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Electrically reversible magnetization at the antiperovskite/perovskite interface

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Using density-functional calculations, we predict the emergence of electrically reversible magnetization at the interface between antiferromagnetic noncollinear antiperovskite GaNMn_3 and ferroelectric perovskite BaTiO_3 . We find that Mn magnetic moments are enhanced and reoriented at the $\text{GaNMn}_3/\text{ATiO}_3$ (001) ($A = \text{Sr}$ and Ba) interface, resulting in a sizable net magnetization along the $[110]$ direction. This magnetization is reversed with ferroelectric polarization of BaTiO_3 through $\sim 20^\circ$ rotation of the noncollinear magnetic moments. The effect is driven by ferroelectric modulation of the antiferromagnetic exchange coupling between the interfacial Mn atoms mediated by the Mn- $3d$ orbital population. Our results open opportunities for controlling the magnetic properties by electric fields by exploiting noncollinear antiferromagnetism at antiperovskite/perovskite interfaces.

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I. INTRODUCTION

Manipulating magnetic properties by electric fields is an active area of research promising significant technological advances [1]. “Standard” methods of controlling magnetism by an applied magnetic field or by passing a spin-polarized current, which exerts a spin torque on magnetization, suffer from significant energy dissipation. Using a voltage instead of an electric current to control magnetic properties is considered to have significant advantages for low-power electronics [2].

Different approaches have been employed to manipulate spin-dependent properties by electric fields. Among them are the field effect on magnetism of dilute ferromagnetic semiconductors [3,4], the voltage effect on coercivity in ferromagnetic metals [5], the voltage-assisted magnetization switching in magnetic tunnel junctions [6,7], the electrical switching of the exchange bias [8], and the electric-field-induced magnetization reversal in single-component multiferroics [9] and ferromagnet-multiferroic heterostructures [10]. From the fundamental science perspective, the importance of this research is evident from the appealing physical phenomena responsible for these properties, such as the effect of electrostatic screening on magnetism [11,12], the voltage-controlled magnetic anisotropy [13–15], and the coupling between spontaneous electric and magnetic polarizations in multiferroics [16] and ferroelectric tunnel junctions [17,18].

Recently, particular attention has been paid to the studies of interfaces between ferroelectric and ferromagnetic materials, where the magnetoelectric coupling between the electric polarization of the ferroelectric and magnetic polarization of the ferromagnet occurs across the interface [19]. In this case, reversal of electric polarization of the ferroelectric as the result of applied electric field produces changes in the electronic structure of the ferromagnet due to the effects of

electrostatic doping or chemical bonding. It has been demonstrated that such coupling affects the magnetization of the ferromagnet [20–27], its Curie temperature [28,29], and the magnetic ordering [30–33].

These studies, however, largely address magnetic properties of collinear ferromagnets. For electric-field-induced magnetization reversal, as often required for device applications, this approach has an intrinsic deficiency. Magnetization reversal in a collinear ferromagnet is equivalent to applying time-reversal symmetry operation. An electric field does not break time-reversal symmetry and hence alone is not sufficient to reverse the magnetization. Utilizing noncollinear antiferromagnetic materials could overcome this deficiency. If there is a net uncompensated magnetic moment due to deviations of the local moments from their equilibrium orientations, reversal of this net moment would not necessarily be equivalent to the time-reversal symmetry transformation. Thus, under certain conditions, an electric field could induce magnetization switching in a non-fully compensated noncollinear antiferromagnet via its effect on the local moment orientations. From this perspective, the ferroelectric-induced interfacial magnetoelectric coupling in heterostructures with noncollinear antiferromagnets may facilitate this switching. In this regard, magnetic *antiperovskite* compounds [34] are especially promising because they possess noncollinear antiferromagnetic configurations [35] and could be structurally matched with ferroelectric perovskite compounds to create epitaxial interfaces [36].

Antiperovskite compounds have the perovskite crystal structure [Fig. 1(a)],¹ where cation and anion positions are interchanged [Fig. 1(b)]. For example, magnetic antiperovskites contain $3d$ transition-metal elements (M) and have chemical formula ABM_3 ($A = \text{Ga, Sn, Zn}$; $B = \text{C, N}$). These materials exhibit a broad variety of functional properties,

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¹The figures were created using VESTA [56] and the SciDraw scientific figure preparation system [57].

