Magnetization Reversal by Electric-Field Decoupling of Magnetic and Ferroelectric Domain Walls in Multiferroic-Based Heterostructures

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We demonstrate that the magnetization of a ferromagnet in contact with an antiferromagnetic multiferroic ($LuMnO_3$) can be speedily reversed by electric-field pulsing, and the sign of the magnetic exchange bias can switch and recover isothermally. As $LuMnO_3$ is not ferroelastic, our data conclusively show that this switching is not mediated by strain effects but is a unique electric-field driven decoupling of the ferroelectric and antiferromagnetic domain walls. Their distinct dynamics are essential for the observed magnetic switching.

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With their rich physics, multiferroics (materials in which magnetic and polar orders coexist) have emerged as some of the most promising materials for multifunctional applications in spintronics, owing to the advantageous possibility of controlling the magnetic state by electric fields and vice versa [1–6]. However, in spite of expectations, the minute magnetoelectric coupling of both order parameters [7] in single-phase multiferroics has hampered device-driven progress and focus is being directed towards exploring interface coupling either via strain [8,9] or by the exchange interaction between an antiferromagnetic (AF) multiferroic and a ferromagnet (FM) giving rise to magnetic exchange bias (EB). An EB manifestation is the magnetic hysteresis loop shift along the field axis, when the system is cooled through the Néel temperature (T_N) in magnetic field. This shift can be either in the "negative" [10] or in the "positive" field direction [11] and it is largely employed in spin valves and magnetic tunnel junctions.

The EB in magnetoelectrics was first explored [12] at the interface of the archetypical magnetoelectric (but not multiferroic) Cr_2O_3 with a FM layer and a sign switch of the EB was observed depending on the electric field applied during the cooling procedure through T_N of Cr_2O_3. Following the original observation of coupled order parameters at domain walls (DW) in hexagonal manganites [13], electric-field-induced suppression of the EB was found using the multiferroic $YMnO_3$ [6], shortly after EB in $YMnO_3$ had been demonstrated [14,15]. Those pioneering works were soon followed by studies [16–20] on $BiFeO_3$, which so far is the only room-temperature multiferroic. Although it has been proposed [16–18] that EB could be related to the ferroelectric and AF domain structure of $BiFeO_3$, which can be modified by an electrical field [17–19,21], strain-mediated coupling has not been excluded [22]. However, to date it has not been demonstrated that the sign of the EB can be reversibly switched at a certain temperature by electric field, without the need to follow the usual field-cooling protocol. In this Letter we show that the sign of EB can be switched and reset by appropriate electric pulses applied at a certain magnetic field, without the need of varying settled temperature. We will show here that electric-field driven decoupling of the ferroelectric and antiferromagnetic domain walls, and their distinct dynamics, are essential for the observed magnetic switching.

We demonstrate this EB resetting for the magnetization of 10 nm thin ferromagnetic $Ni_{81}Fe_{19}$ (Py) film deposited on the basal plane of hexagonal $LuMnO_3$ single crystal (~ 12 μm thick). Py is a soft FM, while $LuMnO_3$ is an AF multiferroic, $T_N = 93$ K [23] and $T_C > 570$ K [24], isostructural to $YMnO_3$ [25]. It has a hexagonal crystal structure [25] and below T_N the Mn moments adopt a triangular arrangement within the basal plane.

Cooling the sample through T_N in magnetic field of 3 kOe applied in the basal plane, resulted in establishing a positive EB field, $H_{eb} = +130$ Oe as evidenced by the negative hysteresis loop shift shown in Fig. 1(a) (black arrow). All measurements were performed at 5 K, cycling H between +3 and −3 kOe. The training effect is common in exchange biased systems. Here it is reflected by the difference between the virgin curve (labeled "v") and the first consecutive loop (labeled "t_1") in Fig. 1(a) and it quickly dies off for further cycles. Hence, in our experiments to minimize training effects, we choose to apply electric field to the second trained curves ("t_2"); however, the results reported in the following are found to be qualitatively similar for any set of magnetization loops.

Applying electric pulse of 40 V ($\approx 3 \times 10^6$ V/m), duration 500 μs and triangular profile, at the descending branch of the magnetization loop, at $H = -145$ Oe (a value chosen to be close to the coercive field), causes

