omega$ was determined from the time of flight (TOF) of the scattered neutrons detected at position sensitive detectors (PSDs). The $T_0$ chopper was set at 50 Hz, a collimator of $1.5^\circ$ 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 41 K and 15 K. The energy of the incident neutron beam was $E_i = 11.46$ meV yielding an energy resolution of $\Delta E = 0.3$ meV at the elastic position.

Figure 1(e) illustrates the $a^*$ - $c^*$ scattering plane. Reciprocal lattice positions at $q = (-1,0,-1)$ and $(0,0,-1.5)$ are the positions of nuclear and magnetic Bragg peaks, respectively. Throughout this paper $q$ is expressed in reciprocal lattice unit, $q = (h,k,l)$. INS spectra with $k_{||} / a^*$ were measured at 41 K and 15 K. Red curves in Fig. 1(e) indicate the measured $q$-ranges for $h\omega = 0,1$ and 3 meV. At 15 K INS spectra that cover wide $q$-range were measured by rotating the crystal by 70 degree in 2 degree steps. The $q$-range in the scan for $h\omega = 0$ meV is indicated by the blue shaded area in Fig. 1(e). The range of out of plane momentum is $q_{||} < 0.41$ Å$^{-1}$. In the following, the out of plane spectra are integrated in the central range $q_{||} < 0.13$ Å$^{-1}$, and we show all spectra in the $(h,0,l)$ plane.

### III. EXPERIMENTAL RESULTS

The INS spectra projected onto the $c^*$ - axis at 41 K and 15 K are shown in Figs. 2(a) and 2(b), respectively. At 41 K a diffuse spectrum of paramagnetic scattering emerges from $l = -1.5$. At 15 K dispersive excitations emerge in the energy range of $2.5$ meV $< h\omega < 4.5$ meV, which is interpreted as spin waves of the Fe$^{3+}$ moments.

Figures 3(a)-3(d) display neutron spectra at 15 K sliced at the energies of 0, 1, 2, and 3 meV in the $a^*$ - $c^*$ plane. The white arcs are because of the absence of the neutron detectors between the detector banks. In Fig. 3(a) the peak at $q = (-1,0,-1)$ is a nuclear Bragg reflection, and the peak at $(0,0,-1.5)$ is a magnetic Bragg reflection. The peaks at other $qs$ are not identified; they may be Bragg reflection from minor grains of crystals. The rings expanding from $(0,0,-1.5)$ in Figs. 3(b)-3(d) imply that a dispersive excitation appears from $(0,0,-1.5)$. The rings are flattened along the $c^*$ - axis, which means that the dispersion along the $c^*$ - axis is steeper than that along the $a^*$ - axis. This is consistent with the naive prediction from the crystal structure that the intrachain interaction along the $c$ - axis is strong compared with the interchain interaction.

The INS spectrum at 15 K projected onto $h\omega - (0,0,l)$ plane by the integrating the neutron intensity in the ranges of $-0.1a^* \leq q \leq 0.1a^*$ along the $a^*$ direction in the scattering plane and $-0.17a^* \leq q \leq 0.17a^*$ perpendicular to the scattering plane is shown in Fig. 3(a). The spectrum projected onto $h\omega - (h,0,-1.5)$ plane by the integration in the ranges of $-0.17a^* \leq q \leq 0.17a^*$ perpendicular to the scattering plane and $-1.6c^* \leq q \leq -1.4c^*$ along the $c^*$ direction is shown in Fig. 3(b). We clearly observed the spin waves of the Fe$^{3+}$ moments around $q = (0,0,-1.5)$, and the flat excitation at about 1.0 meV which is the transition between the lifted states of Kramers doublet of the Nd$^{3+}$ ion. The spin waves of the Fe$^{3+}$ moments are more dispersive along the $c^*$ direction than along the $a^*$ direction, which is consistent with the flattened ring in Figs. 3(b)-3(d).

A series of $h\omega$ dependence of the neutron intensity obtained by the integration in the same $q$-ranges that were used for the display of Figs. 3(a) and 3(b) were fitted by Gaussian functions to investigate the detailed structures of the excitations. The peak energies were plotted as open circles in Figs. 4(a) and 4(b). These data will be used in the analysis section. The white circles around $q = (0,0,-1.5)$ exhibit an anti-crossing between the spin wave of the Fe$^{3+}$ moments and the flat mode of the Nd$^{3+}$ moments, meaning that the Fe$^{3+}$ moments interact with the Nd$^{3+}$ moments.