FIG. 1. (a) Atomic structure of perovskite $ATiO_3$ ($A = \text{Sr}, \text{Ba}$). (b) Atomic and magnetic structure of antiperovskite $GaNm_3$. Arrows denote the magnetic moments of Mn atoms. (c) Frustrated magnetic configuration of $GaNm_3$ in the (111) plane. (d) Atomic structure of the $ATiO_3/GaNm_3$ (001) interface.

such as superconductivity [37] and magnetoresistance [38], as well as magnetovolume [39], magnetocaloric [40], and barocaloric [41] effects. The magnetic antiperovskites are typically metallic and often reveal exotic magnetic order [35]. In particular, $GaNm_3$ is an itinerant magnetic metal with Γ^{5g} noncollinear antiferromagnetic ground state [42,43], as shown in Figs. 1(b) and 1(c). Due to the antiferromagnetic (AFM) coupling between Mn atoms on the triangular lattice in the (111) plane, the local magnetic moments of Mn form a clockwise configuration with the angle of 120° between the directions, canceling the magnetic moments in each plane [42,43]. As the result of this magnetic symmetry, $GaNm_3$ is predicted to be piezomagnetic [44,45] and flexomagnetic [46]. The Néel temperature of $GaNm_3$ is found to be close to room temperature (the reported values range from 270 to 300 K [35–43]).

In this work, we exploit the sensitivity of noncollinear antiferromagnetism in antiperovskites to external stimuli to control it with ferroelectric polarization of perovskites. Using density-functional theory calculations, we predict the electrically reversible magnetization at the interface between antiperovskite $GaNm_3$ and ferroelectric perovskite $BaTiO_3$ [Fig. 1(d)]. The effect stems from the reversible rotation of the noncollinear magnetic moments in response to the

TABLE I. Calculated magnetic moments (μ_B) of Mn atoms in bulk $GaNm_3$ for different in-plane strain ξ .

		m_x	m_y	m_z	m_{total}
$\xi = 0$	Mn1	1.724	1.724	0	2.438
	Mn2	-1.724	0	1.724	2.438
		0	-1.724	-1.724	2.438
$\xi = 1.5\%$	Mn1	1.801	1.801	0	2.547
	Mn2	-1.827	0.062	1.889	2.629
		0.062	1.827	-1.889	2.629

ferroelectric polarization modulation of the antiferromagnetic exchange coupling between the Mn atoms at the interface. Using the ferroelectric effect on noncollinear interface magnetization is a paradigm for voltage-controlled magnetism.

II. METHODS

First-principles calculations are performed with the projector augmented-wave method [47] implemented in VASP code [48] using unconstrained noncollinear magnetic structures [49,50]. The exchange and correlation effects are treated within the generalized gradient approximation [51]. We use the plane-wave cutoff energy of 550 eV and $16 \times 16 \times 16$ and $12 \times 12 \times 1$ k -point meshes in the irreducible Brillouin zone for bulk and interface structures, respectively. The in-plane lattice constant of the interface supercell is constrained to the calculated lattice constant of cubic SrTiO_3 ($a = 3.945 \text{ \AA}$) to simulate epitaxial growth of $GaNm_3$ on a SrTiO_3 substrate. Internal coordinates and c -lattice constant are relaxed until the force on each atom is less than $0.001 \text{ eV/\AA}$.

III. RESULTS

A. Magnetic ground state of bulk $GaNm_3$

First, we ascertain that our calculations correctly predict the ground state of bulk $GaNm_3$. We find that the relaxed lattice parameter is $3.867 \text{ \AA}$, the magnetic moment per Mn atom is $2.438 \mu_B$ (Table I), and the minimum-energy magnetic configuration is Γ^{5g} [52]. These results are consistent with the available experimental data [42,43] and previous theoretical calculations [44–46]. Under the constraint of the in-plane lattice constant $a = 3.945 \text{ \AA}$ (the calculated lattice constant of bulk SrTiO_3), $GaNm_3$ in the heterostructure is exposed to the in-plane tensile strain of $\sim 1.5\%$. The strain leads to a piezomagnetic response, resulting in the net magnetic moment $m_{\text{net}} = m_{\text{Mn1}} + 2m_{\text{Mn2}}\cos(\frac{2\pi}{3} - \delta)$, where Mn1 and Mn2 are the Mn atoms in the horizontal GaMn plane and the Mn_2N plane, respectively [Fig. 1(c)], and δ is the canting angle of m_{Mn2} . We find a small $m_{\text{net}} = 0.05 \mu_B$ and $\delta = 1.6^\circ$ (Table I) in a good agreement with the earlier theoretical calculations [44–46].

