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Magnetic-Field-Induced Polarization Flop in Multiferroic $TmMn_2O_5$

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We discovered a reversible electric polarization flop from the a axis (P_a) to the b axis (P_b) in multiferroic $TmMn_2O_5$ below 5 K by applying a magnetic field of approximately 0.5 T along the c axis. This phenomenon is the first example of the rare-earth (R) compound RMn_2O_5. This magnetic-field-induced polarization flop corresponds to a magnetic phase transition from one incommensurate magnetic (ICM) P_a phase to another ICM P_b phase, which is equivalent to an ICM P_b phase above 5 K under no magnetic field. The spin chirality in the bc plane, which was observed in the P_b phase by polarized neutron diffraction, disappeared in the ICM P_a phase. This indicates that the polarization in the ICM phases of $TmMn_2O_5$ was induced by an $\mathbf{S}_i \times \mathbf{S}_j$–type interaction.

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Recent discoveries of the colossal magnetoelectric effect in $TbMnO_3$ by Kimura *et al.* [1], and in $TbMn_2O_5$ and $DyMn_2O_5$ by Hur *et al.* [2,3], had an impact on the field of the so-called multiferroics and solid state physics. Kimura *et al.* discovered that the electric polarization along the c axis (P_c) can be flopped to P_a in $TbMnO_3$ by an external magnetic field along the b axis (H_b). Thus, it is possible to control the ferroelectric state not only with an external electric field but also with an applied magnetic field. A polarization flop (90° rotation) by a magnetic field and a polarization flip (reversal) by an electric field allow a four-state memory device to be constructed from a single material, which may enable a wide array of new applications.

A rare-earth (R) manganite of the form RMn_2O_5 is one multiferroic material which has been extensively studied, but the origin of its polarization is not yet fully understood [4]. Hur *et al.* reported that in $TbMn_2O_5$, P_b can be flipped by applying H_a. Until now, there has been no report of a polarization flop by applying H in RMn_2O_5. It was believed that the polarization of RMn_2O_5 could appear only along the b axis, and there was no report on P_a and P_c in RMn_2O_5. However, we recently discovered that P_a appears and P_b disappears in $TmMn_2O_5$ as the temperature (T) decreases below 5 K under a zero magnetic field [5]. A magnetic-field-induced phase transition of $TmMn_2O_5$ below 5 K was investigated by Iwata *et al.* [6,7], who observed anomalies in ε_b and changes in P_b as a result of an applied H_c. However, the microscopic origin of such anomalies was unclear. Because of the polarization flop with T and the phase transition from H_c, we expected that the polarization along the a axis could be flopped to the b axis by applying H along the c axis in $TmMn_2O_5$ below 5 K. In this Letter, we show that this magnetic-field-induced polarization flop does indeed occur in $TmMn_2O_5$. This behavior is consistent with a previously reported magnetic phase transition with T [5].

At room temperature, $TmMn_2O_5$ is orthorhombic with a $Pbam$ space group [8]. The dielectric properties of this system are strongly related to magnetic ordering [5], which is described by the magnetic propagation wave vector $\mathbf{q} = (q_x, 0, q_z)$. The magnetic phase of $TmMn_2O_5$ changes from a paramagnetic (PM) phase into a two-dimensionally modulated incommensurate magnetic (2D-ICM) phase below $T_{N1} \sim 44$ K, and a one-dimensionally modulated incommensurate magnetic (1D-ICM) phase with $\mathbf{q} = (q_x, 0, 1/4)$ below $T_D = 36.4$ K. A commensurate magnetic (CM) phase with $\mathbf{q} = (1/2, 0, 1/4)$ forms below $T_{CM} = 34.8$ K, where ε_b exhibits a peak and P_b increases. The CM phase changes into a low-temperature incommensurate magnetic (LT-ICM) phase below $T_{ICM} = 23.4$ K, and P_b decreases abruptly.