Figure 5(a) shows the $h\omega$ dependence of the neutron

![Figure 4](image4.png)

**FIG. 4:** (Color online) Color maps of the inelastic neutron scattering spectra obtained at HRC, along the (a) $l$ and (b) $h$ directions at 15 K. The open circles are the peak positions extracted Gaussian fits and the curves are the calculated spin wave dispersions. Fitting curves reasonably reproduce the experimental data. White area in the middle in the panel (a) is the gap between neutron detectors banks.
intensity obtained by the integration in the \( q \)-range of \( h = [-0.5, 0] \) and \( l = [-1, -0.7] \). The solid curve is fit to the data by Gaussian functions. (b) Constant-\( Q \) scan at \((0, 0, -1.5)\). The spectra were integrated in the range of \( h = [-0.1, 0.1] \) and \( l = [-1.6, -1.4] \). The error bars are inside the symbols. The solid curves are fits to the data by Gaussian functions. The gray shaded areas are the energy resolutions. From the peak position we identify the magnitude of the energy split of the Kramers doublet to be 0.98 meV. Figure 5(b) shows a constant-

The magnitude of the energy gap at the AF zone center of an anisotropy in the \( Fe^3^+ \) ion. The peak energies of the Nd\( ^{3+} \) modes. In Eq. (1), positive

IV. ANALYSIS

In order to identify the magnetic model realized in NdFe\(_3\)(BO\(_3\))\(_4\), we consider the following Hamiltonian:

\[
\mathcal{H} = -\sum_{n.n.} J_1 \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{n.n.n.} J_2 \mathbf{S}_i \cdot \mathbf{S}_j
- \sum_{n.n.} J_3 \mathbf{S}_i \cdot \mathbf{J}_k + \sum_{k} \mathcal{H}_{CF}(\mathbf{J}_k),
\]

where the \( x \)-axis is parallel to the crystallographic \( a \)-axis and the \( z \)-axis is parallel to the \( c \)-axis. \( J_1 \) and \( J_2 \) are the exchange interactions in the nearest and 2nd nearest neighbor paths of the \( Fe^3^+ \) ions as shown in Figs. 6(a) and 6(b). These terms mainly determine the dispersions along the \( c^* \)-axis and \( a^* \)-axis, respectively. \( J_3 \) is the nearest neighbor exchange interaction between the \( Fe^3^+ \) and Nd\( ^{3+} \) moments, which induces the anti-crossing between the \( Fe^3^+ \) and Nd\( ^{3+} \) modes. In Eq. (1), positive

FIG. 5: (Color online) (a) \( \hbar \omega \) dependence of the neutron intensity that is obtained by the integration in the \( q \)-range of \( h = [-0.5, 0] \) and \( l = [-1, -0.7] \). The solid curve is fit to the data by Gaussian functions. (b) Constant-\( Q \) scan at \((0, 0, -1.5)\). The spectra were integrated in the range of \( h = [-0.1, 0.1] \) and \( l = [-1.6, -1.4] \). The error bars are inside the symbols. The solid curves are fits to the data by Gaussian functions. The gray shaded areas are the energy resolutions: Gaussian functions with full width at half maximum of 0.3 meV.

FIG. 6: (Color online) Exchange paths in NdFe\(_3\)(BO\(_3\))\(_4\). \( J_1 \) and \( J_2 \) are the nearest and 2nd nearest neighbor exchange interactions between the \( Fe^3^+ \) moments. \( J_3 \) is the nearest neighbor exchange interaction between the \( Fe^3^+ \) and Nd\( ^{3+} \) moments. The \( x \)-axis is parallel to the \( a \)-axis and the \( z \)-axis is parallel to the \( c \)-axis. The \( y \)-axis is vertical to the \( x \) and \( z \)-axis.
(negative) signs of the exchange parameters correspond to ferromagnetic (antiferromagnetic) exchange interactions. \( H_{\text{CF}} \) is the crystal field Hamiltonian of the Nd\(^{3+}\) ion.

