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Control of the polarization flop direction by a tilted magnetic field in multiferroic $TbMnO_3$

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In spin-driven ferroelectrics, often referred to as magnetoelectric (ME) multiferroics, a domain wall separates two magnetic as well as ferroelectric domains. Therefore, it is expected that the control of such an ME domain wall could result in a large ME effect. Here, we show that the direction of a slanted magnetic field controls whether the electric polarization ($\boldsymbol{P}$) rotates by +90 or −90° upon the $\boldsymbol{P}$-flop transition in a prototypical spiral magnetic ferroelectric $TbMnO_3$. This behavior is discussed in terms of the domain-wall energy of a spiral magnet in a slanted magnetic field.

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Since a 90° rotation of electric polarization by the application of a magnetic field ($\boldsymbol{H}$) in $TbMnO_3$ was discovered by Kimura *et al.*,[1] research into magnetoelectric (ME) multiferroics has become an active field in both physics and technological application research.[1–15] The mechanism of spin-driven ferroelectricity in $TbMnO_3$ and many other cycloidal magnets is explained by the inverse effect of the Dzyaloshinsky-Moriya interaction.[16–19] Yamasaki *et al.*[20,21] confirmed that the electric polarization $\boldsymbol{P}$ relates to the vector spin chirality $\boldsymbol{S}_i \times \boldsymbol{S}_j$ ($\equiv \boldsymbol{C}$) in $R\text{MnO}_3$ when R=Tb or $Gd_{0.7}Tb_{0.3}$ such that

$$\boldsymbol{P} = A\boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j), \tag{1}$$

where $\boldsymbol{e}_{ij}$ is the unit vector connecting the i and j sites. The coefficient A is positive both in $TbMnO_3$ with $\boldsymbol{P} \parallel c$ and in $Gd_{0.7}Tb_{0.3}MnO_3$ with $\boldsymbol{P} \parallel a$. In the $R\text{MnO}_3$ system, therefore, the $\boldsymbol{P}$ flop is regarded as a 90° rotation of $\boldsymbol{C}$ around the b axis along which the spin moments of Mn are modulated. In general, it is essential to investigate the response of $\boldsymbol{C}$ to an external magnetic field to understand the microscopic origin of the gigantic ME effect. Since the $\boldsymbol{P}$ flop in $TbMnO_3$ is of the first-order type, two phases with directions of $\boldsymbol{C}$ differing by 90° can coexist in the vicinity of the $\boldsymbol{P}$-flop phase transition. In a simple case, the $\boldsymbol{C}$ vector can rotate by either +90 or −90°, as shown in Fig. 1. As a result, the multidomain state would appear after a flop process even if the initial state was of single domain. However, several experimental reports contradict this simple prediction. For example, $TbMnO_3$ maintains a large P_c comparable to a single-domain state after a $\boldsymbol{P} \parallel c$-to-$\boldsymbol{P} \parallel a$ flop by increasing H and a re-entrant $\boldsymbol{P}$ flop by decreasing H to 0 T in the absence of a poling electric field.[1,22] These reports imply that the flop direction of $\boldsymbol{C}$ as well as $\boldsymbol{P}$ was unintentionally altered to either +90 or −90° by some unknown mechanism. Another example of the selective rotation of $\boldsymbol{C}$ is the reversal of $\boldsymbol{P}$ by rotating the magnetic field direction in the ab plane at 9 T.[22] By rotating the direction of magnetic field of 9 T, the sign of P_a is reversed, unlike the case in which the magnetic field is swept from 9 to −9 T. This result suggests that the direction of magnetic field plays an important role in the selective rotation of $\boldsymbol{P}$. Here, we report that the direction of rotation of $\boldsymbol{P}$ in $TbMnO_3$ is completely controlled by the direction of magnetic field. The result can be explained by the differences in energy of ME domain walls.