P_b in the CM phase of RMn_2O_5 is generally observed regardless of R, and the CM phase is not significantly affected by a magnetic field, most likely because Mn ions are responsible for P_b. On the other hand, the LT-ICM phase exhibits a variety of properties depending on R, and is sensitive to a magnetic field due to competing magnetic interactions among Mn ions and R ions. Rare-earth ions strongly affect the magnetic and dielectric properties of the LT-ICM phase, and applying a magnetic field parallel to the magnetic moments of R causes large magnetoelectric effects in RMn_2O_5 [9,10]. The polarization can be flipped by a magnetic field in $TbMn_2O_5$ [2], induced in $HoMn_2O_5$, and reduced in $ErMn_2O_5$ [11], which arises from the nature of the LT-ICM phases. The polarization flop in $TmMn_2O_5$ also occurs between the two LT-ICM phases, so a comparison between the magnetic structure of the LT-ICM P_a phase and the LT-ICM P_b phase can provide useful information to better understand the origin of the polarization in RMn_2O_5.

Single crystals of $TmMn_2O_5$ were grown by the PbO-PbF_2 flux method [12]. Two samples, used to measure dielectric properties along the b and a axes, were cut from a single crystal. Conductive silver paste electrodes were painted onto the samples, and dielectric measurements in magnetic fields up to 14.5 T along the c axis were performed at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan. The permittivity, ε_b and ε_a, was measured using an LCR meter (HP4284A) at a frequency of 10 kHz. The polarization, P_b and P_a, was measured using a picoammeter (Keithley, 6485) and integration of induced current. No electric-field poling was performed, because the samples were macroscopically polarized and exhibited a constant polarization in ferroelectric phases without an applied electric field [5]. The tendency became stronger as the crystal quality improved with regard to diffraction, perhaps because the magnetic domains providing the polarization were more robust and less affected by the electric field. The two samples were placed in a magnet, and were measured simultaneously using two sets of instruments.

Neutron diffraction measurements in a magnetic field up to 5 T were performed using a triple axis spectrometer TAS-2, installed at JRR-3 at the Japan Atomic Energy Agency. A $TmMn_2O_5$ single crystal from another batch was mounted on the (h, 0, l) scattering plane with a horizontal-field superconducting magnet. The incident and final energies of neutrons were fixed at 14.3 meV using a pyrolytic graphite (PG) (002) monochromator and an analyzer. A PG filter was inserted in front of the sample to reduce higher-order contamination. The experimental configuration of the collimation was 15′-80′-80′-80′.

Polarized neutron scattering experiments were performed using TAS-1 at JRR-3. A PG (002) reflection and a Heusler (111) reflection were used as a monochromator and analyzer, respectively. A spin flipper was placed in front of the analyzer, and a guide field around the sample was maintained parallel to the momentum transfer **Q** (horizontal field) by a Helmholtz coil. The incident neutron energy was 14.7 meV, and a collimator sequence of 40′-80′-80′-open was used. PG and sapphire filters were located in front of the sample to eliminate higher-order and fast neutrons, respectively. In this configuration, we could analyze the polarization of the diffracted neutrons when the incident beam was unpolarized.

Figure 1(a) shows the temperature (T) dependence of the polarization P_b and P_a around 5 K measured in zero magnetic field. P_b was assumed to be zero at 4.2 K, while P_a was zero at 6.5 K, so that both disappeared in 0 T at each temperature, which was confirmed by measuring their hysteresis loops [5]. The decrease in P_a and the increase in P_b with increasing temperature occur simultaneously, in agreement with the previous report [5]. The magnitude of P_a, about 7 nC/cm^2, was comparable to that of P_b, about 8 nC/cm^2. Although the results were obtained during heating, similar changes were observed during cooling.

Figure 1(b) shows the magnetic field dependence of the polarization P_a and P_b at 4.2 K. P_a was assumed to be zero

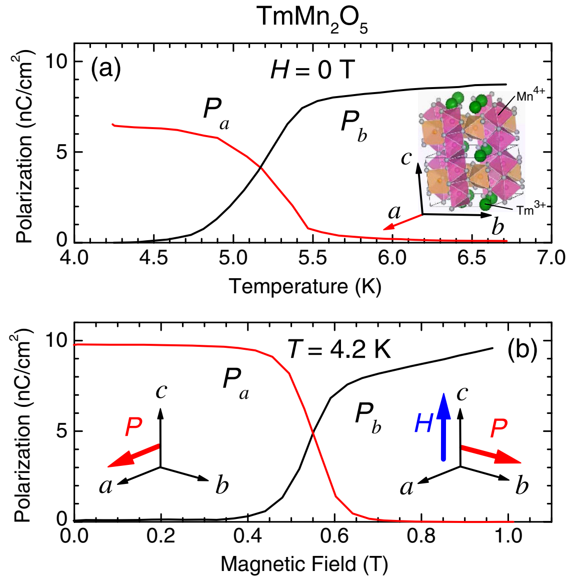

FIG. 1 (color online). (a) Temperature dependence of the polarization P_a and P_b of $TmMn_2O_5$ during heating in zero magnetic field. The inset shows the crystal structure of $TmMn_2O_5$. (b) Magnetic field dependence of P_a and P_b at 4.2 K.

