Magnetoelectric Memory Effect of the Nonpolar Phase with Collinear Spin Structure in Multiferroic $MnWO_4$

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The novel memory effect of a nonpolar paraelectric phase with a collinear spin structure has been observed in a magnetoelectric multiferroic material $MnWO_4$. Since the ferroelectric polarization arises from a noncollinear spin structure, in a new class of magnetoelectric multiferroic materials with a spiral-spin structure, the information of ferroelectric domains should be lost in the collinear spin phase. However, in $MnWO_4$, it has been found that the domain states in the ferroelectric phase are memorized even in the nonpolar phase with a collinear spin structure, when the phase transition is of the first-order type. Here we demonstrate a magnetoelectric memory effect that the ferroelectric single-domain state can be reproduced from the paraelectric phase by a magnetic field. We propose the nuclei growth model, in which the small ferroelectric embryos keep the polarization state in the nonpolar collinear spin phase.

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Magnetoelectric (ME) multiferroic materials, in which magnetic and ferroelectric (FE) order coexist and mutually interact, have recently been attracting much interest because of the possibility to control magnetism by electric fields and vice versa [1–4]. In particular, a new class of multiferroic materials, in which the spiral-spin structure induces ferroelectricity [5], exhibits a gigantic ME effect, such as a magnetic-field- (H-)induced FE phase transition [6–8] and the FE polarization (P) flop [3,9–13] and reversal [14–16]. Among them, an H-induced phase transition between the paraelectric (PE) and FE phase is one of the noticeable phenomena, since the giant nonlinear P response to H, which is especially observed upon the first-order type phase transition, could lead to a new type of storage device, such as an H-controlled FE memory. However, we have to apply not only H but also an electric field (E) in the H-induced FE phase transition, since a FE single-domain state is necessary for such a giant nonlinear ME response. What we demonstrate here, for a multiferroic manganese tungstate ($MnWO_4$), is the reproduction of the FE single-domain state by an H across the phase transition from a PE to a FE phase without an E.

$MnWO_4$ has been known as a mineral species named Hübnerite, since 1865 [17]. The crystal structure of $MnWO_4$ is a Wolframite structure, which belongs to the monoclinic space group $P2/c$ with $\beta \sim 91°$ [18]. One of the characteristics of this crystal structure is a zigzag chain of edge-sharing MnO_6 octahedra along the c axis. $MnWO_4$ is also known to be a frustrated magnet with competing exchange interactions [18,19]. With decreasing temperature, $MnWO_4$ undergoes successive magnetic phase transitions to three long-wavelength antiferromagnetic (AF) ordering states, AF3 ($T_2 < T < T_N$), AF2 ($T_1 < T < T_2$), and AF1 ($T < T_1$) [see Fig. 1(b)]. According to neutron diffraction results at 0 T [18], AF1, AF2, and AF3 are a commensurate collinear-antiferromagnetic phase, an incommensurate cycloidal-spiral-spin phase, and an incommensurate collinear-antiferromagnetic phase, respectively. In AF1 and AF3, Mn^{2+} magnetic moments collinearly align in the ac plane, forming an angle of about 35° with the a axis, whereas in AF2 an additional component along the b axis exists [Fig. 1(b)]. Among the three magnetic phases (AF1–AF3), only the AF2 phase with the spiral-spin structure shows ferroelectricity [10,20,21]. According to the microscopic model proposed by Katsura, Nagaosa, and Balatsky [22], the spin moments on two neighboring sites, $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$, should induce a local dipole moment $\boldsymbol{p}$ given by $\boldsymbol{p} = A\boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$, where $\boldsymbol{e}_{ij}$ 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 interaction [23], predicts the macroscopic uniform P in a magnetic structure with cycloidal-spiral-spin components, and explains the relationship between magnetic structure and P observed in the AF2 phase. In addition, the correlation between the vector spin chirality ($\boldsymbol{C} \equiv \boldsymbol{S}_j \times \boldsymbol{S}_i$) of the spiral-spin structure[24] and P direction has recently been confirmed by spin-polarized neutron diffraction measurement [25]. Since these experimental facts indicate that the vector spin chirality is a key factor for the appearance of ferroelectricity, the information of the P direction in the FE phase with spiral-spin structure should be lost in collinear spin phases without vector spin chirality, such as AF1 and AF3 phases. Nevertheless, it has been found that the PE AF1 phase with collinear spin structure memorizes the information of the FE single-domain states of the AF2 phase.

