Control of the Magnetoelectric Domain-Wall Stability by a Magnetic Field in a Multiferroic $MnWO_4$

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The relation between the orientation of the magnetic field and the flopped ferroelectric polarization has been investigated for multiferroic $MnWO_4$. The ferroelectric single-domain state is retained across the polarization flop process when the direction of the applied magnetic field slightly deviates from the b axis within the ab plane. Furthermore, the electric polarization in the high-field $P \parallel a$ phase is reversed when the $P \parallel b$-to-$P \parallel a$ transition takes place while decreasing and increasing the magnetic fields oppositely canted from the b axis. These results indicate that the symmetry breaking induced by a canted magnetic field determines the direction of the polarization flop, which corresponds to the direction of the vector spin chirality. The stability of the magnetoelectric domain walls in a canted magnetic field play a key role in the directional control of the electric polarization flop phenomenon.

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Magnetoelectric (ME) multiferroics, in which magnetic and ferroelectric (FE) orders coexist, have recently attracted much interest due to their potential use in novel physics fields and applications such as controlling electric polarization (P) by using a magnetic field (H) or controlling magnetic order by using an electric field [1,2]. In particular, a new class of multiferroics, in which magnetic order induces a FE phase transition [3–16], often shows gigantic ME effects, such as the flop (90° rotation) induced by H [3,5,10,11] and a reversal [4,6,9,15–17] of the FE polarization. In recent years, the relation between the magnetic order and the ferroelectricity in some multiferroic materials, such as perovskite $RMnO_3$ ($R =$ Tb and Dy), has been intensively investigated. It has turned out that ferroelectricity appears in the cycloidal-spiral spin phase without centrosymmetry [18,19], in which the spin rotation axis is not parallel to the magnetic modulation vector ($\boldsymbol{Q}$). This correlation between the FE polarization and the cycloidal-spiral spin structure is suggested to be associated with the antisymmetric part of exchange coupling, which is the so-called Dzialoshinskii-Moriya (DM) interaction [20–22]. The microscopic model proposed by H. Katsura *et al.* describes the relationship between an electric dipole moment, $\boldsymbol{p}$, and canted spin moments, $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$, on the neighboring two sites (i and j) as follows:

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

Here, $\boldsymbol{e}_{ij}$ denotes the unit vector connecting the two sites. The coefficient A is a constant which depends on the spin-orbit interaction and the superexchange interaction. This mechanism is often referred to as inverse DM interaction. Equation (1) predicts that macroscopic P should appear in the cycloidal-spiral spin phase. In fact, ferroelectricity has been observed in a number of materials other than perovskite $RMnO_3$ ($R =$ Tb and Dy) exhibiting a cycloidal-spiral spin structure [7,9–11,14]. In addition, the correlation between the vector chirality ($\boldsymbol{C} = \boldsymbol{S}_i \times \boldsymbol{S}_j$) of spiral spin structures and P direction has recently been confirmed by spin-polarized neutron diffraction measurements in $TbMnO_3$, $LiCu_2O_2$, and $MnWO_4$ [23–25].

P flops induced by H have been observed in some multiferroics exhibiting ferroelectricity driven by the spiral spin structure, such as $RMnO_3$, $MnWO_4$ or $LiCu_2O_2$ [3,5,10,11]. With a phenomenological model, M. Mostovoy has proposed that controlling the vector spin chirality ($\boldsymbol{C}$) by using an H which is perpendicular to $\boldsymbol{Q}$ induces the P-flop phenomenon in a cycloidal-spiral spin system [21]. In this model, the $\boldsymbol{C}$ of a spiral spin structure points in the applied H direction, and consequently P flops along the axis perpendicular to both $\boldsymbol{C}$ and $\boldsymbol{Q}$. However, this model cannot explain the P flop observed in well-known ME multiferroic systems, such as perovskite $RMnO_3$ ($R =$ Tb and Dy), since the $4f$-$3d$ exchange interaction between adjacent rare-earth and manganese ions should complicate the response of P to H [21]. From this viewpoint, $MnWO_4$ is a spiral magnetic system which follows Mostovoy's prediction [10]. $MnWO_4$ is crystallized in a wolframite structure ($P2/c$), in which MnO_6 octahedra are aligned in zigzag chains along the c axis, as shown in Fig. 1(a). It is reported that there are three long-wavelength magnetic ordering states in this system, AF1, AF2, and AF3 at low temperatures [see Fig. 1(b)] [10,26–28]. For AF1 and AF3, the magnetic moments are collinearly aligned in the ac plane, forming an angle of about 35° with the a axis, whereas an additional component exists in the b direction in AF2 [Fig. 2(a)] [29]. The magnetic principal axis setting, which is an orthogonal one, is different from the crystallographic monoclinic set-

