Control of the electric polarization flop direction by a canted magnetic field in a magnetoelectric multiferroic MnWO₄

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Abstract. The relationship between the magnetic field direction and the flopped ferroelectric polarization has been investigated for multiferroic MnWO₄. We have observed that the ferroelectric polarization flop direction is switched without applying an electric field, when the direction of an applied magnetic field slightly deviates from the $b$ axis within the $ab$-plane. The polarization flop direction during the phase transition between $P//a$ and $P//b$ phase in a canted magnetic fields has been experimentally determined. The stability of magnetoelectric domain walls in a canted magnetic field would play a key role in the directional control of the electric polarization flop phenomenon.

1. Introduction

Magnetoelectric (ME) multiferroic materials, in which magnetic and ferroelectric (FE) orders coexist, have recently attracted much attention due to their potential uses in novel applications such as controlling electric polarization ($P$) by using a magnetic field ($H$) or vice versa [1,2]. In particular, a new class of multiferroics, in which magnetic order induces a FE phase transition [3,4], often shows gigantic ME effects, such as the flop (90°-rotation) induced by $H$ [3,5]. In recent years, the relation between the magnetic order and the ferroelectricity in some multiferroic materials, such as perovskite TbMnO₃, has been intensively investigated. It has been proven that ferroelectricity appears in the cycloidal-spiral spin phase without centrosymmetry [6], in which the spin rotation axis is not parallel to the magnetic modulation vector ($Q$). 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 Dzialoshinski-Moriya (DM) interaction [7]. According to the microscopic model proposed by Katsura et al.[7], the spin moments on two neighboring sites, $S_i$ and $S_j$, should induce a local dipole moment $p$ given by $p = Ae_j \times (S_i \times S_j)$, where $e_j$ is the unit vector connecting the two sites and $A$ is a constant. This formula, which can be also regarded as the inverse Dzyaloshinskii-Moriya (IDM) interaction, predicts that macroscopic $P$ should appear in the cycloidal-spiral spin phase.

$P$ flops induced by $H$ have been observed in some multiferroics exhibiting ferroelectricity driven by the spiral-spin structure, such as TbMnO₃, MnWO₄ [3,5]. With a phenomenological model, Mostovoy has proposed that controlling the vector spin chirality $C = S_i \times S_j$, which is perpendicular to $Q$, by using an $H$ induces the $P$-flop phenomenon in a cycloidal spiral spin system [8]. In this model, the $C$ of a spiral spin structure points in the applied $H$ direction, and consequently $P$ flops along the axis perpendicular to both $C$ and $Q$. However, this model cannot explain the $P$ flop observed in well-known
ME multiferroic systems, such as perovskite TbMnO$_3$, since the 4$f$-3$d$ exchange interaction between adjacent rare-earth and manganese ions should complicate the response of $P$ to $H$ [8]. From this viewpoint, MnWO$_4$ is a simple spiral magnetic system, which may follow Mostovoy's prediction [5,13]. MnWO$_4$ is crystallized in a wolframite structure ($P2_1/c$), in which MnO$_6$ octahedra are aligned in zigzag chains along the $c$ axis. It has been reported that there are three long-wavelength magnetic ordering states, AF1, AF2, and AF3 in this system at low temperatures (see Fig.1 (a)) [9]. 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 [9]. Among the three magnetic phases, it has been found that only the AF2 phase with the spiral spin structure shows ferroelectricity [5,10,11]. In addition, when an $H$ above 10 T is applied along the $b$ axis at temperatures of around 10 K, the FE $P$ flips from the $b$ to the $a$ axis, as shown in Fig.1 (b) [5,13]. 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 $P$ flop.

We have recently reported that the symmetry breaking induced by a canted $H$ should have a potential for controlling the $P$ direction [12-14], which can be explained by a strong coupling between electric $P$ and spiral magnetism. In this study, we have investigated the influence of the applied $H$ direction on a $P$ flop of MnWO$_4$, which is one of the systems free from the interference of 4$f$ ions in cycloidal ferroelectrics. 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 and lowers the symmetry of the system.

![Diagram](image)

Figure 1 (a) Magnetoelectric phase diagram of MnWO$_4$ in a magnetic field along the $b$ axis. (b) Magnetic field, which is parallel to the $b$ axis, dependence of the electric polarization along the $a$ axis ($P_a$) and $b$ axis ($P_b$).