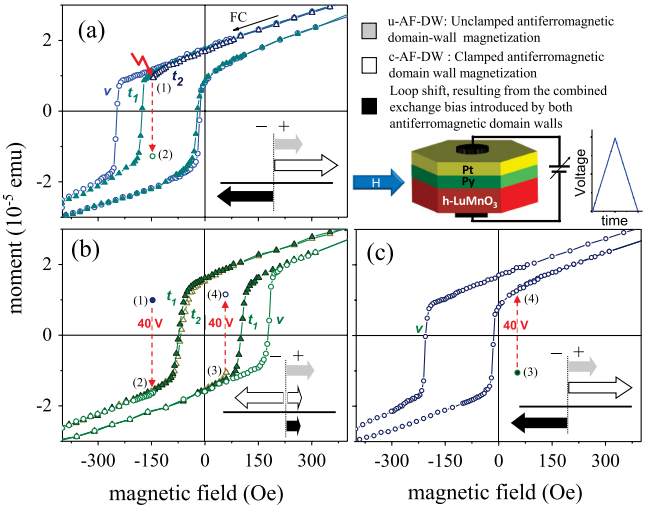

FIG. 1 (color online). In (a) concessive magnetization loops recorded after cooling the sample under 3 kOe field from well above T_N [virgin loop (υ)—circles] and trained loops recorded by subsequent isothermal field cycling (t_1 and t_2)—triangles (solid and empty, respectively). The red dashed arrow indicates the magnetic moment jump from point (1) where electric pulse is applied to point (2). (b) virgin (υ) and trained (t) loops after 40 V pulse at point (1) in panel (a); (c) loop after applying the 40 V pulse at point (3). Legend for the insets is shown in the top right area of the figure, where also a cartoon of the heterostructure and the electric pulse profile are given.

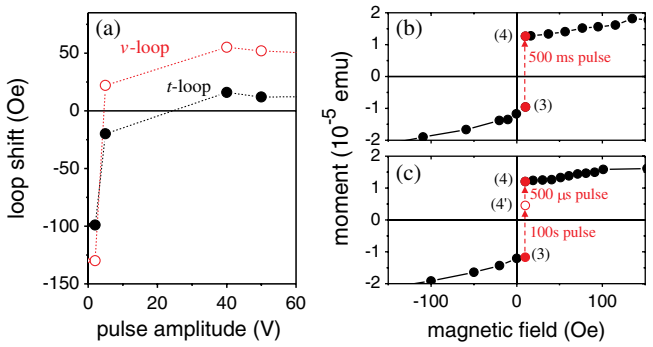

FIG. 2 (color online). Dependence of the magnetic hysteresis loop shift and magnetic moment modifications on the characteristics of electric pulses. (a) Magnetic hysteresis loop shift ($-H_{eb}$) (υ loops and t loops) after the electric pulse as a function of the electric pulse amplitude; (b) magnetization changes after applying 40 V pulse with duration 500 ms; (c) after applying 40 V pulse with duration 100 s, followed by 40 V pulse with duration 500 μs.

an abrupt jump of the Py magnetic moment m(Py) [(1) → (2) in Figs. 1(a) and 1(b)], which also changes its direction. Up to this point we qualitatively reproduced the result discovered using $YMnO_3$ film [6]. Further cycling of magnetic field after the application of this electric pulse [curves υ, t_1, and t_2 in Fig. 1(b)], results in concessive hysteresis loops being close to the mirror image of those before the pulse shown in Fig. 1(a), and the corresponding H_{eb} has its sign opposite ($H_{eb} = -55$ Oe, υ curve, black arrow) to the original one. It is relevant to note that though qualitatively similar, the two sets of loops—before and after the electric pulse—have some differences: H_{eb} is smaller (in modulus) and the coercive field H_C is larger after the pulse (supplemental information [26]). At this point it was tempting to see if at the settled temperature an electric pulse could recover the polarity of the original EB. Indeed, application of electric pulse of 40 V at the ascending branch of the magnetization loop, at $H = +60$ Oe, triggers magnetization reversal [(3) → (4), in Figs. 1(b) and 1(c)]. Subsequent field cycling leads to hysteresis loops [Fig. 1(c)] very similar to those shown in Fig. 1(a) (recorded after the initial field-cooling process). Importantly, comparison to data in Fig. 1(a) indicates that the sign of the EB field ($H_{eb} = +110$ Oe, υ loop, black arrow) has been recovered.

Similar electric switching of magnetization was observed for other pulse amplitudes. For example, after using the same experimental protocol, a pulse of 5 V triggered a jump of the m(Py) to a value very similar to that measured after the 40 V pulse. The subsequent EB ($H_{eb} = -22$ Oe) is, however, smaller compared to the one after applying 40 V. Comparison of the EB after electric pulses in the t loops indicates the same trend, as summarized in Fig. 2(a) where we collect the dependence of the H_{eb} (minus the loop shift) on V for υ and t loops.

Figure 2(a) illustrates that the resulting EB depends on the applied voltage. This indicates that the underlying mechanism of EB switching weakens with decreasing the electrical field amplitude, whereas it was repeatedly observed down to 5 V, no switching was observed below a threshold of about 2 V. Switching was found to be insensitive to pulse polarity.