There are five Kramers doublelets in the crystal field of the Nd\(^{3+}\) ion above \( T_N = 30\) K. The first excited energy is about 8 meV, and second one is about 17 meV as reported in Ref. 29. In the calculation of the low-energy excitations below 6 meV it is assumed that only the ground state in the crystal field of the Nd\(^{3+}\) ion hybridizes with the Fe\(^{3+}\) moments. For this assumption, we introduce the ground state of the crystal field of the Nd\(^{3+}\) ion.

At the Nd\(^{3+}\) site with \( D_3 \) symmetry, the crystal field Hamiltonian can be defined as follow:

\[
H_{\text{CF}} = B_6^C C_6^6 + B_0^C C_0^6 + iB_3^C (C_3^6 + C_{-3}^6) \\
+ B_0^C C_0^6 + iB_3^C (C_3^6 + C_{-3}^6) + B_0^C (C_0^6 + C_{-6}^6).
\]

(2)

The \( B_p \) are the crystal field parameters and the \( C_p \) are the spherical tensor operators. We used the values of the parameter \( B_p \) reported in Ref. 29. Matrix elements of \( J^x, J^y, \) and \( J^z \) in the ground state doublet \( |g\pm\rangle \) are as follow:

\[
\begin{align*}
\langle g_\pm | J^x | g_\pm \rangle = -1.67 \equiv \frac{\beta}{2}, \\
\langle g_\pm | J^y | g_\pm \rangle = \frac{\pm \beta}{2}i, \\
\langle g_\pm | J^z | g_\pm \rangle = \mp 0.98 \equiv \frac{\alpha}{2}, \\
\langle g_\pm | J^z | g_\mp \rangle = (g_\pm | J^y | g_\mp) = (g_\mp | J^x | g_\pm) = 0,
\end{align*}
\]

meaning that the total angular momentum is anisotropic, favoring in-plane. Next we inspect anisotropy within the \( ab \)-plane. The quantization axis is transformed from the \( z \)-axis to the \( x \)-axis because the direction of the spin in the order state is along the \( x(a) \)-axis. Then, the matrix elements of \( J^x, J^y, \) and \( J^z \) in the redifined state \( |g'_\pm\rangle \) are calculated as follow:

\[
\begin{align*}
\langle g'_\pm | J^x | g'_\pm \rangle = \frac{\beta}{2}, \\
\langle g'_\pm | J^y | g'_\pm \rangle = \frac{-\beta}{2}i, \\
\langle g'_\pm | J^z | g'_\pm \rangle = \frac{-\alpha}{2}, \\
\langle g'_\pm | J^z | g'_\mp \rangle = (g'_\pm | J^y | g'_\mp) = (g'_\mp | J^x | g'_\pm) = 0.
\end{align*}
\]

The operator \( B_6^C (C_6^6 + C_{-6}^6) \) leads to an anisotropy within the \( ab \)-plane. In order to quantify this, we express the total angular momentum of the Nd\(^{3+}\) ion in the ground state doublet as

\[
J^x = \frac{\beta}{2} \cos \theta, \quad J^y = \frac{\beta}{2} \sin \theta,
\]

(5)

where \( \theta \) is the angle between the \( a \)-axis and the moment. Thus classical energy of \( B_6^C (C_6^6 + C_{-6}^6) \) becomes

\[
B_6^C (C_6^6 + C_{-6}^6) = \frac{\sqrt{231}}{16} B_6^C \gamma J \left( \frac{\beta}{2} \right)^6 \cos 6\theta,
\]

(6)

where \( \gamma J = -3.80 \times 10^{-5} \) is a Stevens’ factor. Eq. (6) means that the classical energy of the crystal field gives a six-fold anisotropy. Since the sign of the \( B_6^C \gamma J \) is negative, the easy-axis is the \( a \)-axis that is consistent with the magnetic structure 26. The magnitude of the calculated anisotropy energy is 65.2 \( \mu \)eV. We effectively include the six-fold anisotropic energy as \( -D (J^x)^2 \) in the Hamiltonian Eq. (11). The coefficient \( D \) is 23.5 \( \mu \)eV, which is defined by the relation:

\[
-D \left( \frac{\beta}{2} \right)^2 = \frac{\sqrt{231}}{16} B_6^C \gamma J \left( \frac{\beta}{2} \right)^6 \times 2 = 65.2 \ \mu \text{eV}.
\]

(7)