2. Experimental
A single crystal of MnWO$_4$ was grown by the floating zone method [11]. The crystal was oriented using Laue x-ray photography, and cut into a rectangular shape with two kinds of paired faces, which are perpendicular to the crystallographic $a$ and $b$ axes, respectively. Gold electrodes were then sputtered onto each face of the sample for measuring the electric polarization along the $a$ and $b$ axes ($P_a$ and $P_b$). The $P$ value was obtained by integrating the ME or the pyroelectric current, which was measured with an electrometer (Keithley 6517A). Measurements of $P$ in magnetic fields of up to 14.5...
were performed at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan.

3. Results and Discussions
To manipulate the direction of $P$ rotation in MnWO$_4$, we applied $H$ in the direction canted from the $b$ axis, which is one of the magnetic principal axes, within the $ab$ plane, since the canted $H$ should break the two-fold rotational symmetry around the $b$ axis. Figure 2 (a) shows the temperature dependence of the flopped $P$ along the $b$ axis ($P_b$) for two magnetic field directions, where the respective angles between the direction of the field and the $b$ axis ($\Delta \theta$) are $+1.5^\circ$ and $-1.5^\circ$. The data for $P_b$ presented in Fig. 2 (a) were obtained with the procedures schematically shown in Fig. 2 (b). First, the sample was cooled from above $T_N$ in a poling electric field along the $a$ axis, $E_a = +80$ kV/m, and in a magnetic field, $H = 12$ T, along the axis canted from the $b$ axis by $\Delta \theta = \pm 1.5^\circ$ (I and I’ in Fig. 2(b)). At 10.3 K, where the X phase with positive $P_a$ appeared, the poling electric field was removed. Then, $H$ was decreased from 12 T to 8 T, which is shown as II and II’ in Fig. 2 (b). As similar with the case of $\Delta \theta = 0^\circ$ in Fig. 1 (b), $P$ flop from the $a$ axis to the $b$ axis has been observed around 10.7 T. Then, $P_b$ was measured at 8 T while warming temperature (III and III’ in Fig. 2(a)).

Figure 2 (a) Temperature dependence of the electric polarization along the $b$ axis ($P_b$) in the canted magnetic fields ($\Delta \theta = \pm 1.5^\circ$). (b) Data collection procedure for the Fig. 2 (a). (c), (d) The relation between the magnetic field deviation angle from the $b$ axis within the $ab$ plane and $P$-flop directions.
As shown in Fig. 2 (a), we have observed contrastive P-flop behaviors when the H direction deviates in the opposite directions from the b axis. For both canted magnetic field directions, $\Delta \theta = \pm 1.5^\circ$, the finite polarization, which is comparable with that of the single domain state [5], is observed. This result indicates that single domain state is retained during the P-flop process in the canted H. Another noticeable point is that the direction of Pb in the AF2 phase is reversed when $\Delta \theta$ changes in sign. In Figs. 2 (c) and (d), the relation between the magnetic field direction and the P flop direction are schematically shown. $P_a (>0)$ flops to the +b direction, when $\Delta \theta$ is positive ($\Delta \theta > 0$). On the other hand, when $\Delta \theta$ becomes negative ($\Delta \theta < 0$), $P_a (>0)$ flops to the -b direction. Taking account of the IDM interaction, the observed result should also indicate that the vector spin chirality C rotates toward the canted H direction, though it is not experimentally confirmed that the sign of the prefactor $A$ for the $P_a$ phase is the same as that for the $P_b$ phase. These results indicate that the direction of an H canted from the b axis, which lowers the symmetry of the system, determines the P (C) flop direction.

From the microscopic viewpoint, the H-stabilized ME domain-wall model has been proposed to explain the observed phenomena [13]. In this model, the Zeeman energy stabilization lifts the degeneracy of the four types of the ME domain walls, which connect the different spiral spin structures with $\pm P_a$ and $\pm P_b$. In this study, we could experimentally predict the stabilized ME domain wall type in a canted H through C-flop behavior. The observed results indicate that the spiral spin planes gradually rotate as passing perpendicular configuration to the applied H within the ME domain walls. In this situation, the ME domain wall are speculated to be thicker than the magnetic modulation wavelength.

4. Conclusion

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 within the ab-plane causes a reversal of P in the flopped phase. In addition, we have experimentally determined the relationship between the H direction and P-flop direction. The present observation indicates that the P flop direction is controlled by the H through a lift of degeneracy of the magnetic domain walls between the different spiral spin structures, and these domain walls would be thicker than the magnetic modulation wavelength.

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