in 1 T since it was almost constant from 1 T to 14.5 T at 4.2 K, and from 4.2 K to 50 K above 1 T. The change in $P_b(H)$ is consistent with previous results [6], while the corresponding change in $P_a(H)$ is reported for the first time here. The direction of the polarization changed from along the a axis to along the b axis with the application of a magnetic field along the c axis. The results clearly demonstrate a polarization flop of $TmMn_2O_5$, induced by a magnetic field. This flop occurred at 4.2 K in 0.5–0.6 T, which is an extremely weak magnetic field compared with the polarization flops of $MnWO_4$, which requires about 10 T [13], $TbMnO_3$ about 5 T [1], or $LiCu_2O_2$ about 2 T [14], or with the polarization flip of $TbMn_2O_5$ at about 2 T [2]. There is a large difference between the polarization flop of $TmMn_2O_5$ and others. The flop in $TmMn_2O_5$ can be induced by simply decreasing temperature even in zero magnetic field, so the flop occurs easily by nature. P_a at 4.2 K in 0 T in Fig. 1(b) is different from that in Fig. 1(a). This is probably because the actual sample temperature changed rapidly around 5 K due to a first-order phase transition, and the integration of pyroelectrically induced current to obtain the polarization could not be performed smoothly. The polarization measured as a function of H was more reproducible than the polarization as a function of T during the experiment. Although it is not shown in Fig. 1(b), P_a began to decrease in smaller H as temperature increases, which is consistent with the previously obtained phase diagram [7]. P_b increases to 15 nC/cm^2 in 3 T, and then becomes almost constant up to 14.5 T.

Figure 2 shows magnetic (2.535, 0, 2.284) and (2.535, 0, 2.716) Bragg reflection profiles over the range of H and T where the polarization flop occurred. Measurable Bragg

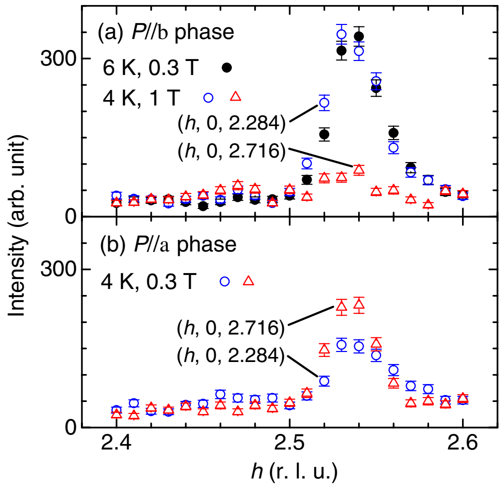

FIG. 2 (color online). Magnetic Bragg reflection profiles (h, 0, 2.284) (circles) and (h, 0, 2.716) (triangles) at (a) 6 K, 0.3 T and 4 K, 1 T (P_b phase) and (b) 4 K, 0.3 T (P_a phase).

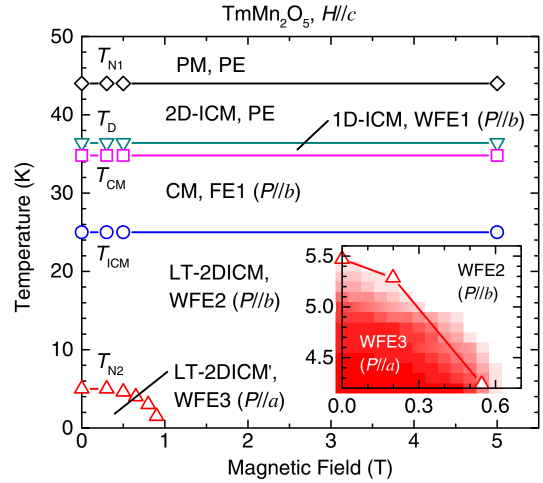

FIG. 3 (color online). Magnetic field-temperature phase diagram of $TmMn_2O_5$ obtained through the present study. The magnetic field was applied along the c axis. The boundaries were determined by the neutron diffraction results. The gradation of the shaded WFE3 phase in the inset indicates the magnitude of P_a. The boundary in the inset was determined by the peaks of ε_a.