Next the operators of total angular momentum \( J \) are approximated as the operators of pseudo-spin \( s = 1/2 \) because the ground state is Kramers doublet and the degree of freedom is two. The connection between operators of the total angular momentum \( J \) and the pseudo-spin \( s \) is determined by the matrix elements Eq. (11). In this approximation the operators of the total angular momentum is redefined as

\[
J^x = \beta s^x, \quad J^y = \beta s^y, \quad J^z = \alpha s^z.
\]

(8)

The Hamiltonian Eq. (11) is, thus, represented by

\[
H = - \sum_{\text{n.n.}} J_1 S_i \cdot S_j - \sum_{\text{n.n.n.}} J_2 S_i \cdot S_j \\
- \sum_{\text{n.n.}} J_3 S_i \left \{ \frac{\beta \gamma \gamma_j}{\alpha s_k} - \sum_k D (\beta s_k)^2 \right \}.
\]

(9)

We subsequently calculate the spin wave spectrum of this Hamiltonian using Holstein-Primakoff (HP) transformations. The HP transformations of the spin operators of the Fe\(^{3+}\) moments and the pseudo-spin operators of the Nd\(^{3+}\) moments are written as

\[
S_i^x = S - a_i^\dagger a_i, \quad S_i^y = \sqrt{\frac{S}{2}} (a_i^\dagger + a_i), \quad S_i^z = \sqrt{\frac{S}{2}} (a_i^\dagger - a_i),
\]

(10)

\[
s_i^x = s - b_i^\dagger b_i, \quad s_i^y = \sqrt{\frac{s}{2}} (b_i^\dagger + b_i), \quad s_i^z = -\sqrt{\frac{s}{2}} (b_i^\dagger - b_i).
\]

(11)

The \( a_i^\dagger, a_i, b_i^\dagger \) and \( b_i \) bosons operator in each sublattices. The quantization axis is parallel to the \( x(a) \)-axis. We introduce spatial Fourier transformation via

\[
c_i^\dagger (q) = \frac{1}{\sqrt{N}} \sum_\mathbf{r_i} c_i^\dagger e^{-i\mathbf{q} \cdot \mathbf{r_i}} \quad (i = 1 \sim 24),
\]

(16)
where \( N \) is the number of unit cells in the system, and \( \{c_i\} = \{a_i, b_i\} \) are the bosons operators on each sublattice. By using this notation we obtain

\[
\mathcal{H} = \sum \sum_{q} A_{ij}(q)c_i^\dagger(q)c_j(q) + \frac{1}{2} \sum_{ij} \left[ B_{ij}(q)c_i^\dagger(q)c_j^\dagger(q) + \text{h.c.} \right]. \tag{17}
\]

The eigenvalues of the matrix \((A + B) (A - B)\) give the squares of the energy of the normal modes\(^{34}\).

\[
(A + B) (A - B) \chi_\alpha(q) = \{\hbar \omega(q)\}^2 \chi_\alpha(q). \tag{18}
\]

The dispersions obtained from this calculation are indicated by the yellow solid curves in Figs. 3(a) and 4(b). In fact we obtained 24 modes of spin waves, but due to the trigonal symmetry of the lattice only 8 modes have non-zero spectral weight. The modes at the highest and second-highest energies around the AF zone center, \(q = (0, 0, -1.5)\), in Fig. 3(a) are two-fold degenerated, and the highest energy mode in Fig. 4(b) is four-fold degenerated. The in the zone center, there are two modes at \(\hbar \omega = 1.12\) meV and 1.23 meV, and another two modes at \(\hbar \omega = 0.32\) meV and 0.61 meV. The 0.32 meV gap is caused by the anisotropy of the Nd\(^{3+}\) moment in the \(ab\) plane. It vanishes if the \(D\) is set to zero. The modes at 1.12 meV and 1.23 meV is the Nd\(^{3+}\) level after hybridizing with the dispersive Fe\(^{3+}\) spin waves. The small splittings of both modes are due to the easy-plane type anisotropy of the Nd\(^{3+}\) ion, i.e., the effect of \(\alpha \neq \beta\). These splittings are the origin of the observed broadenings of the experimental peaks in Fig. 3(b). White circles in Figs. 3(a) and 4(b) are fit by the mean energy of the split modes. \(\chi_\alpha^2\) were calculated for the parameter set with the step sizes of \(\delta J_1 = 0.001\) meV, \(\delta J_2 = 0.001\) meV, and \(\delta J_3 = 0.1\) meV in the ranges of \(|J_1| \leq 1\) meV, \(|J_2| \leq 1\) meV, and \(|J_3| \leq 0.1\) meV. The obtained parameters set for the minimum \(\chi_\alpha^2\) is listed in Table I. The fit to the data provides excellent agreement with the overall spectrum. It should be noted that the anisotropy gap of about 0.57 meV at the zone center is quantitatively reproduced by using the fixed parameter of \(D = 23.5\) meV obtained from reported value of the parameter \(B_{ij}^{6,22}\). It is revealed that the origin of the in-plane anisotropy is the crystal field of the Nd\(^{3+}\) ion.

