Magnetic Biasing of a Ferroelectric Hysteresis Loop in a Multiferroic Orthoferrite

Y. Tokunaga,[1] Y. Taguchi,[1] T. Arima,[1,2,3] and Y. Tokura[1,4]
[1]RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan
[2]Department of Advanced Materials Science, University of Tokyo, Kashiwa 277-8561, Japan
[3]RIKEN SPring-8 Center, Hyogo 679-5148, Japan
[4]Department of Applied Physics and Quantum-Phase Electronics Center (QPEC), University of Tokyo, Tokyo 113-8656, Japan
(Received 6 October 2013; published 23 January 2014)

In a multiferroic orthoferrite $Dy_{0.7}Tb_{0.3}FeO_3$, which shows electric-field-(E-)driven magnetization (M) reversal due to a tight clamping between polarization (P) and M, a gigantic effect of magnetic-field (H) biasing on P-E hysteresis loops is observed in the case of rapid E sweeping. The magnitude of the bias E field can be controlled by varying the magnitude of H, and its sign can be reversed by changing the sign of H or the relative clamping direction between P and M. The origin of this unconventional biasing effect is ascribed to the difference in the Zeeman energy between the $+P$ and $-P$ states coupled with the M states with opposite sign.

DOI: 10.1103/PhysRevLett.112.037203 PACS numbers: 75.85.+t, 75.60.-d, 77.80.Dj

The mutual control of magnetization (M) and electric polarization (P) by electric (E) and magnetic fields (H) has long been a big challenge in condensed matter physics and applications. In multiferroic materials endowed with both P and M, it becomes possible, provided that they are strongly coupled [1,2]. Representative examples are H-induced P reversal [3–6] and its complementary process, namely, E-induced M reversal, as demonstrated recently [7,8]. Another example is the modification of a P-E loop by applying H [9–13]. In some cases, the application of H changes the value of coercive E [9,10], and in other cases, the shape of the P-E curves changes from paraelectriclike to ferroelectriclike [11,12] or from antiferroelectriclike to ferroelectriclike [13]. These effects on the P-E loops thus far reported did not depend on the polarity of H, and the obtained P-E loops in H remained symmetric with respect to the origin.

For ferroelectric ferromagnets with tight P-M clamping, the H effect on P-E loops remains a fundamentally important open question. In these materials, H is anticipated to affect a P-E loop in a sign-dependent manner; this is because P reversal accompanies M reversal in an external H, giving rise to a modification of the Zeeman energy. Thus, an asymmetric P-E loop with respect to the origin is expected, which can be viewed as an H-biasing effect on the P-E loop. In this Letter, we demonstrate such a biasing effect for a multiferroic rare-earth orthoferrite $Dy_{0.7}Tb_{0.3}FeO_3$ in which the E-driven M reversal has recently been attained [8]. The biasing effect of a ferroic hysteresis loop may provide useful functionality, as well as the magnetic counterpart known as "exchange bias" that shows up in antiferromagnetic and ferromagnetic heterostructures [14–19] and has been applied to practical devices [20].

As discussed in Ref. [8], $P(\|c)$ of $Dy_{0.7}Tb_{0.3}FeO_3$ originates not from an inverse Dzyaloshinsky-Moriya (DM) mechanism [21–23] but from symmetric exchange striction between rare-earth (R) $4f$ moments and Fe $3d$ spins, which order antiferromagnetically at 2.65 K and far above room temperature, respectively. The ferromagnetic moment ($\|c$) arises as the canting of antiferromagnetically coupled Fe spins from DM interaction [8]. Therefore, P reversal requires the change of an antiferromagnetic phase factor between 0 and π of either an R $4f$ moment or an Fe spin, i.e., θ_R or θ_{Fe} [8,10,24]. Note that the reversal of the Fe spin is necessarily accompanied by the reversal of a spontaneous M via the DM interaction. In other words, θ_{Fe} and M have a one-to-one correspondence with each other. In consideration of the symmetric exchange striction, the effective interaction energy can be expressed as $E_{int} = -\alpha PMM'$ [24], where α, P, M, and M' denote a coupling constant, electric polarization, ferromagnetic moment, and rare-earth staggered moment, respectively. M' also changes its sign, depending on the value of $\theta_R(= 0 \text{ or } \pi)$, similar to the case of M [8,24]. It should be noted that the direction of the DM vector itself always remains unchanged upon the P reversal here, in contrast to those predicted in polar-distortion-induced DM weak ferromagnets, such as $LiNbO_3$-type $MTiO_3$ (M = Fe, Ni, Mn) [25].