Single crystals of the typical cycloidal magnetic ferroelectric $TbMnO_3$ were grown by a floating-zone method. To monitor the rotation direction of $\boldsymbol{P}$, two thin-plate samples were prepared. The widest surface of one sample had a normal vector forming an angle of 45° both from the a and c axes in the ac plane [see Fig. 2(b)]. In this configuration, the measured polarization value of $\boldsymbol{P}$ corresponds to $P_n = (P_a + P_c)/\sqrt{2}$. The widest surface of the other sample was perpendicular to the a axis. Gold electrodes were sputtered onto the opposite faces of the samples to measure the electric polarization $\boldsymbol{P}$. We obtained the $\boldsymbol{P}$ value from the integration of the pyroelectric current, which was measured with an

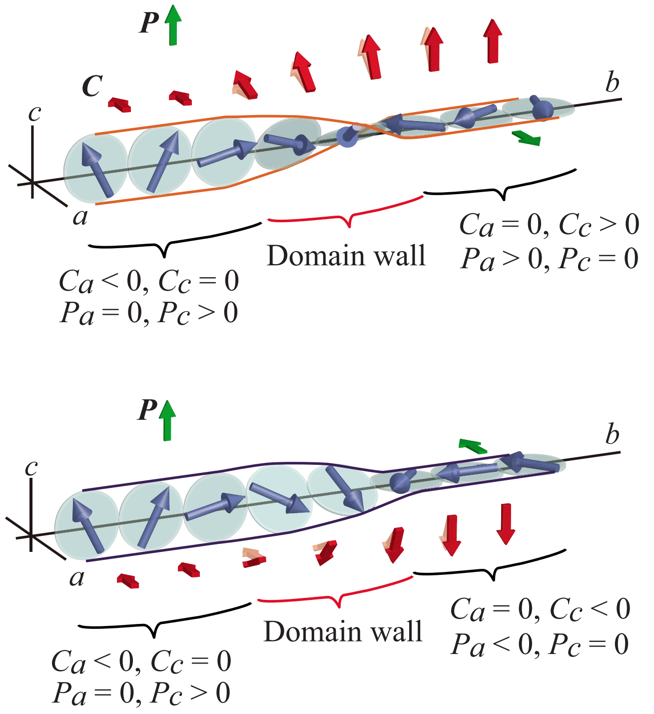

FIG. 1. (Color online) Relation between electric polarization $\boldsymbol{P}$ and vector spin chirality $\boldsymbol{C}$. The vector spin chirality $\boldsymbol{C}$ rotates by either +90 or −90° around the magnetic propagation vector (b axis) following the $\boldsymbol{P}$-flop transition.

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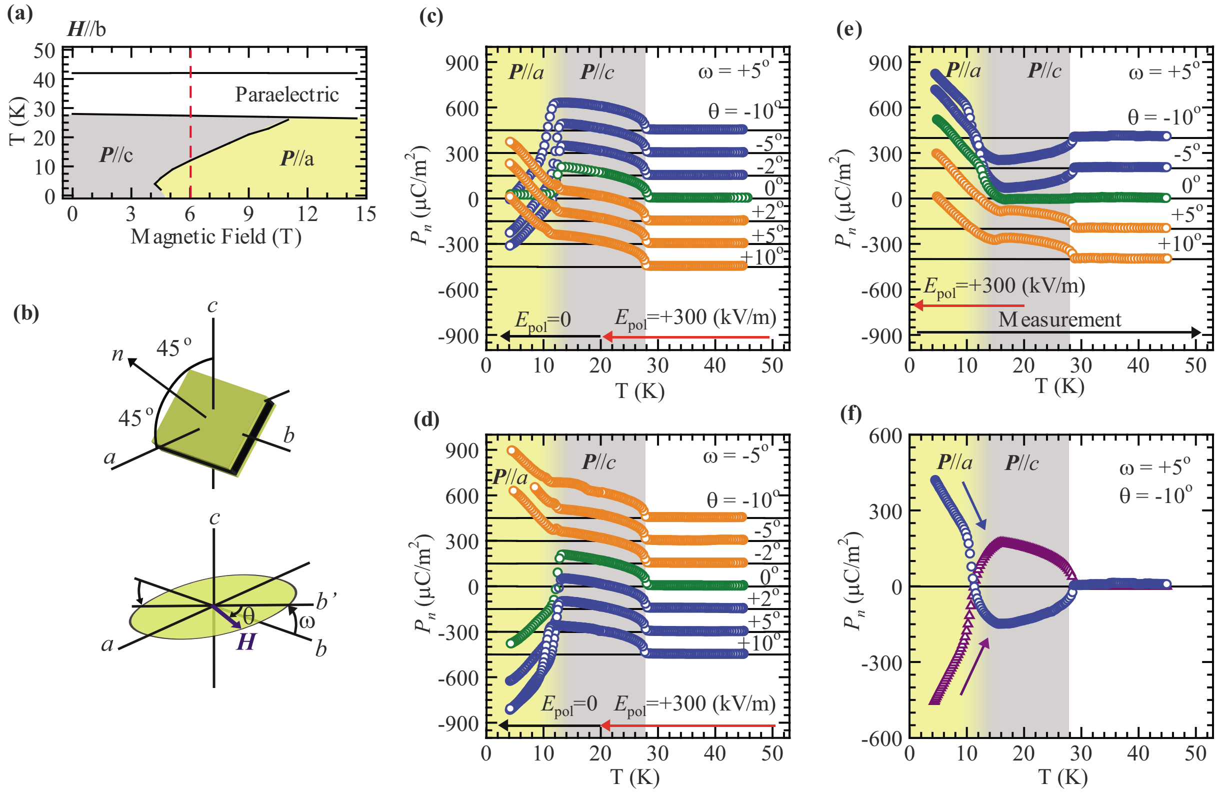