reflections are technically restricted, due to the horizontal-field magnet used to apply H_c. Both reflections correspond to the two-dimensionally incommensurate position $\mathbf{q} = (0.465, 0, \pm 0.284)$, and the integrated intensity of each reflection relates to the magnetic structure factor. The profiles at 6 K in 0.3 T (the high-T P_b phase) and at 4 K in 1 T (high-H P_b phase), shown in Fig. 2(a), are similar in intensity, while those at 4 K in 1 T (P_b phase) and at 4 K in 0.3 T (P_a phase), shown in Figs. 2(a) and 2(b), differ considerably. Similar changes in other reflections were found with the polarization flop as a function of temperature in zero magnetic field [5], and it is clear that the polarization flop coincides with a magnetic structural change.

Figure 3 summarizes the H-T phase diagrams of $TmMn_2O_5$ obtained through this study. The phase boundaries were based on the neutron diffraction results. Dielectric phases are labeled as paraelectric (PE), ferroelectric (FE), and weak ferroelectric (WFE) phases with numbers [5]. We named the LT-ICM phases corresponding to the WFE2 ($P \parallel b$) and WFE3 ($P \parallel a$) phases as the LT-2DICM and LT-2DICM′ phases, respectively. The gradation of the shaded WFE3 phase in the inset in Fig. 3 corresponds to the magnitude of P_a shown in Fig. 1(b).

Unlike $DyMn_2O_5$ [3], remarkable changes in the permittivity and the polarization by a magnetic field were not observed, except for the polarization flop. According to a previous report [7], one more phase boundary was expected around 4 T below 6 K, but no indication of this boundary was observed in the present study. T_{CM} determined by the peaks of ε_b decreased by 0.4 K, and T_{ICM} increased by 0.6 K as H increased from 0 T to 14.5 T. Hence the CM-FE1 phase slightly shrank as H increased, in contrast with the magnetic-field-induced CM-FE phase from an LT-ICM phase in $HoMn_2O_5$ [11,15]. However, a similar shrinking of the CM phase by H was reported in $TbMn_2O_5$ [2] and $ErMn_2O_5$ [11]. A similar H-T phase diagram, with regard to the WFE2 and WFE3 phases, and a similar change in P_b induced by H to Fig. 1(b) were observed in $DyMn_2O_5$ [16].

Here, we discuss the origin of the polarization and the mechanism of its flop in $TmMn_2O_5$. There are two microscopic theories to explain magnetically induced ferroelectricity. One is the inverse Dzyaloshinskii-Moriya interaction, written with neighboring spins of $\mathbf{S}_i \times \mathbf{S}_j$ [17,18], and the other is exchange striction, written $\mathbf{S}_i \cdot \mathbf{S}_j$ [19,20]. Although Chapon *et al.* explained $P_b(T)$ of YMn_2O_5 with the latter model, based on powder neutron magnetic structure analysis [21], we have already pointed out that the former is another possible candidate based on our model-free magnetic structure analysis results for the CM phases of RMn_2O_5 (R = Y, Ho, and Er) [4,9,22]. In these CM phases, Mn^{4+} spins generally form transverse spiral chains along the c axis, whose chirality stacks antiphase on the ac plane and in-phase on the bc plane as illustrated in Fig. 4(c). We consider that they bring alternating microscopic polarizations along the a axis and uniform polarizations along the b axis, respectively, according to the $\mathbf{S}_i \times \mathbf{S}_j$–type interaction [22]. Hence, the macroscopic polarization appears only along the b axis in the CM phase. A similar situation to Fig. 4(c) was observed in the LT-ICM P_b phase of YMn_2O_5 [23]. In other words, the $\mathbf{S}_i \times \mathbf{S}_j$ term could also induce P_b in the LT-ICM phase as well as in the CM phase. If the chirality in one of the two chains in Fig. 4(c) were reversed, the stacking situation would switch, namely, in-phase on the ac plane and antiphase