Because of the trilinear form of the interaction energy, four states out of eight possible combinations for P, M, and M' are energetically stable, namely, the ($P+$, $M+$, $M'+$), ($P+$, $M-$, $M'-$), ($P-$, $M-$, $M'+$), and ($P-$, $M+$, $M'-$) states. These states or domain states are schematically presented in Fig. 1(a) as closed circles in the P-M-M' order-parameter phase space. There are three kinds of composite domain walls that separate the four domain states as described in Ref. [24] in detail, but in this Letter, we focus

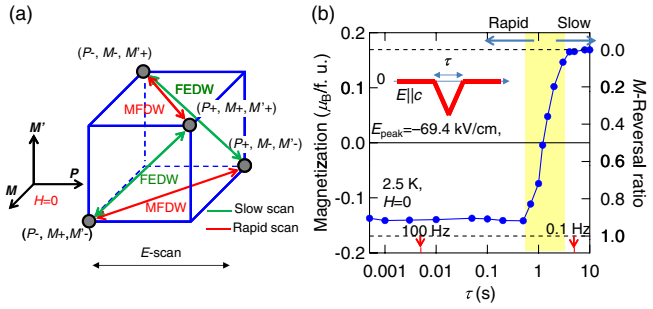

FIG. 1 (color online). (a) Relation among energetically stable domain states and domain walls that can be driven by the E field is displayed in the P-M-M' order-parameter phase space of $Dy_{0.7}Tb_{0.3}FeO_3$ for $H = 0$. Each corner of cube corresponds to the $+$ or $-$ state of the corresponding order parameter. Only four states out of eight (as presented with closed circles) are stable due to the trilinear-type interaction energy among P, M, and M' (see text). FEDW and MFDW denote ferroelectric and multiferroic domain walls, respectively. Green (red) arrow indicates the P-reversal process for a slow (rapid) E scan whose frequency is larger (smaller) than those indicated with yellow in panel (b). (b) Electric-pulse width dependence of M and the M-reversal ratio in $Dy_{0.7}Tb_{0.3}FeO_3$ at 2.5 K. $(P+, M+, M'+)$ initial state is prepared, and a triangle-shaped single E pulse with the peak height of $E_{peak} = -69.4$ kV/cm and temporal width of τ was applied. After the application of the pulse, magnetization was measured (reproduced from Ref [8]).

only on two kinds of domain walls that are driven by E. Such domain walls are represented with red and green arrows in Fig. 1(a). One is the multiferroic domain wall (MFDW) across which both P and M change the sign while keeping M' unchanged, and this is nothing but the antiphase boundary of the Fe antiferromagnetic order. The other is the ferroelectric domain wall (FEDW), across which both P and M' change sign while keeping M unchanged, and this corresponds to the antiphase boundary of the rare-earth antiferromagnetic order [8,24].

Another unique feature of this system is that the E-driven P-reversal process depends on the E-sweeping speed. As shown in Fig. 1(b), when a triangle-shaped single E pulse with a short (long) width τ is applied to a $(P+, M+, M'+)$ state, M is reversed (remains unchanged); therefore, P reversal occurs through the nucleation and propagation of MFDW (FEDW). Such a temporal-scale-dependent feature has been ascribed to a larger inertia of the M' domain wall arising from the strong Ising character of the R $4f$ moment than the M (Fe) domain wall [8]. Namely, upon slow E sweeping, the system prefers to reverse P through the motion of FEDW, which is nothing but the domain wall of the R moment. However, because the reversal dynamics of the Ising-like R moments is slow, it cannot follow rapid E sweeping. On the other hand, the Fe spins can follow much faster dynamics than the anisotropic R moments. Thus, upon decreasing τ, the reversal of P starts to occur through the MFDW or, equivalently, the domain wall of the Fe spin. Therefore, it is the anisotropy of the rare-earth moment that governs the crossover temporal scale. This crossover in the present material takes place in the yellow-colored region in Fig. 1(b), which corresponds to a frequency around several hundreds of mHz at 2.5 K [8]. Hereafter, we refer to the sweeping process with a higher (lower) frequency than this crossover frequency as *rapid* (*slow*) sweeping.