FIG. 2. (Color online) Change in electric polarization of $TbMnO_3$ with sweeping temperature in a slanted magnetic field. (a) Magnetoelectric phase diagram of $TbMnO_3$ in magnetic fields applied along the b axis. Excerpt from Ref. 25. (b) Sample morphology and definition of magnetic field direction in the $\boldsymbol{P}$ measurement. (c) and (e) Electric polarization $P_n = (P_a + P_c)/\sqrt{2})$ in a magnetic field of 6 T in various directions. Measurements started from the single-domain state of (c) and (d) $+P_c$ or (e) $+P_a$. (f) Change in electric polarization P_n with increasing temperature in a magnetic field $\omega = +5°$ and $\theta = -10°$ for different initial states.

electrometer (KEITHLEY 6517A). Prior to each $\boldsymbol{P}$ measurement, the sample was cooled to a ferroelectric phase in a poling electric field (typically 300 kV/m) to form a single-domain state. The direction of the magnetic field was varied by rotating the sample in a cryostat equipped with a 15 T superconducting magnet. The measurements of $\boldsymbol{P}$ in a magnetic field were performed at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan.

First, we investigated whether $\boldsymbol{P}$ flops from the $+c$ direction to the $+a$ or $-a$ direction with sweeping temperature in a magnetic field of 6 T [see the dotted line in Fig. 2(a)] in various directions. Prior to each measurement, the sample was cooled from 45 to 20 K in a positive electric field to form a single-domain state with $P_c > 0$. In this Rapid Communication, the magnetic field direction is represented by two angles ω and θ, as shown in Fig. 2(b). Thus, the a and c components of the magnetic field are given by

$$H_a = H \sin \theta,$$

$$H_c = H \cos \theta \sin \omega. \tag{2}$$

Figure 2(c) shows that the observed P_n value changes in sign upon the $\boldsymbol{P}$-flop transition when $\theta < 0$ and $\omega > 0$ but not when $\theta > 0$ and $\omega > 0$. This means that $\boldsymbol{P}$ flops from the $+c$ to the $-a$ direction in the case of $\theta < 0$ and $\omega > 0$, and from the $+c$ to the $+a$ direction in the case of $\theta > 0$ and $\omega > 0$. The θ dependence on the direction of rotation of the $\boldsymbol{P}$ flop is reversed for $\omega < 0$, as shown in Fig. 2(d). These results clearly indicate that the direction of rotation of $\boldsymbol{P}$ and hence $\boldsymbol{C}$ in the $\boldsymbol{P} \parallel c$-to-$\boldsymbol{P} \parallel a$ transition depends on the direction of the magnetic field. Similar selective rotations of $\boldsymbol{P}$ are also observed for the $\boldsymbol{P}$ flop in the opposite direction, i.e., the transition from the $\boldsymbol{P} \parallel a$ phase to the $\boldsymbol{P} \parallel c$ phase, as shown in Fig. 2(e). The single-domain $\boldsymbol{P} \parallel a$ state with $P_a > 0$ was obtained by cooling the sample from 20 to 4.2 K in a poling electric field. The sign of the obtained P_n value changes following the $\boldsymbol{P}$ flop in the $\theta < 0$ and $\omega > 0$ case but not in the $\theta > 0$ and $\omega > 0$ case. One might think that the bistability of the ferroelectric phases would be affected by the application of H in a slanted direction. This is, however, not the case. Figure 2(f) shows that the $P_a > 0$ state changes into the $P_c < 0$ state while warming up in a 6 T magnetic field with $\omega = +5°$ and $\theta = -10°$, while the $P_a < 0$ state changes into the $P_c > 0$ state in the same condition. It is obvious that the slanted magnetic field controls the direction of rotation of $\boldsymbol{P}$ but not the direction of $\boldsymbol{P}$ itself. Theoretically, two states with opposite $\boldsymbol{P}$ directions that are superimposed with each other by space inversion are degenerate in energy in a slanted magnetic field because the magnetic field does not break the space inversion symmetry. Nonetheless, the present study confirms the selective rotation of the electric polarization direction in a slanted magnetic field. Therefore, we need to take into account the