The observed peculiar EB switching and resetting, triggered by an electric field has no analogue in the conventional exchange bias systems. It requires that the FM moments of the Py become unpinned by electrical pulse, but then pinned again in direction opposite to the initial one. This led us to suggest the ferroelectric domain walls of the $LuMnO_3$ as a prime suspect behind the observed EB reset.

Because of strong uniaxial anisotropy of the hexagonal $LuMnO_3$, only two kinds of 180° ferroelectric (FE) domains with opposite sign of the FE order parameter are expected to exist, with narrow domain walls (FE-DWs) between them that span only a few unit cells [27]. On the other hand, AF domains [28] also exist. Their walls carry [28,29] net magnetic moment. EB at compensated magnetic surfaces, such as (0001) of $LuMnO_3$, owes its existence exclusively to these uncompensated moments. In $LuMnO_3$, the small basal plane anisotropy of the Mn moments should render AF-DWs much wider than the FE-DWs, and their net moment should be in the basal plane [27]. In hexagonal $RMnO_3$ (R = Y, Lu, etc.) it has been shown that FE and AF domains are clamped and two distinct types of AF-DWs exist [13,30]: "clamped" walls (c-AF-DW) formed at the position of all FE-DWs, and "unclamped" walls (u-AF-DW) formed within the large ferroelectric domains. c-AF-DWs are created and clamped

at the center of each of the already existing FE-DWs to minimize the free energy [27,31].

The scenario, which we propose for explaining the observed peculiar effect of the electric pulses on the EB, begins with cooling down the sample in a presence of magnetic field to ensure that the Py moments are aligned. Below T_N, clamped and unclamped AF-DWs are formed. The orientation of the uncompensated moment of the AF-DWs is dictated by the exchange interactions with the ferromagnetic Py moments at the interface. The uncompensated moments in both types of AF-DWs pin m(Py) giving rise to EB as illustrated in Fig. 1 (insets). Once c-AF-DWs are formed at FE-DWs, it is energetically costly to separate them from the FE-DWs [27]. The magnetic hysteresis cycle after the cooling procedure [Fig. 1(a)] is similar to the one for conventional EB systems, the only difference being that two different types of AF-DWs contribute to pinning. Whereas u-AF-DWs do not correlate with FE domains and thus should always provide EB unaffected by the multiferroicity, this is not the case for the c-AF-DWs which contribution to EB should be affected by FE-DW motion under electric field.

Suggesting the way in which the electric field assists the magnetization rotation is crucial for understanding the EB switching and subsequent reset. Since no irreversibility is found on the dielectric response of $LuMnO_3$ up to 40 V (see the supplemental information [26]) switching of overall polarization can be ruled out as a driving force. The experimental results from Fig. 1 clearly indicate that under application of the electric pulse, some AF-DWs have been unpinned—at least for a short period of time—with the concomitant collapse of the pinning chain providing the EB and the DW-magnetic moments can freely rotate under the external magnetic field. Subsequent pinning of the AF-DWs should lead to a new EB, eventually of sign opposite to the initial one. The c-AF-DWs are the candidates to play such key role.

We propose that applying a pulse [at point (1) in Figs. 1] with a suitable amplitude and duration could quickly move the FE-DW away from its initial position [Fig. 3(a)] leaving behind unpinned the c-AF-DW that was sitting at its center [Fig. 3(b)]. Unclamping of AF-DW from the FE-DW during the electric pulse leaves the former unpinned as the polarization-induced changes of exchange interactions and single-ion anisotropy are no longer active [27,31] and thus AF-DW magnetic moment is free to rotate under the influence of the external (negative) magnetic field. Therefore, during the pulse the AF-DW magnetic moment cannot provide an effective pinning force to m(Py) and this allows the magnetic field to reverse it instantly.

After the electric pulse, AF-DW should be reestablished at a FE wall (which could be in a new position or back at the initial one, depending whether its motion was reversible or irreversible). Importantly, the magnetic moment of the newly pinned c-AF-DW will be in a direction opposite to the one before the electrical pulse since its orientation will be dictated by the reversed m(Py)

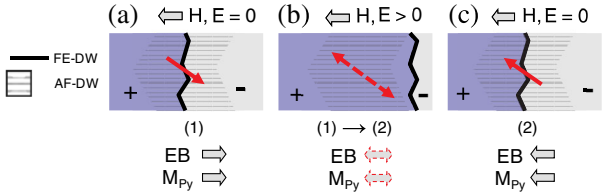

FIG. 3 (color online). A sketch (top view of the basal plane) of the position of clamped AF (dashed area) and FE domain walls (in black) pair at different points of the hysteresis loops depicted on Figs. 1 and 2. From left to right: at point (1); during the magnetization jump from (1) to (2) caused by the first electric pulse, when "unclamping" takes place; at point (2) where a "clamping" is reestablished but the direction of the AF domain-wall moment is reversed. The red arrows inside the figures represent the net magnetic moment of the AF domain wall when it is clamped (solid arrow—pinned moment) and unclamped (broken arrow—unpinned moment). The arrows above and below the figures represent the directions of the characteristics to which they are attached (H—magnetic field; M_{Py}—magnetization of the permalloy; EB—exchange bias).