Single crystals of $Dy_{0.7}Tb_{0.3}FeO_3$ were grown by a floating zone method. The orientation of the crystal was determined by a back-Laue x-ray diffraction method. A plate with a dimension of 1 mm × 2 mm × 31 μm with the widest face normal to the c axis was cut out from the single crystal bar. Electrodes were formed on both of the widest faces by a heat-treatment-type silver paste to make a capacitor structure. The temperature and $H(\|c)$ were controlled with a superconducting magnet (PPMS, Quantum Design), and the P-E curves with $E\|c$ were measured with a ferroelectric tester (Premier II, Radiant). E-linear paraelectric components were subtracted from the obtained P-E curves [26]. Prior to each measurement, the initial state was prepared with a magnetoelectric- (ME-) poling procedure. The M-H curves were measured by a superconducting quantum interference device (SQUID) magnetometer (SQUID-VSM, Quantum Design), and the coercive magnetic field (H_c) was found to be ~1060 Oe at 2.5 K and ~440 Oe at 2 K, respectively, as shown in Fig. 3(e).

In Fig. 2(a), we show the H dependence of the P-E loop measured at $f = 0.1$ Hz (slow scan) with a $(P+, M+, M'+)$ state being the initial state. As an initial trial, $H = 500$ Oe ($< H_c$) and $T = 2.5$ K was selected. The P-E loop does not show an appreciable change upon application of H and remains symmetric with respect to the origin at $H = +500$ Oe as well as at $H = 0$. On the other hand, it can be clearly seen from Figs. 2(b)–2(d) that the P-E loop measured with rapid E sweeping ($f = 100$ Hz) shows an apparent shift along the E-axis direction upon the application of H, where the direction depends on the polarity of H.

Such an E-sweeping-speed-dependent H effect can be explained as follows. At $H = 0$ and $E = 0$, all four states in the order-parameter phase space have the same energy. However, under H and in the absence of E, an energy difference arises. The energies of two states out of the four become lower compared to the others by $2MH$ due to Zeeman energy, as shown in Figs. 2(e)–2(g). As mentioned above, whether or not P reversal is accompanied by M reversal depends on the E-sweeping speed. When the E-sweeping speed is low ($f = 0.1$ Hz), P reversal is not accompanied by M reversal, and it occurs through the nucleation and propagation of FEDWs, as depicted with green arrows in Fig. 2(e). Therefore, the final state should be $(P-, M+, M'-)$ with the same $M+$ as the initial state $(P+, M+, M'+)$. In the presence of H, both states have the same Zeeman energy gain ($-MH$), and the effect of H on