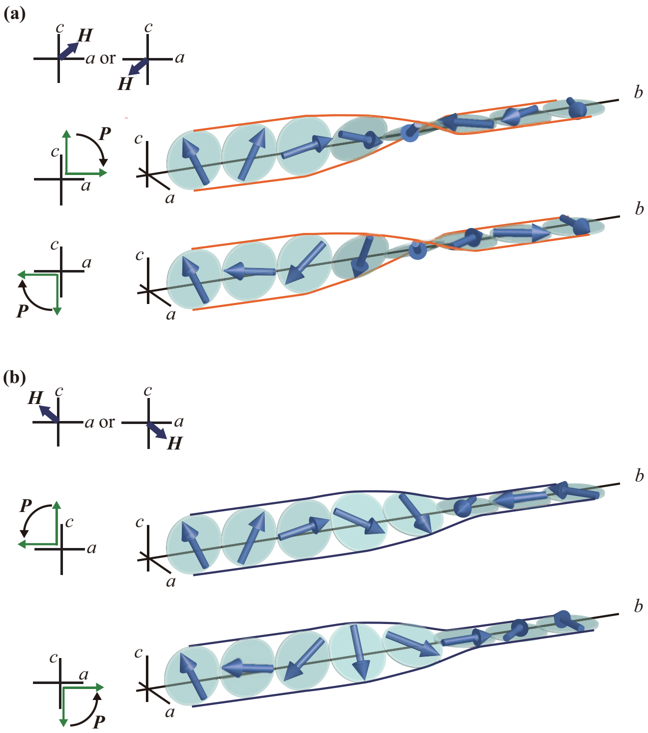

FIG. 3. (Color) Possible magnetoelectric domain walls in a cycloid magnet TbMnO$_3$ upon an electric polarization flop transition. (a) Electric polarization flops from the $+c$ ($-c$) direction to the $+a$ ($-a$) direction in the case of $\omega>0$ and $\theta>0$, as well as $\omega<0$ and $\theta<0$. (b) Electric polarization flops from the $+c$ ($-c$) direction to the $-a$ ($+a$) direction in the case of $\omega>0$ and $\theta<0$, as well as $\omega<0$ and $\theta>0$.

stability of the domain wall in the slanted magnetic field. Since the electric polarization flop transition is of the first-order type, $\boldsymbol{P}\parallel a$ and $\boldsymbol{P}\parallel c$ domains can coexist at the $\boldsymbol{P}$-flop transition, separated by ME domain walls. For simplicity, we assume that the ME domain walls are perpendicular to the b axis.[23] A domain wall appears as a twist in the spin-spiral plane of ±90°. Figure 3 schematically shows the ME domain walls between the $\boldsymbol{P}\parallel c$ and $\boldsymbol{P}\parallel a$ phases. The present measurements of the direction of rotation of $\boldsymbol{P}$ indicate that two among the four types of walls between the $\boldsymbol{P}\parallel a$ and $\boldsymbol{P}\parallel c$ domains are stabilized in a slanted magnetic field, as shown in Fig. 3. It should be noted here that higher-energy and lower-energy domain walls are interchanged with each other by a mirror operation, which is broken in a slanted magnetic field. Consequently, the $P_c>0$ state is selectively transformed into the $P_a>0$ state in a slanted magnetic field with $H_a>0$ and $H_c>0$ or with $H_a<0$ and $H_c<0$. Furthermore, this model straightforwardly explains the result shown in Fig. 2(f).

