

Magnetic structure of multiferroic β -Tb₂(MoO₄)₃

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1. Introduction

β -Tb₂(MoO₄)₃ (TMO) undergoes 1st order phase transition at 432 K (T_C) from tetragonal $P\bar{4}2_1m$ (Phase I) to orthorhombic $Pba2$ (Phase II) and show both ferro-electricity and -elasticity below T_C . The dielectric constant disobeys the Currie-Weiss law showing a step at T_C ^[1], while the spontaneous polarization gradually increases without saturation with decreasing temperature^[2]. To explain the ferro-electric and -elastic phase transition, a thermodynamical free-energy has been proposed from a group-theoretical calculation of the zone boundary M -point of $P\bar{4}2_1m$ ^[3], and a soft optical mode at the M -point has been observed by inelastic neutron scattering (INS)^[4]. Therefore, the phase transition is classified as both “improper” ferro-electric and -elastic types and the material typifies the improper phase transition. TMO exhibits antiferromagnetic phase transition at extremely low temperature 0.45 K (T_N)^[5]. In addition, magnetic anisotropy has been observed in phase II. Furthermore, the magnetoelectric effect that the electric polarization is induced at 78 K in phase II by an external magnetic field has been observed recently^[6,7]. These facts indicate that some magnetic mechanism exists, which closely relates to ferro-electricity and -elasticity. To examine the mechanism, we performed INS experiment using a spectrometer HRC at BL-12 in J-PARC in the period 2017A. A magnetic QENS spectrum appeared below room temperature, of which intensity increases and width narrows in the elastic scattering region with decreasing temperature. Therefore, the magnetic diffractions are expected to be observed. Thus, we aimed to determine the magnetic structure of TMO in Phase II.

2. Experiment

Colorless and transparent single crystals of TMO grown by using the FZ method^[8] were grinded thoroughly and annealed 2h at 600°C. The powdered sample of 3.7272 g was enclosed in a V-Ni sample cell with He gas, after measuring its mass and height. The sample sell was set into 10 K top-loading refrigerator, although we planned to use 4K refrigerator. The lowest temperature was 13K. The measurements were performed using a high-resolution neutron powder diffractometer, Super-HRPD, at BL08 in J-PARC. The measurement time was established longish to collect enough statistics even in the low angle (LA) bank, in addition to the back scattering (BS) bank and 90-degree (QA) bank, and the measurement temperature points were configured fewer. The measurements were performed at 13, 50, 100, 150, 200, 250, and 300 K (16h at 13K, the others are 10h). Rietveld analyses were performed for the data of all banks by using a software, Z-Rietveld^[9]. The atomic displacement parameters were isotopic and constrained the same value for Tb and Mo, and anisotropic for O.

3. Results

Figure 1 shows the diffraction pattern of TMO at 13 K. Many sharp peaks can be seen even in the region $d < 1$ Å. However, no magnetic diffraction peak is found. If any component of magnetic moment exists at Tb³⁺, the magnetic diffraction appears at the positions such as 100, 010, 101 *etc.*, which do not satisfy the reflection conditions of $Pba2$. Thus, we changed the purpose

of the experiment from the magnetic structure analysis to accurate structure analysis to examine the origin of spontaneous polarization switched by external magnetic field. The Rietveld calculations were converged with the R_{wp} =1.6-1.8 %. Obtained Crystal structure are shown in FIG. 2. The structure at 532 K is drawn by using a previous

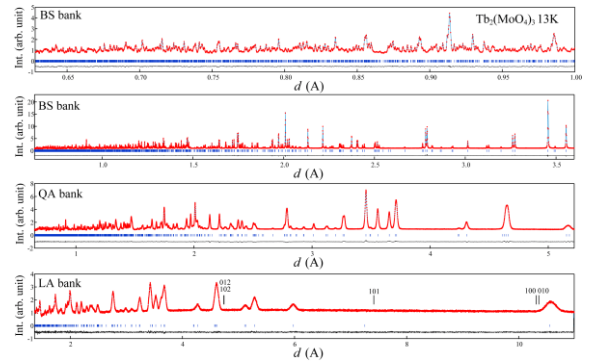


FIG.1 Diffraction pattern of TMO at 13K.