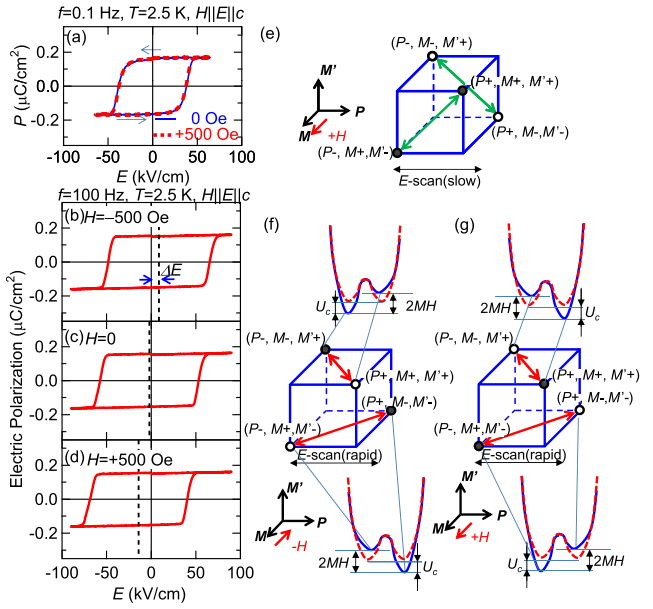

FIG. 2 (color online). (a) P-E loops measured at $f = 0.1$ Hz (slow scan) at 2.5 K. Dotted (solid) line corresponds to the loop measured in $H = +500$ Oe (0 Oe). P-E loops measured at $f = 100$ Hz (rapid scan) in (b) $H = -500$, (c) $H = 0$, and (d) $H = +500$ Oe, respectively. Vertical dashed lines indicate the center of the hysteresis loop, which corresponds to the bias field ΔE. (e) Schematic of P-reversal paths for slow E scan ($f = 0.1$ Hz) in the presence of $H(>0)$. Filled (open) circles represent states with lower (higher) energy due to Zeeman energy induced by $H(>0)$ along the c axis. P reversal occurs through the nucleation and propagation of FEDW without changing the sign of M. (f),(g) Schematic paths of P reversal for rapid E scan ($f = 100$ Hz) in a (f) negative and (g) positive H field. P reversal occurs through the MFDW without changing the sign of M'. Filled (open) circles represent states with lower (higher) energy by an amount of $2U_c \equiv 2MH$ due to the Zeeman energy. Free energy with double minimum show asymmetric deformation that depends on this Zeeman energy at $E = 0$ (blue solid curves). The energy difference $2U_c$ is totally compensated when $E = \Delta E$ is applied (red dashed curves).

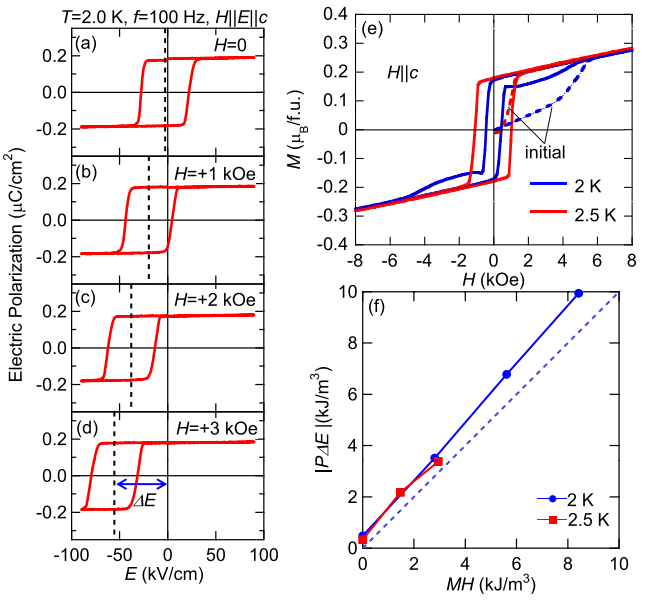

FIG. 3 (color online). (a)–(d) P-E loops measured in $H = 0$, +1, +2, and +3 kOe, respectively, at $T = 2$ K and at $f = 100$ Hz (rapid scan). Each loop was measured after preparing an initial state of ($P+$, $M+$, $M'+$) by an ME poling. Dotted lines indicate center of the hysteresis loop, corresponding to bias field ΔE. (e) M-H loop measured after zero-field cooling at 2 (blue line) and 2.5 K (red line). Dotted lines correspond to initial curves. (f) Comparison between $|P\Delta E|$ and MH obtained from P-E loops and M-H curves (filled symbols). ΔE, P, M values are the bias E field at H, saturation value of polarization, and weak-ferromagnetic moment at each temperature. The dotted line represents the relation that $|P\Delta E| = MH$.

the free energy with the double minimum associated with the $\pm P$ states is merely a parallel shift by an amount of $-MH$ along the energy axis while keeping the symmetry with respect to $E = 0$. Thus, the P-E loops show no shift along the E axis and remain symmetric with respect to the origin, as observed in Fig. 2(a).

On the other hand, for the rapid E sweep ($f = 100$ Hz), P reversal occurs through the nucleation and propagation of MFDWs, as displayed in Figs. 2(f) (for $H < 0$) and 2(g) (for $H > 0$). These processes are accompanied by an M reversal, and the final state should be ($P-$, $M-$, $M'+$). In contrast to the slow E-sweep case, the application of H differentiates the final state energy from that of the initial state due to the Zeeman energy, $2MH$. This situation is schematically depicted in Figs. 2(f) and 2(g) as asymmetrically distorted double-minimum potential (blue solid curves) in the absence of E, and the energy difference ($2U_c$) will be totally compensated by the application of $E = \Delta E$ that satisfies $-P\Delta E = MH(= U_c)$, as depicted with red dashed curves. Therefore, the P-E loop should be shifted along the E axis by $\Delta E = -MH/P$. Thus, the amount of the shift is proportional to H, and its sign depends on the polarity of H; if the initial state is prepared to be ($P+$, $M-$, $M'-$) by an ME-poling process, then the final state after P reversal will be ($P-$, $M+$, $M'-$), as displayed with arrows in the bottom planes of the cubes in Figs. 2(f) and 2(g).