A single crystal of $MnWO_4$ was grown by the floating zone method. The crystal was oriented using Laue x-ray photographs, and cleaved into a thin plate with wide faces perpendicular to the crystallographic b axis. Gold elec-

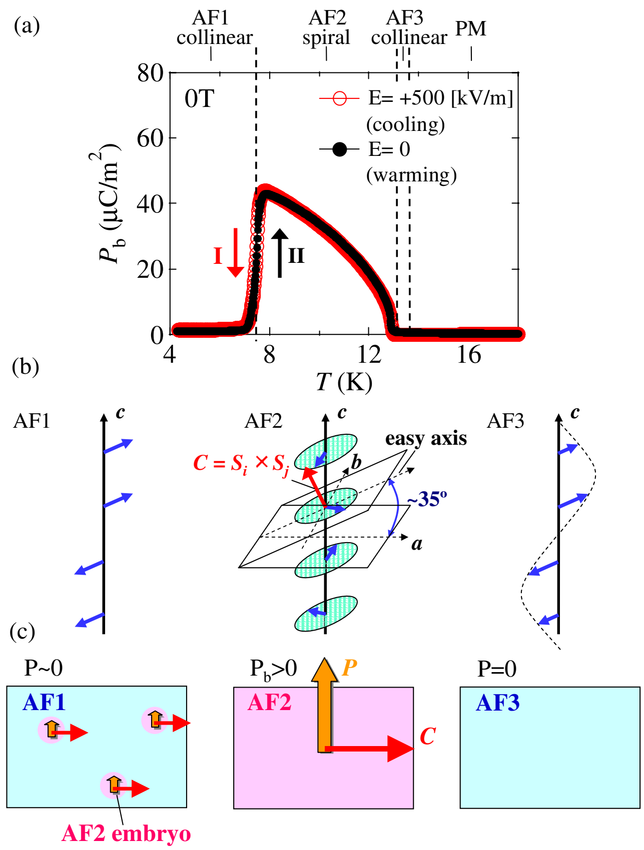

FIG. 1 (color online). (a) Temperature dependence of electric polarization along the b axis (P_b). Open circles represent the cooling process with a poling electric field, $E = +500$ kV/m (I), and filled circles represent the warming process without a poling electric field (II). (b) Respective schematic magnetic structures of the AF1, AF2, and AF3 phases. (c) The nuclei growth model of the ferroelectric AF2 embryo. Orange (light grey) block arrow and red (dark grey) arrow represent ferroelectric polarization (P) and vector spin chirality ($\boldsymbol{C}$), respectively. The pink (circular grey) region in the AF1 phase represents an AF2 embryo.

trodes were sputtered onto the opposite faces of the sample for measurements of electric polarization along the b axis (P_b). The measurements of P_b in a magnetic field up to 14.5 T were performed at the High Field Laboratory for Superconducting Materials, Institute for Research, Tohoku University, Japan. The P_b value was obtained by integrating the ME current, which was measured with an electrometer (Keithley 6517A). Magnetic-field directions were controlled by rotating the sample in a cryostat equipped with a 14.5 T superconducting magnet. Before each measurement of P_b, an electric field of $+500$ kV/m was applied to the sample. The poling electric field was turned off before the measurements.