result [10]. There is no significant temperature dependence for the interatomic distances such as Tb-Tb, Tb-O, Mo-O, and O-O. However, MoO₄ tetrahedra rotate in Phase II (FIG. 2). The rotation angles increase with decreasing temperature as the order parameter. Principal axes are crystallographic *a* and *c* for Mo1, and *b* and *c* for Mo2, respectively (FIG. 3). The distance between the centroids of positive and negative charges is independent of temperature with constant value of 1.863 Å and contrasts with that of actual spontaneous polarization (FIG. 4). Above results show an image of ferroelectric phase transition mechanism, that is, 1. The order parameter is a rotational mode of MoO₄ tetrahedra at the zone boundary *M*-point in Phase I. 2. The tetrahedra rotationally jump at *T_C* and the jumping displacement induces an initial spontaneous polarization. 3. The initial spontaneous polarization is independent of temperature. 4. Therefore, another origin of the spontaneous polarization apart from the atomic displacement is needed.

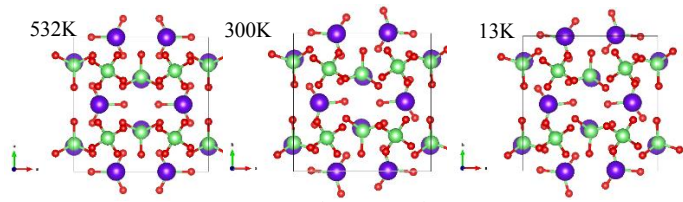


FIG.2 Crystal structure of TMO

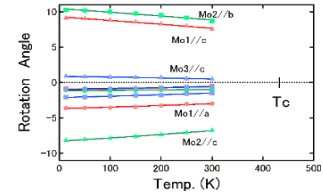


FIG.3 Rotation angle of MoO₄

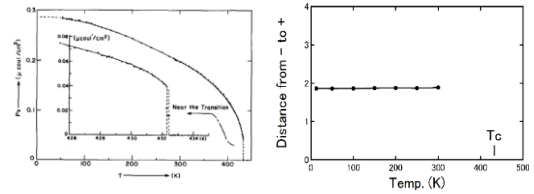


FIG.4 Spontaneous polarization of GMO [2].

Distance from - to + charge of TMO.

In our INS experiment, the crystal field (CF) excitation levels melt with increasing temperature while a QENS spectrum appears. This indicates that the magnetic moment of Tb³⁺ which precess random at room temperature is integrated into the direction of CF with decreasing temperature. Thus, we calculated the direction and strength of CF. First, we made the unit cell which was shifted Tb1 (Tb2) to *ab*-plane, and adjusted occupancies of the surface atoms to be that total molecules are *Z*=4. Then, electric field vector in a super-cell [(*N*+1) × *N* × *N* for Tb1, and *N* × (*N*+1) × *N* for Tb2 (*N*=4-14 of even number)] was calculated at Tb³⁺ position that the nearest to the centroid of super-cell. Obtained direction and strength were plotted vs 1/*N* and extrapolated to 1/*N*=0. The result is illustrated in FIG. 5. The strengths of CF are strong as 248.82 MV/cm for Tb1 and 258.08 MV/cm for Tb2, respectively. The CF vector orientates to the canted and twisted direction in Tb-Tb dimer and is the polar vector. The angle changes about 4 deg. from 13 K to 300 K. It is predicted that if the magnetic moments order in the direction of CF below *T_N*, the arrows at middle Tb should orientate opposite direction, because magnetic moment is the axial vector.

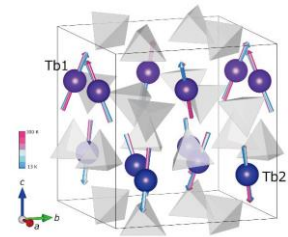


FIG. 5 Direction of CF

4. Conclusion

In this experiment, no magnetic diffraction is observed at 13 K. However, above results still indicates that some magnetic mechanism should exist as the origin of polarization. The results show that the spatial order of the magnetic moments is not formed at 13 K while they precess around the CF with similar relaxation times. To examine the details, magnetic structure analysis under magnetic field is needed.

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