実験報告書様式（一般利用課題・成果公開利用）

MLF Experimental Report	提出日 Date of Report 2017/07/26
課題番号 Project No. 2017A0231 実験課題名 Title of experiment Spectroscopic study on the crystalline electric field excitations in NdB_4 実験責任者名 Name of principal investigator Hiroki YAMAUCHI 所属 Affiliation Materials Sciences Research Center, JAEA	装置責任者 Name of responsible person Shin-ichi ITOH Hideki YOSHIZAWA 装置名 Name of Instrument/（BL No.） HRC (BL12) 実施日 Date of Experiment 2017.06.19 – 06.21

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

A polycrystalline powder sample of neodymium tetraborides, NdB_4, was prepared by crushing single crystals. The high-quality single crystals were grown by the floating zone method in a four-ellipsoidal mirror-type image furnace. The sample had a total mass of 10.4 g. The ^{11}B isotope enriched to 99.5% was used wherever possible to keep away from the strong neutron absorption of ^{10}B contained in natural boron. No impurity phase was observed by neutron powder diffraction experiments. The powdered sample was wrapped in a thin Al foil shaped to 3 cm (height) x 2 cm (width) x 0.8 cm (thickness) and mounted inside a standard Al can with He exchange gas. The sample can was placed inside a GM cryostat and cooled down to 3 K.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Inelastic neutron scattering (INS) measurements were performed by the time-of-flight technique using the chopper spectrometer HRC (BL12) at MLF/J-PARC. The power of the accelerator was approximately 150 kW. The rotation frequency of the Fermi chopper was 200 Hz. In the experiment, two settings for multiple incident energies of neutrons were used mainly with E_i = 51.17 meV and 11.47 meV to target a wide range of (Q, ω) space, and secondarily with E_i = 25.51 meV and 8.01 meV for better energy resolution. The energy resolutions $\Delta E/E_i$ were 1.1%, 0.55%, 0.81%, and 0.44% for incident energies described above, respectively. Data were collected at 30 K, 20 K (in the paramagnetic phase I), 9 K (in the high-temperature intermediate phase II), and 3 K (in the lowest-temperature phase IV).

The crystalline electric field (CEF) removes the ten-fold degeneracy of $4f^3$ ground multiplet of Nd^{3+} (J = 9/2), leading to five Kramers doublets under the tetragonal point symmetry. Figure 1 shows the INS spectra with E_i = 51.17 meV. The spectra are obtained by integrating the data over the Q range of 1.5–2.5 Å^{-1}. The low-energy INS spectra integrated over the Q range of 0.5–1.5 Å^{-1} are shown in FIG. 2. At 30 K, apparent peaks are observed approximately at 3.0 meV and 12.5 meV. As clearly seen in FIG. 3, these peaks show no dispersion

2. 実験方法及び結果（つづき） Experimental method and results (continued)

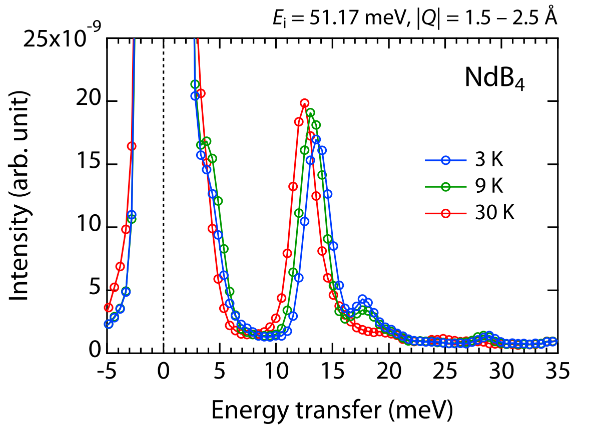

FIG. 1. INS spectra of NdB_4 with 51.17 meV incident energy neutrons at 3 K, 9 K, and 30 K.

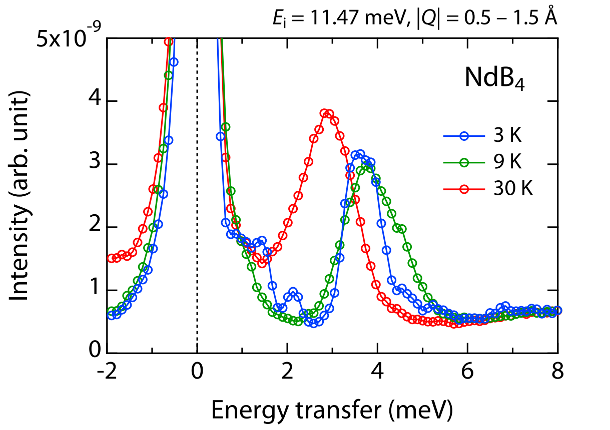

FIG. 2. Low-energy INS spectra of NdB_4 with incident energy E_i = 11.47 meV at 3 K, 9 K, and 30 K.

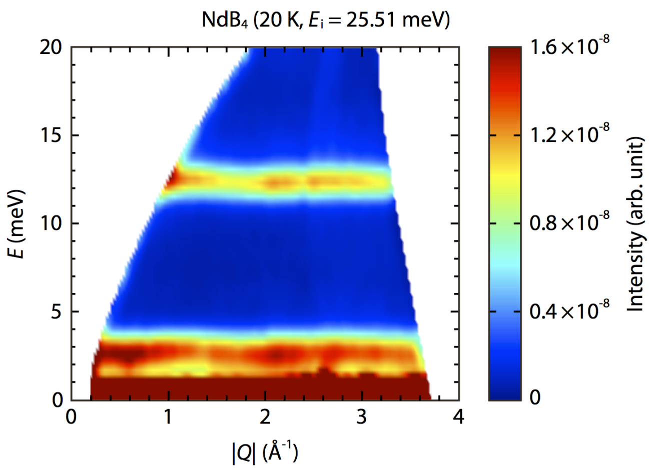

FIG. 3. Contour map of the INS intensity of NdB_4 measured with E_i = 25.51 meV at 20 K.

over the entire Q range and the intensities decrease as the Q increases, indicating CEF excitations (G–E1 and G–E2). Additionally, these two excitations show peak shifts with decreasing temperature. This behavior is also consistent with the fact that the two peaks are CEF excitations. At 9 K, new small peaks emerge around 17.5 meV and 28.5 meV without energy dispersion and increase in intensity with decreasing temperature. Thus, they are considered to be CEF excitations (G–E3 and G–E4). In conclusion, present study succeeds to reveal the CEF level scheme of 0–3.0–12.5–17.5–27.5 [meV]. This scheme can also explain the weak traces around 14.5 meV (E1–E3) and 24.5 meV (E1–E4) at 30 K. The fact that the excitation intensities of G–E3 and G–E4 in the paramagnetic state are very weak should reflect the small mixing of the wave function components in this system. On the basis of this postulation and the additional fact that the excitation intensities of G–E1 and G–E2 are very strong, we calculated the tetragonal CEF parameters B_{lm} and obtained the set of B_{20} = -0.87 [K], B_{40} = 0.071 [K], B_{60} = -0.76 [mK], and B_{44} = B_{64} = 0 [K] that roughly explained the intensity ratio and the peak position of the INS spectrum at 30 K. This result provides the existence of the pseudo-quartet ground state consisting of |5/2> and |7/2> with the small splitting of 3 meV, as the origin of the unusual physical properties of NdB_4. In the future, using these parameters as default, we will obtain the refined solution that can explain other physical quantities while taking the local symmetry of Nd^{3+} ions into account.