B. Atomic structure of the $GaNm_3/\text{ATiO}_3(001)$ interface

We analyze the interface stability of $GaNm_3/\text{ATiO}_3(001)$ using $GaNm_3/\text{SrTiO}_3(001)$ heterostructures, and find that the $\text{NMn}_2/\text{TiO}_2$ interface [Fig. 1(d)] is the most energy-favorable configuration (Appendix A). To investigate the

FIG. 2. (a) Atomic structure of GaNMn₃ between two GaNMn₃/ATiO₃ (A = Sr, Ba) interfaces. The colored triangles denote the (111) plane in each GaNMn₃ layer. (b) Relative Ti-O displacement in the TiO₂ layers in GaNMn₃/SrTiO₃ (001) and GaNMn₃/BaTiO₃ (001) heterostructures. Numbers 1 to 5 on x axis in (b) denote TiO₂ layers counted from the bottom interface to the top interface.

magnetic structure of the GaNMn₃/ATiO₃(001) interface, we consider a 4GaNMn₃ · NMn₂/4ATiO₃ · TiO₂ supercell with the in-plane lattice constant being constrained to the calculated value for bulk SrTiO₃, $a = 3.945$ Å. By comparing the energies of different magnetic configurations, we find that the noncollinear antiferromagnetic order of bulk GaNMn₃ is preserved in the whole supercell with some perturbations at the interface (Appendix B). Due to the same interface terminations on top and bottom interfaces [Fig. 2(a)], we can analyze the effect of ferroelectric polarization direction (in the case of BaTiO₃) on the interface magnetic structure by performing a single calculation with a fixed polarization

orientation. In particular, for polarization of BaTiO₃ pointing up in the supercell structure of Fig. 2(a), the bottom interface corresponds to polarization pointing to GaNMn₃ ($P > 0$) and the top interface corresponds to polarization pointing away from GaNMn₃ ($P < 0$).

Figure 2(b) shows in the calculated relative Ti-O displacement in the supercells of GaNMn₃/SrTiO₃ and GaNMn₃/BaTiO₃. While the Ti-O displacement is symmetric across the SrTiO₃, there is a clear polar displacement across the BaTiO₃, indicating the presence of ferroelectricity in this material. Table III shows the Mn2-O, Mn2-Ti, and Mn1-Mn2 interatomic distances at the GaNMn₃/SrTiO₃ ($P = 0$) and GaNMn₃/BaTiO₃ interfaces with polarization pointing to ($P > 0$) and away from ($P < 0$) the interface. We find a notable difference in the Mn2-Ti bond length depending on the polarizations state, which has importance for the magnetism of the interface.

C. Magnetoelectricity of the GaNMn₃/ATiO₃ (001) interface

Figure 3 shows the calculated magnetic structure across the GaNMn₃ layer in the GaNMn₃/ATiO₃ supercells. As expected, in the middle of the GaNMn₃ layer, the Mn moments resemble those in bulk GaNMn₃ under 1.5% tensile strain. The interface affects significantly the magnetism of GaNMn₃. For GaNMn₃/SrTiO₃, the magnitude of the interfacial magnetic moment m_{Mn1} is strongly reduced, while that of interfacial m_{Mn2} is strongly enhanced [Fig. 3(a)]. The direction of interfacial m_{Mn2} is canted with $\delta = 7.2^\circ$ [Fig. 3(c)]. Similar variation in magnitudes of the interfacial magnetic moments is seen in GaNMn₃/BaTiO₃ [Fig. 3(b)]. In this case, however, the ferroelectric polarization of BaTiO₃ strongly affects the magnetic moment directions, so that different orientations of interfacial m_{Mn2} appear in the two polarization states [Figs. 3(c)–3(e)]. For $P > 0$, the interfacial m_{Mn2} is significantly canted with $\delta = 18.1^\circ$, while for