V. DISCUSSION

In \(\text{RFe}_2(\text{BO}_3)_4\), the magnitude of the electric polarization by the \(\text{R}^{3+}\) and Fe\(^{3+}\) ions are locally determined by the magnetic moments.\(^{22,23}\) In case of NdFe\(_2\)(BO\(_3\))\(_4\) the existence of the in-plane anisotropy favoring order along the \(a\)-axis by the Nd\(^{3+}\) and/or Fe\(^{3+}\) ions is a key to the emergence of the multiferroicity. In the analysis section, uniaxial anisotropy of the Fe\(^{3+}\) moments is not considered for the simplicity. In this section, we discuss possible magnetic anisotropies in the \(ab\)-plane of the Fe\(^{3+}\) moments.

The conventional origin of anisotropy in Fe\(^{3+}\)-based magnets is magnetic-dipole interaction or single-ion anisotropy. The magnetic-dipole interaction between spins \(S_i\) and \(S_j\) is represented by

\[
\mathcal{H}_{\text{dip}} = \sum_{i,j} \frac{(g\mu_B)^2}{r_{ij}^3} \{S_i \cdot S_j - 3 (S_i \cdot e_{ij})(S_j \cdot e_{ij})\}, \tag{19}
\]

where \(r_{ij}\) and \(e_{ij}\) are respectively the distance and the unit vector along the bond between \(i\) and \(j\). For a collinear in the \(ab\)-plane, the dipole-interaction energy is independent of the angle to the \(a\)-axis. This is due to the threefold screw-axis symmetry along the \(c\)-axis, which also dictates that further neighbor interactions vanish. Thus, the magnetic-dipole interaction is not the origin of the anisotropy in the \(ab\)-plane.

Next, we consider the single-ion anisotropy of the Fe\(^{3+}\) moments. There is only one inequivalent site for the Fe\(^{3+}\) ion and the local anisotropy is uniquely determined. Since the screw axis \(S_1\) or \(S_2\) is along the Fe\(^{3+}\) chain, the FeO\(_6\) octahedra are transformed by \(2\pi/3\) rotation around the \(c\)-axis one another. Therefore, three local coordinates, \(\{X_i, Y_i, Z_i\}\), can be defined on the FeO\(_6\) octahedra for the anisotropy. Here \(\{i = 1, 2, 3\}\) are the labels of the Fe\(^{3+}\) sites. Since the Fe\(^{3+}\) moments are collinear in the \(ab\)-plane, we discuss the anisotropy only in the \(ab\)-plane. Then, the general single-ion anisotropy to 4th order in the Fe\(^{3+}\) spin-operators is expressed by

\[
\mathcal{H}_{\text{aniso}} = \sum_{i=1,2,3} \left[ a_{x^2} \left(S_i^{X_i}\right)^2 + a_{y^2} \left(S_i^{Y_i}\right)^2 + a_{xy} S_i^{X_i} S_i^{Y_i} \right. \nonumber \\
+ \left. a_{x^4} \left(S_i^{X_i}\right)^4 + a_{y^4} \left(S_i^{Y_i}\right)^4 \right] + a_{x^2y^2} S_i^{X_i} \left( S_i^{Y_1}\right)^2 + a_{x^2y^2} S_i^{X_i} \left( S_i^{Y_1}\right)^3. \tag{20}
\]