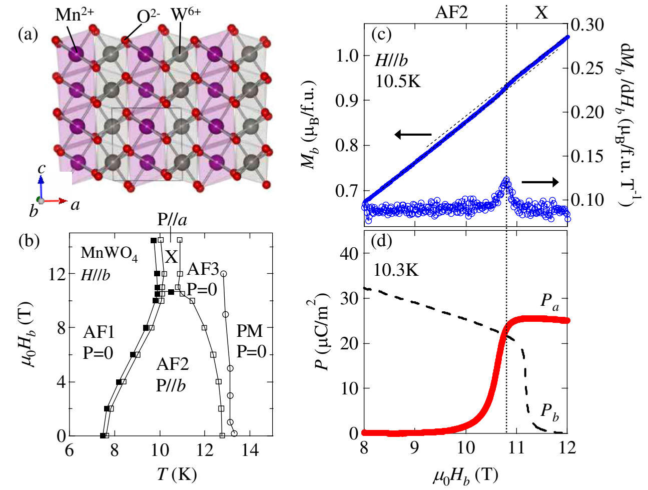

FIG. 1 (color online). (a) Crystal structure of $MnWO_4$ as viewed along the b axis: each cation (Mn^{2+} and W^{6+}) is surrounded by an octahedron of oxygen atoms. (b) Magnetoelectric phase diagram of $MnWO_4$ in magnetic field (H) parallel to the b axis [10]. Open and closed squares represent the data points in the warming (increasing H) and cooling (decreasing H) runs of pyroelectric (or magnetoelectric) current measurements, respectively. Open circles represent Néel temperatures in various magnetic fields. (c, d) Dependence of (c) magnetization (M_b) and (d) electric polarization (P) on the magnetic field applied along the b axis.

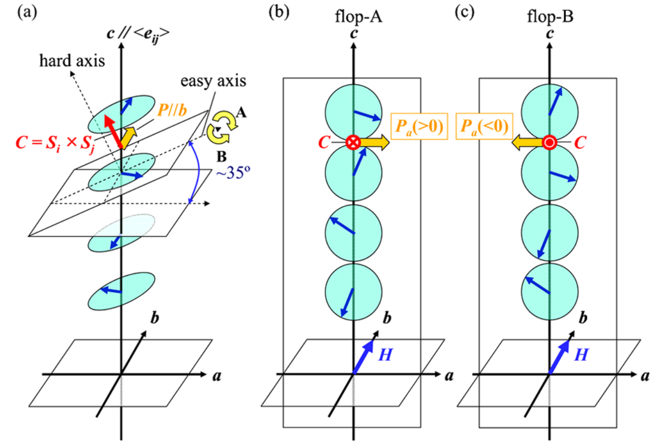

FIG. 2 (color online). (a) Magnetic structure of AF2 with polarization along the b axis ($P \parallel b$). Crystallographic axes (a, b, and c axes) and magnetic principle axes (easy, hard, and b axes) are shown. A and B represent the two possible rotating directions in which the spiral spin plane flops. (b, c) The most probable magnetic structures in the H-induced FE phase (X phase) for (b) $P_a > 0$ and (c) $P_a < 0$. The directions of polarization are drawn on the basis of Eq. (1). The negative sign of the coefficient A in Eq. (1) is deduced from [25].

ting. We define the magnetic principal axes within the ac plane as the easy and the hard axis, respectively, as shown in Fig. 2(a). Among the three magnetic phases, it has been found that only the AF2 phase with the spiral spin structure shows ferroelectricity [10,27,28]. In addition, when an H above 10 T is applied along the b axis at temperatures of around 10 K, the FE P flops from the b to the a axis, as shown in Fig. 1(b) [10]. The most noticeable feature of this material is that $MnWO_4$ is a simple P-flop system with only one kind of magnetic ions, Mn^{2+} ($S = 5/2$), and is hence suitable for the investigation of H-induced P flops.