FIG. 3. (a), (b) Magnetic moments of Mn atoms in GaNMn₃/SrTiO₃ (a) and GaNMn₃/BaTiO₃ (b) systems. (c)–(e) Magnetic configurations of GaNMn₃/ATiO₃ in the GaNMn₃ (111) planes for A = Sr (c) and A = Ba (d), (e) for polarization pointing to GaNMn₃ ($P > 0$) (d) and polarization pointing away from GaNMn₃ ($P < 0$) (e). Mn magnetic moments are indicated by the red arrows, the length of which is scaled to the moment magnitudes shown in (a) and (b). The induced net magnetic moments at the interfaces are indicated by the block arrows, the length of which is scaled to the net moment magnitudes shown in (f). (f) Layer-dependent net magnetic moment in GaNMn₃. The y-axis labels refer to the GaNMn₃ layer number counted from the bottom ($P > 0$, $P = 0$) or top ($P < 0$) interface.

$P < 0$, the direction of interfacial $m_{\text{Mn}2}$ is almost unchanged ($\delta = 0.6^\circ$).

The variation in the magnitudes and orientations of the interfacial $m_{\text{Mn}1}$ and $m_{\text{Mn}2}$ produces a nonzero net magnetic moment m_{net} along the [110] direction at the interface [Figs. 3(c)–3(f)]. For the nonpolarized $\text{GaMnN}_3/\text{SrTiO}_3$ ($P = 0$), the resulting interfacial magnetic moment m_{net} is rather small ($m_{\text{net}} = 0.04 \mu_B$). On the contrary, for the polarized $\text{GaMnN}_3/\text{BaTiO}_3$, there is a large net magnetic moment induced by the ferroelectric polarization at the interface. Remarkably, this induced magnetic moment changes its sign from positive ($m_{\text{net}} = 1.28 \mu_B$) for $P > 0$, to negative ($m_{\text{net}} = -0.56 \mu_B$) for $P < 0$, indicating that polarization switching leads to the reversal of the net interfacial magnetic moment. We note that the predicted 180° switching of the interfacial magnetization is produced by only $\sim 20^\circ$ rotation of the non-collinear magnetic moments. This is different from collinear magnetic systems, which require full reversal of magnetic moments [30–33].

IV. DISCUSSION

To understand this behavior, we employ a simple model which involves a coexistence of the itinerant and localized magnetism in GaMnN_3 . The former is described within the Stoner model, where the magnetic moment emerges through the exchange splitting of the spin bands as the result of competition between the exchange energy (Coulomb interaction) and the kinetic (band) energy. The latter involves the exchange interactions between the localized magnetic moments on the triangular lattice in the (111) plane, as described by the Heisenberg model.

According to the Stoner criterion, the magnetic moment appears when $N_M(E_F)I_M > 1$, where $N_M(E_F)$ is the local density of states (DOS) on atom M at the Fermi energy (E_F) in a nonmagnetic state, and I_M is the Stoner exchange parameter (see, e.g., Ref. [53]). In bulk GaMnN_3 , as seen from Fig. 4(a), there is a peak in the Mn 3d DOS at E_F , which originates from the Mn1 d_{xy} orbitals [Fig. 4(d)] [or equivalently by symmetry Mn2 d_{xz} (Mn2 d_{yz}) orbitals, not shown]. These states are not dispersive because hopping between the Mn sites in the MnGa planes is weakened by the presence of Ga. As the result, the DOS at E_F is high, $N_{\text{Mn}}(E_F) = 1.70 \text{ states}/(\text{eV spin})$. Taking $I_{\text{Mn}} = 0.78 \text{ eV}$ [54], we obtain $N_{\text{Mn}}(E_F)I_{\text{Mn}} = 1.326$. Therefore, the intra-atomic exchange favors the formation of the local magnetic moment on the Mn atom in bulk GaMnN_3 . In addition to the central peak, there are other peaks in the Mn 3d DOS in Fig. 4(a). Peak 1 at $E = -2.6 \text{ eV}$ forms the bonding state from the Mn1 d_{xy} orbitals [Fig. 4(c)] and the Ga 4p orbitals [Fig. 4(b)]. Peak 2 at $E = -1 \text{ eV}$ and peak 3 at $E = 1 \text{ eV}$ represent the bonding and antibonding pair resulting from the hybridization Mn $d_{xz,yz}$ orbitals [Fig. 4(c)] on the octahedral Mn sublattice. N 2p orbitals lie at lower energies [Fig. 4(b)] and do not strongly hybridize with the Mn d states.