To observe the relation between a bias E field and Zeeman energy in a more quantitative manner and also to see whether the bias effect persists even for $H > H_c$, we investigated the H dependence of the P-E loops for $f = 100$ Hz at 2 K. This experiment was performed at 2 K for the following reasons: At 2.5 K, an available maximum $|E|(\lesssim 90$ kV/cm) in the present experimental condition prevents us from obtaining a loop with full polarization and evaluation of the shift of the P-E loops for $H \gtrsim 1$ kOe, while at 2 K, a full polarization loop with a larger bias effect can be expected due to the reduced coercive E and the narrower P-E loop as compared with the

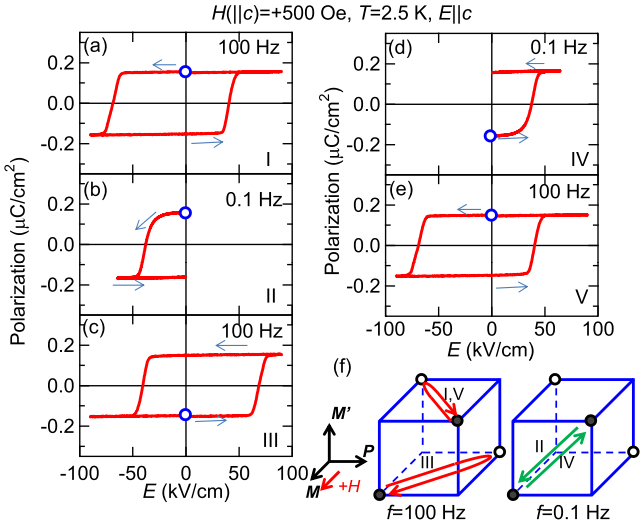

FIG. 4 (color online). (a)–(e) Isothermal electric switching of the sign of bias field under a fixed $H(=+500\ \mathrm{Oe})$ at 2.5 K. An initial state ($P+$, $M+$, $M'+$) is prepared by an ME poling, and (a) a full P-E loop is driven at 100 Hz. Then, (b) half a loop is driven at 0.1 Hz. Next, (c) a full P-E loop is driven at 100 Hz. Then, (d) half a loop is driven at 0.1 Hz again. After this, (e) a P-E loop is driven again at 100 Hz. In (a)–(e), open circles indicate starting points of each P-E loop. (f) P-reversal paths in P-M-M' phase space at 100 and 0.1 Hz in a positive H. I–V correspond to each process appearing in (a)–(e). Closed (open) circles indicate states with lower (higher) energy.

case at 2.5 K. As shown in Figs. 3(a)–3(d) [27], the P-E loop clearly shifts to a larger E field with negative sign as the H field is progressively increased. Notably, the loop for $H > +2$ kOe, which is apparently larger than H_c, displaces with a large bias E field, locating the origin of the P-E plane even outside of the loop. By using these P-E data, as well as the M-H data presented in Fig. 3(e), the experimentally obtained values of $-P\Delta E$ and MH are compared in Fig. 3(f). They show relatively good agreement with the relation that $-P\Delta E = MH$, validating the interpretation of the bias effect in terms of the Zeeman energy difference. The small vertical displacement may be due to some defects inside the crystal that pin down the magnetic domain wall of the Fe spin (MFDW). We have also confirmed the reproducibility and robustness of this bias effect against E cycling [26].

