# MLF Experimental Report

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| 課題番号 Project No.<br>2017A0185<br>実験課題名 Title of experiment<br>Crystal field excitations of multiferroic $\beta$-$Tb_2(MoO_4)_3$<br>実験責任者名 Name of principal investigator<br>Fumihito Shikanai<br>所属 Affiliation<br>Faculty of Education, Shimane University | 提出日 Date of Report<br><br>装置責任者 Name of responsible person<br>Shinichi Itoh<br>装置名 Name of Instrument/(BL No.)<br>BL12<br>実施日 Date of Experiment<br>2017.11.09-2017.11.13 |

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.**

$\beta$-Terbium molybdate, $\beta$-$Tb_2(MoO_4)_3$. Ceramic samples of 122.57 g [φ4cm×4cm (φ9mm×4cm×19)] were wrapped in Al foil and set to a sample container (self-made) by Al wire. He gas was enclosed in an Al-can with the sample. We initially planned this experiments with a single crystal, however we could not perform it. Some high quality large single crystals were obtained by the days of the experiment, however we had no time to align the crystal

axis, because there was no device in our laboratory. Although it is an afterthought, by using a large amount of ceramic sample advised by the responsible person, we could capture the reliable data and the overall picture of the excitations of this material while maintaining psychological margin during the experiment. ,

**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.

The sample can was set to the 3K refrigerator. We measured the magnetic excitation levels at low temperature focusing on the crystal field (CF) levels under 100 meV. The inelastic data (details and $q$-dependences of the levels) and temperature dependences of them were collected with various $E_i$ using a high-resolution chopper spectrometer (HRC) in BL12 of J-PARC. $Tb_2(MoO_4)_3$ (TMO) is in multiferroic phase in all the measurement temperature, between the room-temperature and 3K, because there is no phase transition (ferroelectric phase transition 432 K, antiferromagnetic phase transition 0.45 K). In this experiment, the benefit of multi $E_i$ method is demonstrated, we could obtain the data for eight kinds of $E_i$ form 6 meV to 643 meV in a few long run measurements. Each data includes a few levels which are particularly clear in it. This indicates a forte, high-resolution of the spectrometer HRC. Figure 1 shows inelastic neutron scattering (INS) maps of TMO with $E_i$=26.3 meV at various temperature. Nondispersive excitation levels are clearly observed 5, 7, 10, and 20 meV. These levels melt with increasing temperature while a quasi-elastic neutron scattering (QENS) spectrum appears. The data of $E_i$=8.14

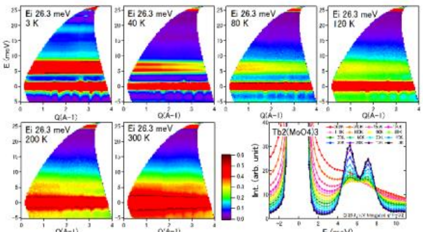

FIG.1 INS map of TMO $E_i$=26.3

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

meV simultaneously measured are shown in FIG.2. Intensity of QENS spectrum increases with decreasing temperature and of which width decreases. The result indicates that the magnetic moment of $Tb^{3+}$ which precess random at room temperature is integrated into the direction of the CF with decreasing temperature. It is predicted that the QENS spectrum will disappear above ferroelectric phase transition temperature 432K, and the magnetic moments will be ordered below antiferromagnetic phase transition temperature 0.45 K, although the temperature region were not measured in this experiment. The relaxation time at 3-10 K is estimated as 40 ps. Inverse of relaxation times obeys the Curie–Weiss law in temperature region above 100 K while the behavior in low temperature is characterized by the crystal field. However, it is necessary to perform more high-resolution experiments to confirm them.