This behavior changes at the interface. Figures 4(e)–4(h) show the calculated local DOS of the Mn atoms in the $\text{GaMnN}_3/\text{SrTiO}_3$ supercell. Away from the interface, the Mn-DOS [Figs. 4(e) and 4(f)] is similar to that in bulk GaMnN_3 [Fig. 4(a)]. However, the interfacial DOS is notably different

FIG. 4. Local and orbital-resolved densities of states for bulk GaMnN_3 (a)–(d) and the local DOS on Mn atoms for the $\text{GaMnN}_3/\text{SrTiO}_3$ interface (e)–(h) in a nonmagnetic state. The dashed vertical line denotes the Fermi energy.

[Figs. 4(g) and 4(h)]. For the interfacial Mn2 atom, which lies in the GaMn (001) plane (being the termination plane of GaMnN_3 in the supercell), the DOS is narrowed down [Fig. 4(h)]. This is due to breaking periodicity of GaMnN_3 along the z direction and thus the reduced number of the nearest neighbors involved in the interfacial Mn2 atom bonding. Absence of the Ga and Mn atoms under the interfacial Mn2 lowers peaks 1, 2, and 3 in the DOS, which originate from the Mn-Ga and Mn-Mn hybridizations, bringing more weight to the Mn2-DOS central peak and narrowing the 3d band [Fig. 4(h)]. We note that bonding of the Mn2 3d orbitals with the 2p orbitals of O lying in the TiO_2 plane does not have a strong effect on the Mn2 3d DOS at the interface. This is seen from comparison of the interfacial Mn DOS in the $\text{GaMnN}_3/\text{SrTiO}_3$ structure and the surface Mn DOS in a freestanding GaMnN_3 (001) slab (see Fig. 8 in Appendix C).

Contrary to Mn2, the DOS of the interfacial Mn1 atoms which lie in the GaMn plane (second from the interface) is wider than the bulk DOS [compare Figs. 3(g) and 3(e)]. This is due to the change in the bond length between Mn1 and Mn2 atoms at the interface as compared to the bulk. The Mn1–Mn2 bond length is $2.755 \text{ \AA}$ in bulk GaMnN_3 , while it is $2.716 \text{ \AA}$ at the $\text{GaMnN}_3/\text{SrTiO}_3$ interface. The reduced bond length enhances the bonding energy and thus shifts the Mn–Mn bonding peak 2 to a lower energy and peak 3 to a higher energy, widening the interfacial Mn1 DOS. The narrower the band, the easier it is for the Coulomb interaction to spin-polarize electrons by pushing more electrons from the spin-down states to the spin-up states. Therefore, the narrowed DOS of the Mn2 atom implies the enhanced magnetic moment, whereas the broadened DOS of the Mn1 atom leads to the reduced magnetic moment.

FIG. 5. (a) Simplified supercell of $\text{GaNMn}_3 \cdot \text{NMn}_2/\text{SrTiO}_3 \cdot \text{TiO}_2$. (b) Schematic of AFM exchange interactions in the (111) plane. (c) Fitted Mn1-Mn2 AFM exchange parameter J_{12} and Mn2-Mn2 AFM exchange parameter J_{22} for each Ti position. (d) J_{22}/J_{12} for each Ti position. (e) Calculated m_{net} according to Eq. (1) for each Ti position. (f) Calculated number of 3d electrons for different Mn atoms. Positive (negative) Δz_{Ti} indicates Ti moving toward (away) from the GaNMn_3 slab.