Figure 1(a) shows the temperature dependence of P along the b axis (P_b) at 0 T. The P_b data shown in Fig. 1(a) were collected by the following procedures. First, a single crystal sample was cooled from above T_N, and P_b was measured by applying a poling electric field along the b axis (open circles), $E = +500$ kV/m. Below 7.6 K, where the PE AF1 phase appears, the poling field was removed. Then the P_b was measured by warming the sample (filled circles). As shown in Fig. 1(a), the P_b value in the warming process without a poling E (II) is the same as that obtained in the cooling process with a poling E (I). In addition, it has been observed that P_b in the FE AF2 phase in the warming process is negative, when the $E < 0$ in the cooling process (not shown). A similar phenomenon is also described in Ref. [20]. These results indicate that the domain states of the FE AF2 phase are memorized even in the PE AF1 phase without vector spin chirality, and this "memory effect" makes it possible to reproduce the FE single-domain states without a poling E in the phase transition from the PE (AF1) to the FE (AF2) phase.

It has been found that an H can also reproduce the FE single-domain state through the memory effect of the AF1 phase. Figure 2(a) shows the H dependence of P_b. The procedures for the P_b measurement in Fig. 2(a) are schematically displayed in Fig. 2(b). Before each measurement, the sample was cooled from above T_N in an electric field E (-500, 0, or 500 kV/m) at 0 T (I). At 4.3 K (PE AF1), the poling field E was removed, and then P_b was measured while increasing H in the a direction up to 6 T (II). As displayed in Fig. 2(a), the H-induced FE phase transition occurs around 3 T. The noticeable point is that the sign of the H-induced FE P depends on the direction of the poling E at 0 T. In addition, the H-induced P value is as large as that of the FE single-domain state, which is shown by an orange (light grey) line in Fig. 2(a). These results mean "ME memory effect," which means we can magnetically read out the electrically written information of the FE single-domain state from the PE state.

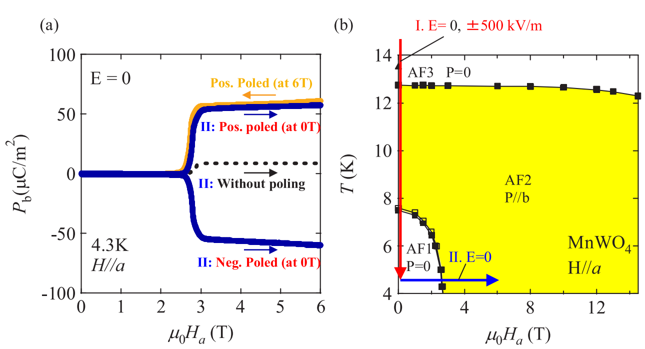

FIG. 2 (color online). Memorized ferroelectric domain states reproduction by a magnetic field. (a) Magnetic-field dependence of electric polarization along the b axis (P_b) at 4.3 K. The magnetic field is applied along the a axis. Blue (dark grey) lines represent the ME memory process, and the orange (light grey) line represents the magnetic-field dependence of the FE single-domain state obtained by applying an electric field with $+500$ kV/m at 6 T. (b) Magnetoelectric phase diagram in magnetic fields parallel to the a axis. The procedures I and II for the measurement of the ME memory phenomenon are also schematically shown. The process II is displayed in (a).