[point (1) ⟶ (2) in Fig. 1], which reaches about 90% of its saturation value, and the polarity of the applied field. This will impose a pinning direction opposite to that before the electrical pulse, as observed in Figs. 1(b) and sketched in Fig. 3(c).

When the second electrical pulse is applied at point (3) of Fig. 1, the EB will be reset; i.e., the initial EB will be recovered. Note that, in this scenario and in agreement with experimental data, the changes of magnetization and EB are independent of the voltage polarity. A threshold V should exist to unpin the c-AF-DW from FE-DW center. Indeed, if the displacement of the FE-DW is not large enough, the magnetic moments of the AF-DW will not be unpinned. This is in agreement with the results from Fig. 2(a), which reveal that electrical pulse of 2 V is incapable to switch magnetization. Similarly, one should expect that if the speed at which the FE-DW travels under the electric-field stimulus is not fast enough, the AF wall would be able to keep "clamped" to it during the excursion and no effect will be observed. To verify this prediction we have performed experiments using $V(t)$ pulses of distinct duration (rising-falling) time. In Figs. 2(b) and 2(c) we show the switching [(3) ⟶ (4′)] induced by a pulse of $V = 40$ V with a duration of 500 ms and 100 s, respectively. It is clear that the magnetization is only partly switched for longer (smaller dV/dt) pulses. In a subsequent experiment, if a slower pulse [100 s, Fig. 2(c)] is followed by another 40 V pulse with duration 500 μs [(4′) ⟶ (4)] the magnetization jump is further enhanced until the saturated final state is recovered.

The two types of AF domain walls, the clamped and the unclamped ones play quite distinct roles in the proposed scenario. While the former could change the sign of the unidirectional anisotropy imposed on the Py moments after each subsequent electric pulse, the later always keep the initially established direction. Thus while the unclamped

AF walls will always contribute to the initial EB established via field-cooling procedure through T_N (gray arrows in Fig. 1), the clamped walls could alternatively produce either positive or negative EB after each concessive electric pulse (white arrows in Fig. 1). The difference in the hysteresis loops prior and after application of electrical pulse should also depend on the number of clamped AF-DWs that are left behind the FE-DW excursion and thus on the pulse amplitude as actually observed in our experiments and summarized in Fig. 2(a). It is worth noting that the situation with domain walls pinned in two opposite directions would lead to an overall decrease in EB and an increase of H_C as experimentally observed.

Finally, the observation of interface-mediate exchange coupling in $LuMnO_3$ is relevant because, in this case and in contrast to $BiFeO_3$ [22], strain is not expected to play a role in domain coupling and switching as $LuMnO_3$ is not ferroelastic. The piezomagnetic response at the domain walls appears to be crucial.

In conclusion, we have shown that at a settled temperature, the sign of EB can be switched by an electric pulse and reset after applying certain magnetic field followed by a second electric pulse. This phenomenon has no analogy in the conventional EB based on antiferromagnetic but nonmultiferroic materials. It constitutes a clear evidence of reversible control of magnetization using electric field without varying the settled temperature. The scenario proposed relies on the distinct role played by the AF domain walls: clamped vs unclamped to the FE ones. The clamped AF-DW's appear to be responsible for the electrical tunability of the torque exerted on the FM moments. Since the unclamped AF-DWs are often born on structural defects, while the number of clamped is predetermined by the number of FE domains, one should be able to tune the hysteresis loops and the exchange bias by controlling the ratio between them (for example, introducing structural defects by irradiation or varying the number of FE domains by the thickness of the multiferroic).

The proposed scenario results from the dynamics of the AF and FE domain walls rather than from their density, which itself may determine the absolute values of EB as found in $BiFeO_3$ [16,19]. It is based on the assumption that the AF and the FE domain walls cannot respond in tandem to the external stimulus, thus implying distinct dynamic properties and effective masses. It requires the ability to push FE domain walls away from the AFM ones; owing the dimensions of the later and typical FE domain-wall motion velocities, responses down to the picoseconds regime could be achieved. Further studies on coupled FE and AF domain-wall dynamics are needed to get a more detailed microscopic understanding. In any event, the possibility of ultrafast switching and modulating the exchange bias at fixed temperature by electric field opens new possibilities, particularly if the same phenomena could be identified in room-temperature multiferroics.

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Note add in proof.—When this manuscript was completed, we learned of two very recent references [32,33] reporting isothermal EB sign switching using Cr_2O_3 and $BiFeO_3$, respectively. However, we note that the suggested mechanisms behind the claimed effects are completely different from the one proposed in our work.

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