Next, we demonstrate that the sign of the bias field can be changed at a fixed temperature, as displayed in Fig. 4, by fully exploiting the fact that the P-reversal process in this system depends on the E-sweeping speed. Here, H was fixed at $+500$ Oe throughout the experiments. Prior to the measurements, the initial ($P+$, $M+$, $M'+$) state was prepared by an ME-poling process. As plotted in Fig. 4(a), a P-E loop was driven at first for 100 Hz (rapid scan), and the loop showed a negative bias field, similar to the result shown in Fig. 2(d). Here, the state of the system changes between ($P+$, $M+$, $M'+$) and ($P-$, $M-$, $M'+$) [path I in Fig. 4(f)], and the $P+$ state coupled with the $M+$ state has a lower energy than ($P-$, $M-$) under positive H. Then, half a loop was driven at 0.1 Hz [Fig. 4(b)]. Because this process is not accompanied by M reversal due to its slow sweeping speed, the state changes from ($P+$, $M+$, $M'+$) to ($P-$, $M+$, $M'-$) [path II in Fig. 4(f)]. Again, a full loop was driven at 100 Hz as shown in Fig. 4(c). At this time, the initial state $P-$ coupled with $M+$ has lower energy than ($P+$, $M-$) under positive H, resulting in the opposite sign of the bias field. Here, the state of the system changes between ($P-$, $M+$, $M'-$) and ($P+$, $M-$, $M'-$) [path III in Fig. 4(f)]. By driving half a loop again at 0.1 Hz [Fig. 4(d)], the state changes from ($P-$, $M+$, $M'-$) to ($P+$, $M+$, $M'+$) [path IV in Fig. 4(f)]. Then, the initial state is recovered, and the loop at 100 Hz exhibits a negative bias field again [Fig. 4(e) and path V in Fig. 4(f)]. Thus, by only changing the sweeping speed of E, all four states can be accessed, and in turn, the sign of the bias E field can be isothermally switched without changing the polarity of H.

Apart from its frequency-dependent feature, such a magnetically tunable, antisymmetric bias effect on the ferroelectric hysteresis loop is expected to be a generic feature in ferroelectric ferromagnets where the signs of P and M are tightly clamped. This effect may bear some analogy to the bias effect on the ferromagnetic hysteresis loop known as "exchange bias" [14–16], which is often observed in the ferromagnet and antiferromagnet [16], ferromagnet and magnetoelectric [17], and ferromagnet and multiferroic [18,19] bilayered heterointerface systems and is useful for practical applications. They essentially originate from spin exchange interaction at the interface between the ferromagnetic and antiferromagnetic layers, which stabilizes a specific M direction in the ferromagnetic layer. On the other hand, the bias effect on a ferroelectric loop has seldom been reported thus far, except for that observed in a $La_{0.3}Sr_{0.7}MnO_3/BiFeO_3$ bilayer system with an atomically controlled interface [28]. In this case, however, the magnitude and the sign of the bias field are determined beforehand by the built-in potential of the interface and cannot be modified by an external field. In the present case, the bias effect originates not from interfacial but from the bulk magnetoelectric effect, and its magnitude can be tuned by H, and the sign can be reversed by H or E. The frequency dependence of the bias effect is dominated by the dynamical properties of MFDW and FEDW. In the present case, the crossover frequency for switching on or off the bias effect may be controlled by, for example, chemically tuning the anisotropy of the rare-earth moment that governs the dynamics of the FEDW. The magnetically tunable, antisymmetric bias effect on a P-E loop as demonstrated here may add new functionality to ferroelectric ferromagnet systems and lead to further exploration of emergent electromagnetism in condensed matter.

In summary, we have demonstrated a gigantic and antisymmetric magnetic-field-induced bias effect on a

P-E hysteresis loops in a multiferroic $Dy_{0.7}Tb_{0.3}FeO_3$ where M reversal is driven by a rapid E sweeping due to tight clamping between P and M. The magnitude of the bias E field can be controlled by H, and its polarity can be reversed by changing the sign of H or by changing the relative direction of P and M. The difference in the Zeeman energy for the $+P$ and $-P$ states coupled with the M states with opposite sign is ascribed to the origin of the bias effect.

This work was in part supported by a Grant-in-Aid for Young Scientists (A) (No. 25707032) and Grants-in-Aid for Scientific Research from the MEXT, Japan, and the Funding Program for World Leading Innovative R&D on Science and Technology (FIRST Program) on "Quantum Science on Strong Correlation."