The H-induced P value through the ME memory process shows the H-sweeping path dependence, when the H is reversed. We have performed two kinds of H-reversal processes, as schematically depicted in Figs. 3(c) and 3(d). One is the H reversal along the a axis [see Fig. 3(c)]. The H dependence of P_b in this process is shown in Fig. 3(a). Before the measurement in Fig. 3(a), the poling field, $E = +500$ kV/m, was applied in a magnetic field along the a axis to obtain the FE single-domain state. After the poling process, the poling field was removed, and then an H was swept from 13 T to -13 T along the a axis (1 and 2). As shown in Fig. 3(a), P_b in the FE AF2 phase appears in the same direction as the initial poling direction. It has also been found that P_b does not decay even after the following sweep from -13 T to 13 T (3 and 4). Another H-reversal process is performed with rotating the H direction within the ab plane [see Fig. 3(d)]. The H-direction dependence of P_b in this process is shown in Fig. 3(b). Here, θ denotes the angle between the a axis and the H direction as shown in the inset. Before each measurement in Fig. 3(b), the sample was cooled down to 4.3 K in a poling electric field, $E = +500$ kV/m, and a magnetic field along the a axis ($\theta = 0°$), respectively, and then the poling electric field was turned off. By rotating an H, P_b vanishes between $\theta =$ 30° and 150°. Taking into account the fact that the PE AF1 phase with collinear spin structure is stabilized in an H along the b axis ($\theta = 90°$) at 4.3 K [10,20], the observed results indicate that the FE-to-PE phase transitions occur in the H-rotating process, as is similar to the H-direction fixed process in Fig. 3(a). As θ exceeds 150°, the FE AF2 phase reappears. The interesting point is the contrasting sign change of P_b in the reentrant FE AF2 phase. As shown in Fig. 3(b), in low magnetic fields below 10 T, P_b appears in the same direction to the initial state. On the other hand, in magnetic fields higher than 12 T, P_b appears in the opposite direction to the initial poled state. These results indicate that the sign of P_b in the reentrant FE AF2 phase depends on the H-sweeping path. We have also confirmed that the P_b does not decay by repeating the H-rotating processes (not shown).

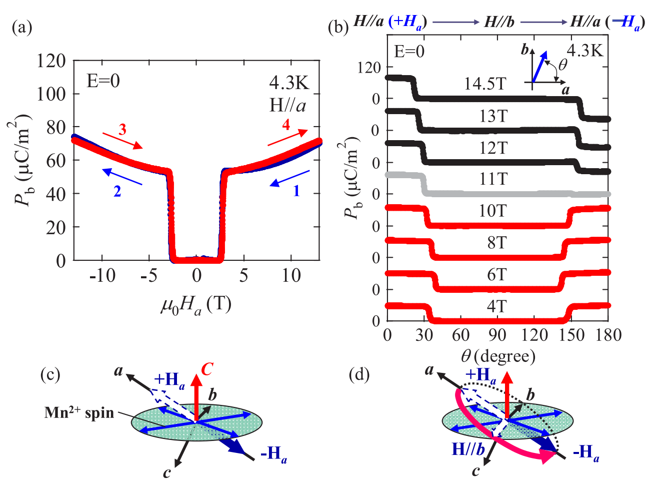

FIG. 3 (color online). Changes in electrical polarization with reversing magnetic field along several paths at 4.3 K. (a) With sweeping a magnetic field along the a axis. (b) With rotating a magnetic field of several field strengths within the ab plane. (c) and (d) Magnetic-field reversal processes are schematically shown for (a) and (b), respectively. $\boldsymbol{C}$ represents the vector chirality before magnetic-field reversal processes.

Taking into account the fact that the inverse Dzyaloshinskii-Moriya interaction is the origin of the P in the FE phase of $MnWO_4$ [25], the vector spin chirality ($\boldsymbol{C}$), which induces the FE polarization, should be retained in the AF1 phase. In that case, we should attribute the P response in the H-reversal processes to the change of the $\boldsymbol{C}$ direction. However, this scenario is inconsistent with the fact that $\boldsymbol{C}$ is not observed in the PE AF1 phase by the spin-polarized neutron diffraction measurements [25]. Here, we propose the interpretation based on the nuclei growth model of the FE embryo, which is a polar nucleus of the AF2 phase [20] [see Fig. 1(c)]. In this model, the existence of small FE AF2 embryos, which are smaller than the detection limit of the neutron diffraction measurement, is assumed in the AF1 phase. The $\boldsymbol{C}$ (or P) direction of the embryos is identical with the former AF2 phase. Then, the single-domain state with the preserved P direction would be reproduced in the PE-to-FE phase transition through the nuclei growth of the FE embryos, as shown in Fig. 1(c). Such embryos of the low symmetry phase in the high symmetry phase are also reported in some shape memory alloys, which show a first-order martensite type structural phase transition [26]. The common factor of these embryo models seems to be a metastability of the low symmetry phase in the first-order phase transition. Indeed, we have confirmed that the AF3 phase with similar collinear spin structure, which appears across the second-order phase transition from the FE AF2 phase, does not show such a memory effect as the AF1 phase does. The proposed scenario indicates that the similar effect could also be expected in other ME multiferroic materials, such as CuO [27], which show a first-order PE-FE transition.