The directions of m_{Mn1} and m_{Mn2} are determined by the AFM exchange interactions between nearest interfacial Mn atoms. To illustrate the effect of ferroelectric polarization on the AFM exchange coupling and magnetic moments, we consider a smaller supercell structure of $\text{GaNMn}_3 \cdot \text{NMn}_2/\text{SrTiO}_3 \cdot \text{TiO}_2$, as shown in Fig. 5(a). We first optimize the atomic structure of the supercell and then move the Ti atoms along the z direction toward or away from the GaNMn_3 slab. This captures the effect of ferroelectric polarization, since the displacement of the interfacial Ti atoms is found to provide the dominant change between the interfacial structures with different polarization states (Table II). For each Ti position, we calculate a series of total energies as a function of the canted angle δ , and then fit the results to the Heisenberg model [45]: $E(\delta) = -4J_{12}m_{\text{Mn1}}m_{\text{Mn2}}\cos(\frac{2\pi}{3} - \delta) - 2J_{22}m_{\text{Mn2}}m_{\text{Mn2}}\cos(\frac{2\pi}{3} + 2\delta)$, to find J_{12} and J_{22} , which are the exchange-coupling parameters between Mn1-Mn2 and Mn2-Mn2, respectively [Fig. 5(b)]. As is evident from Fig. 5(c), all

the calculated values of J_{12} and J_{22} are negative, reflecting the AFM exchange between the Mn atoms. When Ti atoms move toward the GaNMn_3 slab, both the Mn1-Mn2 and Mn2-Mn2 AFM exchange parameters are reduced, but the effect of the displacement on J_{12} is stronger, which changes the ratio of J_{12} to J_{22} so that it crosses 1 at a small negative displacement [Fig. 5(d)]. Therefore, when the Ti atoms are closer to the interface, the AFM exchange interaction between Mn2-Mn2 is stronger ($J_{22}/J_{12} > 1$), making m_{Mn2} be canted toward antiparallel and hence the net magnetic moment to be parallel to m_{Mn1} . On the contrary, when Ti atoms are further from the interface, Mn1-Mn2 AFM exchange is stronger ($J_{22}/J_{12} < 1$), making m_{Mn1} and m_{Mn2} be canted toward antiparallel and leading to the net magnetic moment to be antiparallel to m_{Mn1} . This behavior is seen in Fig. 5(e), revealing that m_{net} changes its sign when the Ti displacement changes from positive to negative.

The predicted variation of J_{12} and J_{22} as a function of displacement of Ti atoms can be understood in terms of the change in the number of 3d electrons on the Mn sites. The latter occurs due the screening charge in GaNMn_3 induced by the interface polarization when Ti^{4+} ions are displaced from their equilibrium positions. It is well known that the atoms with the nearly half filled 3d band, such as Mn and Cr, have strong tendency towards the AFM order because the Pauli exclusion principle forbids the electron hopping onto the orbital which is already occupied by an electron with the same spin [53]. Therefore, GaNMn_3 favors the AFM Mn-Mn exchange. On the other hand, when the bands are more than half filled, as is for Fe, Co, and Ni, the electron hopping favors the FM order. Doping electrons into the half-filled bands weakens the AFM interaction and gradually transforms the exchange from antiferromagnetic to ferromagnetic [55]. This trend is consistent with our results. Figure 5(f) shows the calculated number of the Mn 3d electrons (n_{3d}) which is obtained by integrating the valence charge density within a sphere of radius $r_a = 1.323 \text{ \AA}$ centered on the Mn sites. It is seen that the change of n_{3d} on the Mn1 and Mn2 sites [Fig. 5(f)] correlates with the change of J_{12} and J_{22} [Fig. 5(a)]: when Ti atom moves closer to the interface, both Mn1 n_{3d} and Mn2 n_{3d} increase as J_{12} and J_{22} do; the increase of Mn1 n_{3d} is larger than Mn2 n_{3d} in agreement with the larger increase of J_{12} compared to J_{22} . We conclude, therefore, that the interfacial Mn-Mn AFM exchange interactions are primarily controlled by the screening charge altering the Mn 3d orbital population, in response to the polarization induced by Ti displacement, and producing the Mn moment canting and the resulting net magnetic moment.

V. CONCLUSION

In conclusion, we have shown that the noncollinear magnetization intrinsic to antiperovskite GaNMn_3 is strongly

TABLE II. Interfacial Mn2-O, Mn2-Ti, and Mn1-Mn2 interatomic distances ($\text{\AA}$) along the z direction for $\text{GaNMn}_3/\text{ATiO}_3$ ($A = \text{Sr, Ba}$). $P = 0$ corresponds to $\text{GaNMn}_3/\text{SrTiO}_3$; $P > 0$ ($P < 0$) corresponds to $\text{GaNMn}_3/\text{BaTiO}_3$ with polarization pointing to (away from) the interface.