[1] S.-W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).
[2] Y. Tokura and S. Seki, Adv. Mater. **22**, 1554 (2010).
[3] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London), **429**, 392 (2004).
[4] Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, Phys. Rev. Lett. **96**, 207204 (2006).
[5] S. Ishiwata, Y. Taguchi, H. Murakawa, Y. Onose, and Y. Tokura, Science **319**, 1643 (2008).
[6] J. S. White, T. Honda, K. Kimura, T. Kimura, Ch. Niedermayer, O. Zaharko, A. Poole, B. Roessli, and M. Kenzelmann, Phys. Rev. Lett. **108**, 077204 (2012).
[7] J. T. Heron, M. Trassin, K. Ashraf, M. Gajek, Q. He, S. Y. Yang, D. E. Nikonov, Y.-H. Chu, S. Salahuddin, and R. Ramesh, Phys. Rev. Lett. **107**, 217202 (2011).
[8] Y. Tokunaga, Y. Taguchi, T. Arima, and Y. Tokura, Nat. Phys. **8**, 838 (2012).
[9] K. Kimura, H. Nakamura, S. Kimura, M. Hagiwara, and T. Kimura, Phys. Rev. Lett. **103**, 107201 (2009).
[10] Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, Phys. Rev. Lett. **101**, 097205 (2008).
[11] B. Kundys, A. Maignan, C. Martin, N. Nguyen, and C. Simon, Appl. Phys. Lett. **92**, 112905 (2008).
[12] T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B **71**, 224425 (2005).
[13] H. Kuroe, T. Hosaka, S. Hachiuma, T. Sekine, M. Hase, K. Oka, T. Ito, H. Eisaki, M. Fujisawa, S. Okubo, and H. Ohta, J. Phys. Soc. Jpn. **80**, 083705 (2011).
[14] J. Nogues and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
[15] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956).
[16] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **105**, 904 (1957).
[17] X. He, Y. Wang, N. Wu, A. N. Caruso, E. Vescovo, K. D. Belashchenko, P. A. Dowben, and C. Binek, Nat. Mater. **9**, 579 (2010).
[18] V. Laukhin, V. Skumryev, X. Martí, D. Hrabovsky, F. Sánchez, M. V. García-Cuenca, C. Ferrater, M. Varela, U. Lüders, J. F. Bobo, and J. Fontcuberta, Phys. Rev. Lett. **97**, 227201 (2006).
[19] L. W. Martin, Y. H. Chu, M. B. Holcomb, M. Huijben, P. Yu, S. J. Han, D. Lee, S. X. Wang, and R. Ramesh, Nano Lett. **8**, 2050 (2008).
[20] E. Y. Tsymbal, O. N. Mryasov, and P. R. LeClair, J. Phys. Condens. Matter **15**, R109 (2003).
[21] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).
[22] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
[23] I. A. Sergienko and E. Dagotto, Phys. Rev. B **73**, 094434 (2006).
[24] Y. Tokunaga, N. Furukawa, H. Sakai, T. Arima, Y. Taguchi, and Y. Tokura, Nat. Mater. **8**, 558 (2009).
[25] C. J. Fennie, Phys. Rev. Lett. **100**, 167203 (2008).
[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.112.037203 for the details of the subtraction of the E-linear component from P-E loops and robustness of the magnetic bias effect against E-field cycling.
[27] As indicated by the fact that the initial magnetization process of the M-H loop [see Fig. 3(e)] is located outside of the second one, the ferroelectric-ferromagnetic state is not stable at $H = E = 0$ and $T = 2$ K but stable only under the application of E or H. At 2.5 K, on the other hand, the ferroelectric-ferromagnetic state is stable at $H = E = 0$ if the temperature is approached from the higher side or the sample is once poled by E or H. At 2 K, after switching of the E and H, the system relaxes to an antiferroelectric antiferromagnetic state within several minutes. Thus, the P-E loop at $H = 0$ in Fig. 3(a) was measured immediately after a ME-poling process.
[28] P. Yu, W. Luo, D. Yi, J. X. Zhanga, M. D. Rossell, C.-H. Yang, L. You, G. Singh-Bhalla, S. Y. Yang, Q. He, Q. M. Ramasse, R. Erni, L. W. Martin, Y. H. Chu, S. T. Pantelides, S. J. Pennycook, and R. Ramesh, Proc. Natl. Acad. Sci. U.S.A. **109**, 9710 (2012).