It has been reported recently that the symmetry breaking caused by H in a canted direction should have a potential for exerting control over the P direction [17,30], which can be explained by a strong coupling between electric P and spiral magnetism. In this study, we have investigated the effect of the applied H direction on a P flop in a free-from $4f$-$3d$ exchange interaction in cycloidal ferroelectrics by using $MnWO_4$ as the test material. It has been found that the rotation direction of P upon the flop is determined by the direction of H, which is inclined from the b axis. We have also demonstrated that the direction of the P flop can be controlled through a magnetic channel without using an electric channel, and that a slight change of the H direction can reverse the sign of the flopped P.

A single crystal of $MnWO_4$ was grown by the floating zone method [28]. The crystal was oriented using Laue x-ray photography, and cut into a thin plate with the wide faces perpendicular to the crystallographic a axis. Gold electrodes were then sputtered onto the opposite faces of the sample for measuring the electric polarization along the a axis (P_a). The P_a value was obtained by integrating the ME current, which was measured with an electrometer (Keithley 6517A). Measurements of P_a in magnetic fields of up to 12 T were performed at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan. Magnetization was measured in magnetic fields parallel to the b axis by using a vibrating-sample magnetometer.

Figures 1(c) and 1(d) display the respective H dependence of the magnetization along the b axis (M_b) and P in $H \parallel b$. As reported in [10], the magnetic structure in the FE phase with $P \parallel a$ has not yet been identified. In this Letter, we refer to this phase as the X phase. As shown in Fig. 1(c), a small anomaly of M_b is observed around 10.7 T, which emerges as a peak of the derivative dM_b/dH_b. At this H, FE P rotates from the direction of the b axis toward the direction of the a axis, as shown in Fig. 1(d). This behavior indicates that the AF2 and X phases are different magnetic phases, and suggests that the P flop is caused by an H-induced magnetic phase transition. The probable magnetic structure of the X phase is discussed later.

To control the direction of P rotation in $MnWO_4$, we applied H in the direction canted from the b axis, which is one of the principal magnetic axes, within the ab plane, since the canted H should break the twofold rotational symmetry around the b axis. We have observed a contrastive P-flop behavior when the H direction slightly deviates from the b axis. Figures 3(a) and 3(b) show the dependence of P_a on H for two magnetic field directions, where the respective angles between the direction of the field and the

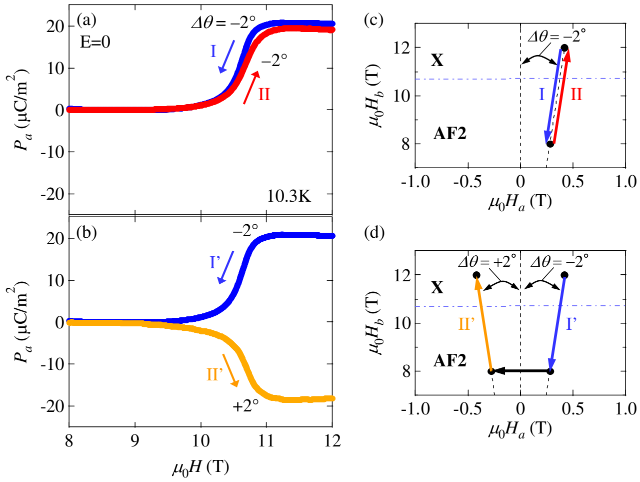

FIG. 3 (color online). (a) Dependence of P_a on the magnetic field (H). Considering P_a, the poling direction determined by the applied electric field, $E_a = +500$ kV/m, at 12 T is defined as the positive direction. The processes for decreasing and increasing H are denoted with I and II, respectively. The deviation of the direction of H from the b axis ($\Delta\theta$) is $-2°$ for both processes, as shown in (c). (b) Dependence of P_a on H. The processes corresponding to the decreasing and increasing of H are denoted with I′ and II′, respectively. $\Delta\theta$ is $-2°$ for process I′, and the rotation was from $-2°$ to $+2°$ at 8 T before process II′, as shown in (d).