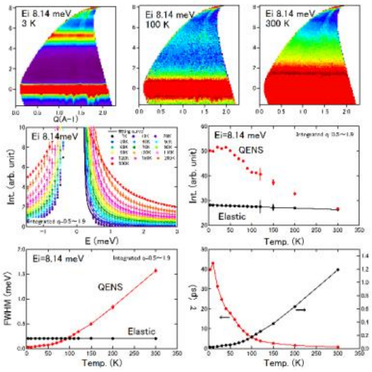

FIG.2 Analytic results of QENS

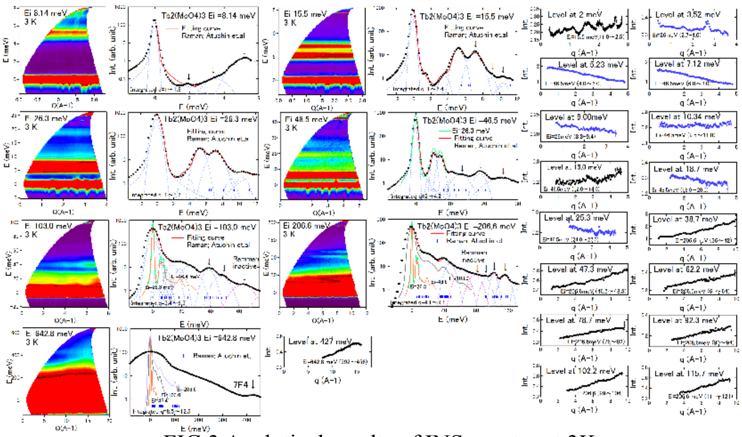

FIG.3 Analytical results of INS spectra at 3K.

To determine the other levels of CF, the data with various $E_i$ were analysed (FIG. 3). The positions of peaks founded in low Ei data (↓ in FIG. 3) were fixed, and of which width and intensity to need to refine were refined. All the widths were convoluted by that of elastic peak, and the ratio of intensities were fixed to those in low $E_i$ as much as possible. This analysis was repeated several times until convergence. The levels of 0.00, 3.52, 5.23, 7.12, 9.00,10.34, 18.7, and 25.3 meV (blue dots in FIG. 3) were assigned as the CF levels from their *q* dependences. Levels at 62.2 and 78.7 meV are the Raman inactive modes of which near energies had reported as the CF excitations in $Tb_2Ti_2O_7$, but they show opposite *q* dependence for those in TMO in FIG. 3. An excitation level $^7F_4$ ($J = 4$ of $Tb^{3+}$) can be found in the data of $E_i$=642.8 meV. To assign $2J+1$=13 CF levels to above obtained levels, the levels 0, 5.23, and 7.12 meV with strong intensity, 18.7 and 25.3 meV with wide width were assumed as the double degeneracy. CF parameters were obtained using the Hamiltonian $H_{CF}^{(C1)}$ of which degree is up to the 2*J*th order. $H_{CF}^{(C1)}$ can almost be reproduced at any level, but many candidates are obtained (FIG. 4). The parameters were refined after obtaining initial parameters from the Monte Carlo method. Because of the site symmetry at $Tb^{3+}$ in TMO is $C_1$, representation of all the crystal filed levels are A. However, actual eigen states are classified into two states which include the state $M_J$=0 (red levels in FIG.4) or not include it (blue levels in FIG.4). The levels belonging to the different representation can accidental degenerate. Currently, we are calculating and confirming the physical properties such as magnetization and specific heat under a magnetic field from the level of FIG. 4. It is predicted that there is another CF level below 1 meV which is not measured this experiment.

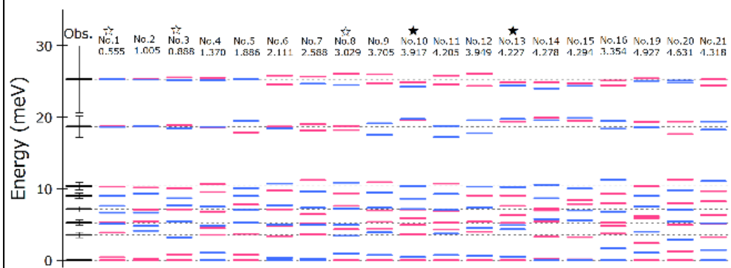


FIG. 4 Candidates of the obtained crystal field levels