The \(a_{x^2}, a_{y^2}, a_{xy}, a_{x^4}, a_{y^4}, a_{x^2y^2}, a_{x^2y^2}, a_{x^2y^3}\), and \(a_{x^2y^3}\) are independent coefficients. Here we define the the local coordinate \(\{X_1, Y_1, Z_1\}\) as the same as the global one \(\{x, y, z\}\). Then the relation between the spin operators defined on the local coordinates \(\{X_2, X_3, Y_2, Y_3, Z_2, Z_3\}\) and the

| \(J_1\) [meV] | \(J_2\) [meV] | \(J_3\) [meV] | \(D\) [meV] (fixed) | \(\chi_\alpha^2\) |
|---|---|---|---|---|
| 23.5 | 0.993 |
those defined on the global one is as follows:

\[
\begin{align*}
S^x_2 &= -\frac{1}{2}S^x_0 + \frac{\sqrt{3}}{2}S^y_0, \\
S^y_2 &= -\frac{\sqrt{3}}{2}S^x_0 - \frac{1}{2}S^y_0, \\
S^z_2 &= S^z_0,
\end{align*}
\tag{21}
\]

where the \(x\) - axis is parallel to the crystallographic \(a\) - axis and the \(z\) - axis is parallel to the \(c\) - axis. These relations are substituted into Eq. (20) to express the single-ion anisotropy in global coordinates. Hereafter we classically calculate the anisotropy energy of the collinear AF structure in the \(ab\) - plane. The \(Fe^{3+}\) spin operators are classically expressed by

\[
\begin{align*}
(S^x_0, S^y_0, S^z_0) &= (S \cos \theta, S \sin \theta, 0), \\
(S^x_0, S^y_0, S^z_0) &= (-S \cos \theta, -S \sin \theta, 0), \\
(S^x_0, S^y_0, S^z_0) &= (S \cos \theta, S \sin \theta, 0),
\end{align*}
\tag{23}
\]

where the \(Fe^{3+}\) moments are functions of the angle \(\theta\) between the \(a\) - axis and the \(Fe^{3+}\) moments in the \(ab\) - plane. It is found that energy is independent on the angle \(\theta\). Consequently, the single-ion anisotropy does not give the anisotropy of the \(Fe^{3+}\) moment in the \(ab\) - plane.

In the multiferroic compound \(Ba_2CoGe_2O_7\) with the metal-ligand hybridization mechanism, it was reported that an interaction between the electric polarization determines the magnetic anisotropy in the easy-plane. We, hence, consider the electric-polarization interaction in \(NdFe_3(BO_3)_4\) using the mechanism, where the local electric-polarization at the \(Fe^{3+}\) site is expressed by \(p_i = f \sum_j (e_i \cdot S_j)^2 e_i\). Here \(e_i\) is a unit vector along the bond to ligands (in this case oxygen), and \(f\) is a coupling constant related with the metal-ligand hybridization and the spin-orbit interaction. The polarization interaction is represented by \(J_p \sum_{ij} p_i \cdot p_j\). \(J_p\) is ferroelectric coupling constant between the electric polarizations \(p_i\). The energy of the polarization interaction was calculated as a function of angle between the \(a\) - axis and the \(Fe^{3+}\) moments in the \(ab\) - plane. It was, then, found that the energy is independent on the direction of the \(Fe^{3+}\) moments in the \(ab\) - plane. Thus, the polarization interaction does not cause the uniaxial anisotropy in the \(ab\) - plane.

Accordingly, at the \(Fe^{3+}\) site the conventional sources of magnetic anisotropy such as the magnetic-dipole interaction and single-ion anisotropy, and the polarization interaction do not lead to the \(a\) - axis anisotropy under the restriction that the crystal symmetry is preserved. This means that the \(Fe^{3+}\) moment does not have any uniaxial anisotropy in the \(ab\) - plane unless there is any disorder which breaks the threefold rotation symmetry, for instance, lattice distortion, and quantum and thermal fluctuations. The direction of the \(Fe^{3+}\) moment, therefore, is determined by the anisotropy of the \(Nd^{3+}\) moment through the \(f-d\) coupling. It can be said that the magnetic anisotropy of the \(Nd^{3+}\) moments by the crystal field drives the multiferroicity in \(NdFe_3(BO_3)_4\).