Assuming FE AF2 embryos in the AF1 phase, we can explain the P behavior in the H-reversal processes in terms of the response of $\boldsymbol{C}$ in the embryos to H. In the H-sweeping process along the a axis, $\boldsymbol{C}$ only tilts toward the a axis without any sign reversal. Therefore, the P direction of the initial state should be retained [see Fig. 3(c)]. In the H-rotation processes shown in Fig. 3(b), the P responses can also be attributed to the $\boldsymbol{C}$ direction changes, which are determined by the competition between the Zeeman energy and the magnetic anisotropy, as reported in other ME multiferroic materials with spiral-spin structure [28,29]. When the former energy is smaller than the latter one, the rotating H cannot reverse $\boldsymbol{C}$ as shown in Fig. 4(a), and the P direction should be unchanged as observed below 10 T in Fig. 3(b). On the other hand, when the Zeeman energy is large enough to overcome the magnetic anisotropy energy, the H-induced spin cone is rotated by a rotating H, and the $\boldsymbol{C}$ is reversed,

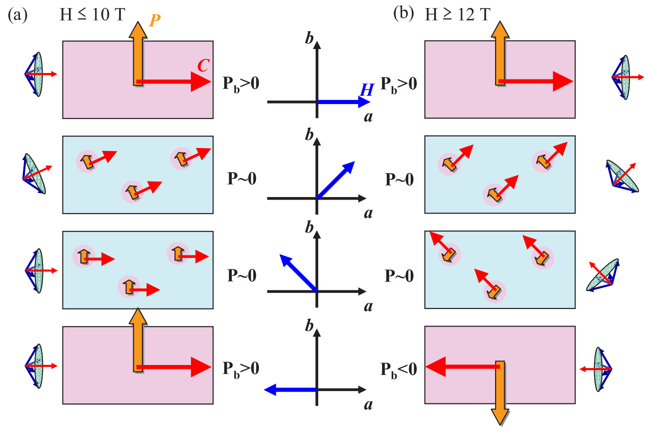

FIG. 4 (color online). Schematic drawing of the embryo model for the magnetoelectric memory effect in the rotating magnetic field. (a) The vector spin chirality behavior in the rotating magnetic field within the *ab* plane below 10 T. The orange (light grey) block arrow and red (dark grey) arrow represent ferroelectric polarization (P) and vector spin chirality ($\boldsymbol{C}$), respectively. Pink (circular grey) regions in the AF1 phase represent AF2 embryos. (b) The directional change of the vector spin chirality with rotating a magnetic field above 12 T within the *ab* plane.

as shown in Fig. 4(b). In this case, the P direction should also be reversed as displayed in Fig. 4(b), and we have observed such a behavior in Fig. 3(b) above 12 T.

In summary, we present the first observation of the new type of magnetic-field- (H-)induced ME effect, ME memory effect, in multiferroic $MnWO_4$. The feature of the ME memory effect, which enables us to read out the information of the single-domain polarization state without using an electric field, would suppress the polarization fatigue, and may lead to a new type of ME storage device. The H-sweeping path dependence of the FE polarization indicates that the origin of the observed memory effect could be attributed to small ferroelectric embryo existence.

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