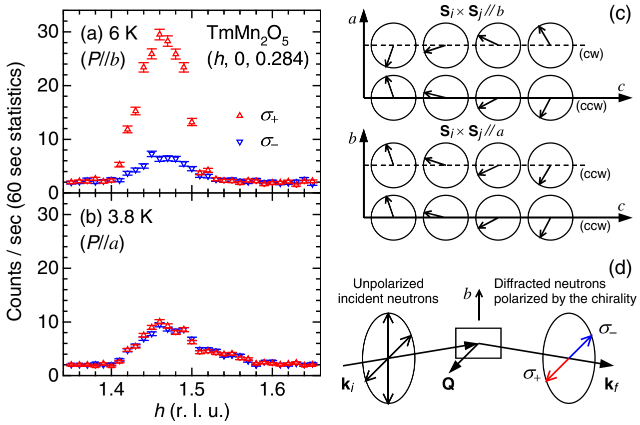

FIG. 4 (color online). (a) Polarized neutron diffraction results of $TmMn_2O_5$ at 6 K ($P \parallel b$) and (b) 3.8 K ($P \parallel a$). The sample was electric-field cooled along the b axis. (c) Images of the chirality and transverse spiral chains along the c axis stacking antiphase on the ac plane and in-phase on the bc plane. (d) The experimental configuration of the polarized neutron diffraction. The incident neutrons were not polarized, and the diffracted neutrons polarized by the chirality were analyzed.

on the bc plane, and the macroscopic polarization would flop, accompanied by a change in the magnetic structure.

To confirm this idea, we measured the spin chirality ($\langle \mathbf{S}_i \times \mathbf{S}_j \rangle$) by analyzing the polarization of the magnetically scattered beam. Similar experiments were performed on several multiferroic compounds such as $TbMnO_3$ [24] and $LiCu_2O_2$ [25]. σ_+ and σ_- in Fig. 4 denote counts of the diffracted neutrons with spins parallel to $+\mathbf{Q}$ and $-\mathbf{Q}$, respectively. The diffracted neutrons are polarized by the magnetic chiral term, and the difference between σ_+ and σ_- corresponds to the spin chirality present in the plane perpendicular to $\mathbf{Q}$ as shown in Fig. 4(d). Figures 4(a) and 4(b) show the magnetic reflection profiles of polarized neutrons in the LT-2DICM-WFE2 P_b phase at 6 K and in the LT-2DICM′-WFE3 P_a phase at 3.8 K. The (1.465, 0, 0.284) reflection roughly parallel to the a axis strongly relates to the bc chirality. The results show that the bc chirality exists at 6 K, but disappears or cancels out at 3.8 K. In this experiment, we could not show the ac chirality because it is technically difficult to observe the chirality on the ac plane for (q_x, K, q_z) magnetic Bragg reflection.

In contrast to the above $\mathbf{S}_i \times \mathbf{S}_j$ model, it is impossible to explain the polarization flop from P_b to P_a by a $\mathbf{S}_i \cdot \mathbf{S}_j$–type interaction because the axis of the polarization is determined by the crystal structure of the paramagnetic phase and $\mathbf{q}$ but both of them hardly change with the flop. We thus conclude that P_b and P_a in the LT-ICM phase of RMn_2O_5 were induced by the $\mathbf{S}_i \times \mathbf{S}_j$ term. Nonetheless, the increase in P_b of the CM phase cannot be explained by only the $\mathbf{S}_i \times \mathbf{S}_j$ term because this term does not depend significantly on whether $\mathbf{q}$ is commensurate or not. The most likely scenario is that the $\mathbf{S}_i \cdot \mathbf{S}_j$ term induces P_b only in the CM phase, adding on P_b produced by the $\mathbf{S}_i \times \mathbf{S}_j$ term, which should be proved in future studies.

In summary, an electric polarization flop from along the a axis to along the b axis was induced by applying a magnetic field along the c axis in $TmMn_2O_5$ below 5 K for the first time in the RMn_2O_5 system. This polarization flop was accompanied by a magnetic phase transition between two incommensurate phases with the same $\mathbf{q}$ and different spin chirality. Appearance of the polarization along the a axis and similar polarization flop phenomena may have been overlooked in other RMn_2O_5.

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