b axis ($\Delta\theta$) are $-2°$ and $+2°$. The data for P_a presented in Figs. 3(a) and 3(b) were collected with the procedures schematically shown in Figs. 3(c) and 3(d), respectively. First, the sample was cooled from above T_N in a poling electric field along the a axis, $E_a = +500$ kV/m, and in a magnetic field, $H = 12$ T, along the direction canted from the b axis by $\Delta\theta = -2°$. At 10.3 K, where the X phase with positive P_a appeared, the poling electric field was removed. Then, P_a was measured as H decreased from 12 T to 8 T, which is shown as I in Fig. 3. As shown in Figs. 3(a) and 3(b), P_a disappears around 10.7 T due to a P flop from the a axis to the b axis. Then, P_a was measured as H increased from 8 T to 12 T. Without changing the H direction ($\Delta\theta = -2°$), which is shown as II in Fig. 3(a), the P_a value after another P flop from the b axis to the a axis was almost the same as that obtained before the first P flop. This result indicates that a series of processes I and II reproduces the FE single-domain state in the X phase, which is realized by applying a poling electric field. On the other hand, when the H direction is changed within the ab plane to $\Delta\theta = +2°$ at 8 T after the I′ process in Fig. 3(b), the sign of P_a is opposite to that before the I′ process. This result indicates that the FE single-domain state where the sign of P is reversed appears in the X phase after the processes I′ and II′. It is noteworthy that in both cases shown in Figs. 3(a) and 3(b), the FE single-domain state is not destroyed even across the P-flop processes without applying any poling electric field. Moreover, the contrasting results indicate the existence of a correlation between the H direction and the direction of the P rotation.

Figure 4(a) shows the details of the relation between P_a and the direction of the H as the latter increases after process I with $\Delta\theta = -2°$. All measurements were carried out as similar processes, which are denoted with II or II′ in Fig. 3. Before each measurement, the sample was warmed up above Néel temperature at 12 T, after which it cooled down to 10.3 K while applying an electric field, $E_a = +500$ kV/m, to obtain a single-domain state. As shown in Fig. 4(a), P flops from the direction of b to that of a at around 10.7 T for the H direction in the range $-4° \leq \Delta\theta \leq +4°$. However, the direction of P_a in the X phase is reversed when $\Delta\theta$ changes in sign, as shown clearly in Fig. 4(a). These results indicate that the direction of an H canted from the b axis, which lowers the symmetry of the system, determines the P flop direction, and maintains the FE single-domain state during the P-flop process.

Figure 2(a) displays the magnetic structure of AF2 with $P \parallel b$. Taking account of the P direction in the X phase, which is parallel to the a axis, and the inverse-DM interaction, the most probable magnetic structure of the X phase is a cycloidal spiral in which the spins rotate within the ac plane and the vector chirality ($\boldsymbol{C}$) is along the b axis, as shown in Figs. 2(b) and 2(c) . This magnetic structure is consistent with the theoretical predictions [21]. In this case, the P flop can be induced by a 90° rotation (flop) of the spiral spin plane around the easy axis [see Fig. 2(a)]. In addition, we can attribute the magnetization anomaly which occurs upon the P flop around 10.7 T in Fig. 1(c) to the spin flop transition.

If the spiral spin plane flops between the two directions, $-90°$ (A) and $+90°$ (B), in H, as shown in Fig. 2(a) with equal probability, comparable volumes of the ac-cycloidal-spiral domains would appear, where the $\boldsymbol{C}$ along the b axis have opposite signs ($C_b > 0$ and $C_b < 0$). In this case, the information of the FE single-domain state should be lost after the P-flop process since the P direction depends on the sign of C_b, and the polarizations along the a axis in the two kinds of domains have opposite signs ($P_a > 0$ and $P_a < 0$), as shown in Figs. 2(b) and 2(c), respectively. Indeed, we have observed such behavior, described in Fig. 4(a), when the H is applied along the b axis, $\Delta\theta = 0°$. When the H direction is canted from the b axis within the ab plane ($\Delta\theta \neq 0°$), H also contains the hard-axis component. This component of H can lift the degeneracy of the four types of magnetic domain walls between the AF2 ($\pm P_b$) and X phases ($\pm P_a$), which might appear during the P-flop process. Since each magnetic domain wall correlates with the relative configuration of the different spiral spin structures of the AF2 and the X phases, more stable magnetic domain walls in canted H make the flop direction of $\boldsymbol{C}$ unique, and the nature of the FE single domain is maintained even after the P flop. In addition, the dependence of the sign of P_a on $\Delta\theta$ observed in Fig. 4(a) can be attributed to the selection of the type of magnetic domain wall by the hard-axis component of H.