In the ME domain wall, the orientation of the twist of the spin spiral is determined by the tilting direction of the magnetic field. Such selectivity of ME domain walls by the application of a slanted magnetic field could be universal in cycloidal magnetic ferroelectrics because the magnetic field in a slanted direction lowers the symmetry of the system. The degeneracy in energy of twist-type magnetic domain walls in a cycloidal magnet can be lifted by the symmetry breaking. When the energy separation is large enough to overcome the thermal agitation, the cycloid can rotate only in one direction. The resulting control of the $\boldsymbol{P}$ rotation direction is applicable to magnetic manipulation of $\boldsymbol{P}$ in various multiferroics.[24]

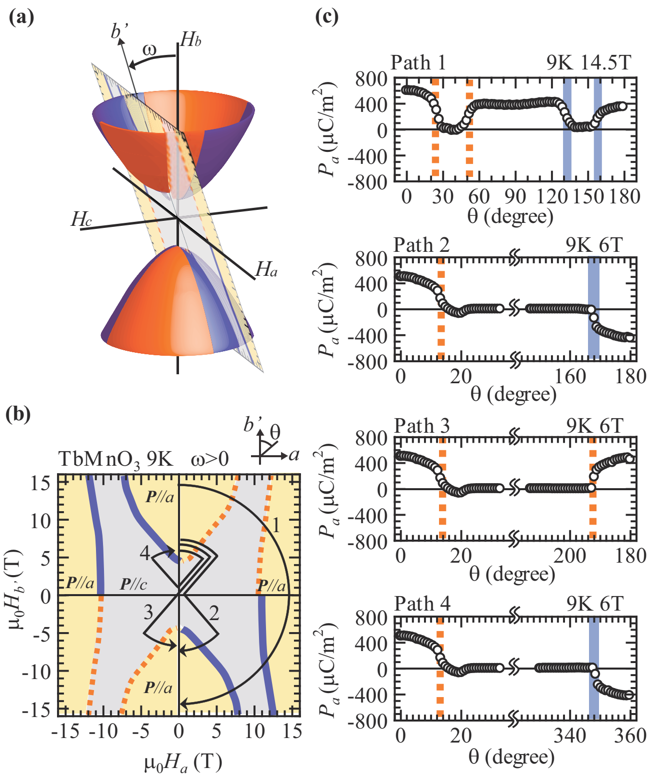

FIG. 4. (Color) Changes in electric polarization of TbMnO$_3$ with sweeping magnetic fields along several paths at 9 K. (a) Three-dimensional magnetoelectric phase diagram with different types of phase boundaries. Higher-H_a boundaries are omitted for clarity. (b) Two-dimensional magnetoelectric phase diagram of a section of the phase diagram shown in (a). Magnetic field sweeping paths for the present magnetoelectric measurements are shown by arrows. (c) Changes in electric polarization along the a axis (P_a) with sweeping a magnetic field along the paths shown in (b).

By making use of the selectivity of the $\boldsymbol{P}$-flop direction in a slanted magnetic field, the signs of P_a and P_c can be controlled by changing the $\boldsymbol{H}$ direction. Figure 4(b) shows the ME phase diagram at a sample temperature of 9 K in slanted magnetic fields with $\omega>0$ [see Fig. 4(a)]. In these conditions, the boundary between the two ferroelectric phases can be classified as one of two types, as indicated by orange and blue in Fig. 4(b), corresponding to Fig. 3. Across an orange boundary, the sign of electric polarization is not changed between the $\boldsymbol{P}\parallel a$ and $\boldsymbol{P}\parallel c$ phases. On the other hand, the sign of the electric polarization is changed across a blue boundary. Figure 4(c) shows the changes in P_a with sweeping magnetic fields along several paths indicated in Fig. 4(b). Along paths 2 and 4, the magnetic field was swept across one orange and one blue boundaries, and thus, $\boldsymbol{P}$ changes in direction from $+a$ to $+c$ and then to $-a$. As a result, P_a is reversed over the whole process. On the other hand, paths 1 and 3, which cross an even numbers of blue and orange boundaries, do not cause a sign reversal of $\boldsymbol{P}$. The relationship between the ***H*** direction and the ***P***-flop direction can explain the previously reported P_a reversal by a rotation of ***H*** direction.[22]

In summary, we have discovered the source of the selectivity that controls the direction of the polarization flop in magnetoelectric $TbMnO_3$ in a slanted magnetic field. The selectivity originates from the stability of magnetoelectric domain walls in the magnetic field. Using this stability, the sign of the electric polarization can be controlled by the slanted direction of magnetic field in the ***P***-flop transition. Such selectivity of ME domain walls in a slanted magnetic field is likely a universal feature of the magnetic field response of multiferroics having a cycloidal magnetic order.

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