The multiferroic mechanism of \(RFe_3(BO_3)_4\) is spin-dependent metal-ligand hybridization model, where the relation between the electric polarization and the magnetic moment is locally determined by the symmetry of \(O^{2-}\) ions around the magnetic ion. In a collinear magnetic structure the local magnetic anisotropy is a casting vote in the determination of the magnetic structure, and, consequently, in the determination of the electric polarization as well. In \(NdFe_3(BO_3)_4\) the crystal field of the \(Nd^{3+}\) ion is revealed to be the origin of the magnetic anisotropy, which determines the bulk structure of multiferroics. This is in contrast with the multiferroic materials of which the mechanism is the spin current model, where the relation is determined by the geometry of neighboring magnetic moments.

VI. CONCLUSION

We performed INS measurements to explore the magnetic excitations, to establish the underlying Hamiltonian, and to reveal the detailed nature of hybridization between the \(4f\) and \(3d\) magnetism in \(NdFe_3(BO_3)_4\). Overall spectra are reasonably reproduced by spin-wave calculation including spin interaction in the framework of weakly-coupled \(Fe^{3+}\) chains, \(f-d\) coupling, and single-ion anisotropy derived from the \(Nd^{3+}\) crystal field. Hybridization between the \(4f\) and \(3d\) magnetism is probed as anti-crossing of the \(Nd\)- and \(Fe\)-centered excitations. The anisotropy gap observed at the AF zone center is explained by the crystal field of the \(Nd^{3+}\) ion in the quantitative level. Magnetic anisotropy of the \(Fe^{3+}\) ion allowed in the present crystal structure is small so that it cannot be dominant. Combination of the measurements and calculations revealed that the hybridization between \(4f\) and \(3d\) magnetism propagates the local magnetic anisotropy of the \(Nd^{3+}\) ion to the \(Fe^{3+}\) network, resulting in the bulk magnetic structure. In the multiferroics of the spin-dependent metal-ligand hybridization type, the local magnetic anisotropy controls the electric polarization, meaning that the local symmetry of the rare-earth ion is a driving force for the non-local multiferroicity in \(NdFe_3(BO_3)_4\).

Acknowledgment

We thank H. Matsuda, and K. Asoh for their contribution to the single crystal growth. The neutron scattering experiment was approved by the Neutron Scattering Program Advisory Committee of IMSS, KEK (Proposal No.
This work was supported by KAKENHI (24340077). S. Hayashida was supported by the Japan Society for the Promotion of Science through the Program for Leading Graduate Schools (MERIT).