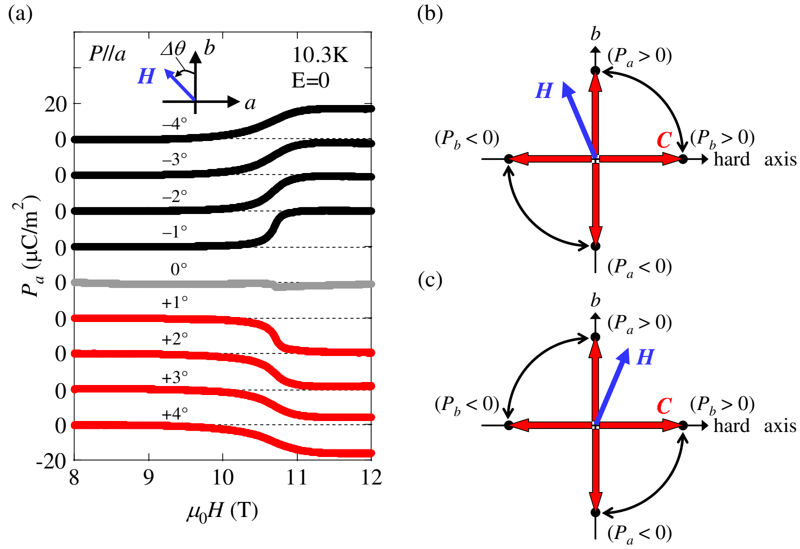

FIG. 4 (color online). (a) Dependence of P_a on the magnetic field H as measured while increasing the magnetic field in various directions ($\Delta\theta$) at 10.3 K. The sample was positively poled ($P_a > 0$) at 12 T, after which it underwent a P flop to $P \parallel b$ while decreasing the magnetic field inclined at $\Delta\theta = -2°$ before each measurement. (b, c) Rotation of the vector spin chirality (***C***) in a canted H. The P directions corresponding to ***C*** are also shown. The displayed ***C***-flop behavior appears if the ME domain wall is thinner than half of the magnetic modulation wavelength.

We roughly estimate that the difference in Zeeman energy between the two types of thin domain walls in an H inclined by 1° can exceed the thermal energy if the area of the wall is 10^1 nm^2. The typical size of a domain in multiferroics is at least 100 nm, judging from the widths of superlattice peaks. Our model can therefore explain the selective rotation of P in a canted field. In Figs. 4(b) and 4(c), we schematically show the possible ***C***-flop processes, which can be realized when the domain wall is thin. It should be noted that the degeneracy of the ***C*** flop directions, which correspond to those of P, is lifted by the hard-axis component of H, which breaks the twofold rotational symmetry along the b axis. This scenario regarding a canted H induced symmetry breaking should be common for all P-flop systems with spiral spin structures. Indeed, we have recently confirmed a similar phenomenon in perovskite RMnO$_3$ (R = Tb and Dy), which is the prototypical P-flop system [31].

In summary, we have found that the FE single-domain state is retained after a P-flop process induced by the application of H when the direction of the latter deviates from the b axis within the ab plane. It was also demonstrated that the change of the sign of the deviation angle between H and the b axis causes a reversal of P in the flopped phase. The present observation indicates that the H-induced FE phase with $P \parallel a$ should have a cycloidal-spiral spin structure, in which spiral spins exist within the ac plane, and the P flop direction is controlled by the H through a lift of degeneracy of the magnetic domain boundaries between the AF2 and the X phase.

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