1 T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) 426, 55 (2003).
2 T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, Phys. Rev. Lett. 92, 257201 (2004).
3 T. Kimura, G. Lawes, and A. P. Ramirez, Phys. Rev. Lett. 94, 137201 (2005).
4 G. Lawes, A. B. Harris, T. Kimura, N. Ragdo, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. 95, 087205 (2005).
5 Y. Yamakami, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, Phys. Rev. Lett. 96, 207204 (2006).
6 K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. 97, 097203 (2006).
7 T. Kimura, J. C. Lashley, and A. P. Ramirez, Phys. Rev. B 73, 220401 (2006).
8 S. Park, Y. J. Choi, C. L. Zhang, and S-W. Cheong, Phys. Rev. Lett. 98, 057601 (2007).
9 Y. Naito, K. Sato, Y. Kobayashi, Y. Kobayashi, and M. Sato, J. Phys. Soc. Jpn. 76, 023708 (2007).
10 H. Murakawa, Y. Onose, S. Miyahara, N. Furukawa, and Y. Tokura, Phys. Rev. Lett. 105, 137202 (2010).
11 H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
12 M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006).
13 I. A. Sergienko and E. Dagotto, Phys. Rev. B 73, 094434 (2006).
14 C. Jia, S. Onoda, N. Nagaosa, and J. H. Han, Phys. Rev. B 76, 144424 (2007).
15 T. Arima, J. Phys. Soc. Jpn. 76, 073702 (2007).
16 A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, G. P. Vorob'ev, Yu. F. Popov, A. P. Pyatakov, L. N. Beznamerykh, and E. A. Popova, JETP Lett. 81, 272 (2005).
17 A. K. Zvezdin, G. P. Vorob'ev, A. M. Kadomtseva, Yu. F. Popov, A. P. Pyatakov, L. N. Beznamerykh, A. V. Kuvardin, and E. A. Popova, JETP Lett. 83, 509 (2006).
18 A. M. Kadomtseva, A. K. Zvezdin, A. P. Pyatakov, A. V. Kuvardin, G. P. Vorob'ev, Yu. F. Popov, and L. N. Beznamerykh, JETP 105, 116 (2007).
19 A. K. Zvezdin, A. M. Kadomtseva, Yu. F. Popov, G. P. Vorob'ev, A. P. Pyatakov, V. Yu. Ivanov, A. M. Kuz'menko, A. A. Mukhin, L. N. Beznamerykh, and I. A. Gudim, JETP 109, 68 (2009).
20 A. M. Kadomtseva, Yu. F. Popov, G. P. Vorob'ev, A. P. Pyatakov, S. S. Krotov, and K. I. Kamilov, Low Temp. Phys. 36, 511 (2010).
21 U. Adem, L. Wang, D. Fausti, W. Schottenhamel, P. H. M. van Loosdrecht, A. Vasiliev, L. N. Beznamerykh, B. Büchner, C. Hess, and R. Klingeler, Phys. Rev. B, 82, 064406 (2010).
22 A. I. Popov, D. I. Plokhov, and A. K. Zvezdin, Phys. Rev. B 87, 024413 (2013).
23 T. Kurumaji, K. Ohgushi, and Y. Tokura, Phys. Rev. 89, 195126 (2014).
24 J. A. Campé, C. Cascales, E. Gutiérrez-Puebla, M. A. Monge, I. Rasines, and C. Ruiz-Valerio, Chem. Mater. 9, 237 (1997).
25 N. Tristan, R. Klingeler, C. Hess, B. Büchner, E. Popova, I. A. Gudim, and L. N. Beznamerykh, J. Magn. Magn. Mater. 316, 621 (2007).
26 P. Fischer, V. Ponomjakushin, D. Sheptyakov, L. Keller M. Janoschek, B. Roessli, J. Schefer, G. Petukhovskii, L. Beznamerykh, V. Temperov and D. Velikonov, J. Phys.: Condens. Matter 18, 7975 (2006).
27 M. Janoschek, P. Fischer, J. Schefer, B. Roessli, V. Ponomjakushin, M. Meven, V. Petricek, G. Petukhovskii, and L. Beznamerykh, Phys. Rev. B 81, 094429 (2010).
28 A. M. Kuz'menko, A. A. Mukhin, V. Yu. Ivanov, A. M. Kadomtseva, and L. N. Beznamerykh, JETP Lett. 94, 294 (2011).
29 M. N. Popova, E. P. Chukalina, T. N. Stanislavchuk, B. Z. Malkin, A. R. Zakirov, E. Antic-Fidancev, E. A. Popova, L. N. Beznamerykh and V. L. Temperov, Phys. Rev. B 75, 224435 (2007).
30 L. N. Beznamerykh, S. A. Kharlamova, and V. L. Temperov Crystallogr. Rep. 49, 855 (2004), translated from Kristallografiya, 49, 945 (2004). Original Russian Text Copyright (c) 2004 by Beznamerykh, Kharlamova, Temperov.
31 S. Itoh, T. Yokoo, S. Satoh, S. Yano, D. Kawana, J. Suzuki, and T. J. Sato, Nucl. Inst. Meth. Phys. Res. A 631, 90 (2011).
32 S. Yano, S. Itoh, S. Satoh, T. Yokoo, D. Kawana, and T. J. Sato, Nucl. Inst. Meth. Phys. Res. A 654, 421 (2011).
33 S. Itoh, T. Yokoo, D. Kawana, H. Yoshizawa, T. Masuda, M. Soda, T. J. Sato, S. Satoh, M. Sakaguchi, and S. Muto, J. Phys. Soc. Jpn. 82, SA033 (2013).
34 R. Sachidanandam, T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B 56, 260 (1997).
35 M. Soda, M. Matsumoto, M. Månsson, S. Ohira-Kawamura, K. Nakajima, R. Shiina, and T. Masuda, Phys. Rev. Lett. 112, 127205 (2014).
36 E. F. Shender, Ž. Eksp. Teor. Fiz. 83, 326 (1082) (Sov. Phys. JETP 56, 178 (1982)).
37 C. L. Henley, Phys. Rev. Lett. 73, 2788 (1994).