	Mn2-O	Mn2-Ti	Mn1-Mn2
$P = 0$	2.087	2.138	1.866
$P > 0$	2.074	1.983	1.933
$P < 0$	2.065	2.253	1.842

TABLE III. Formation energies ΔE (eV/interface) for different interfaces in the $\text{GaNMn}_3/\text{SrTiO}_3$ (001) heterostructure.

	$\text{NMn}_2/\text{TiO}_2$	NMn_2/SrO	GaMn/TiO_2	GaMn/SrO
ΔE	-4.785	-2.295	-2.965	-2.187

TABLE IV. Calculated total energies of GaNMn₃/SrTiO₃ supercell for different initial magnetic configurations at the interface.

	IF1	IF2	IF3	IF4
Energy (meV/supercell)	0	608	627	855

affected at the interface with a perovskite ATiO₃ ($A = \text{Sr}$ and Ba). Our first-principles calculations predict the enhancement and reorientation of Mn magnetic moments, resulting in a sizable net magnetization along the [110] direction. In the case of BaTiO₃, we find that the switching of ferroelectric polarization reverses the net magnetization of GaNMn₃ through $\sim 20^\circ$ rotation of the noncollinear magnetic moments. Magnetization switching by electric means is the holy grail of voltage-controlled spintronics, and thus our results pave a route to achieve this functionality by exploiting ferroelectrically controlled noncollinear magnetism at antiperovskite/perovskite interfaces.

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APPENDIX A: GaNMn₃/ATiO₃(001) INTERFACE FORMATION ENERGY

The interface stability of the GaNMn₃/SrTiO₃ (001) heterostructure was analyzed using symmetric supercells $4\text{GaNMn}_3 \cdot \text{NMn}_2/4\text{SrTiO}_3 \cdot \text{TiO}_2$, $4\text{GaNMn}_3 \cdot \text{NMn}_2/4\text{SrTiO}_3 \cdot \text{SrO}$, $4\text{GaNMn}_3 \cdot \text{GaMn}/4\text{SrTiO}_3 \cdot \text{TiO}_2$, and $4\text{GaNMn}_3 \cdot \text{GaMn}/4\text{SrTiO}_3 \cdot \text{SrO}$ to simulate four possible interfacial atomic configurations between GaNMn₃ and SrTiO₃: NMn₂/TiO₂, NMn₂/SrO, GaMn/TiO₂, and

FIG. 6. (a)–(d) Tested GaNMn₃/SrTiO₃ (001) interface configurations: NMn₂/TiO₂ (a), NMn₂/SrO (b), GaMn/TiO₂ (c), and GaMn/SrO (d).

GaMn/SrO. Figure 6 shows the fully relaxed atomic structures of these interfaces. The interface formation energies ΔE were calculated using the following relations:

$$\Delta E_{\text{NMn}_2/\text{TiO}_2} = \frac{1}{2}(E_{\text{sc}} - 4E_{\text{GNM}} - 4E_{\text{STO}} - E_{\text{Ti}} - 2E_{\text{O}} - E_{\text{N}} - 2E_{\text{Mn}}),$$

$$\Delta E_{\text{NMn}_2/\text{SrO}} = \frac{1}{2}(E_{\text{sc}} - 4E_{\text{GNM}} - 4E_{\text{STO}} - E_{\text{Sr}} - E_{\text{O}} - E_{\text{N}} - 2E_{\text{Mn}}),$$

$$\Delta E_{\text{GaMn}/\text{TiO}_2} = \frac{1}{2}(E_{\text{sc}} - 4E_{\text{GNM}} - 4E_{\text{STO}} - E_{\text{Ti}} - 2E_{\text{O}} - E_{\text{Ga}} - E_{\text{Mn}}),$$

$$\Delta E_{\text{GaMn}/\text{SrO}} = \frac{1}{2}(E_{\text{sc}} - 4E_{\text{GNM}} - 4E_{\text{STO}} - E_{\text{Sr}} - E_{\text{O}} - E_{\text{Ga}} - E_{\text{Mn}}),$$

where E_{sc} is the total energy of the supercell, E_{GNM} , E_{STO} , E_{Ti} , E_{Sr} , E_{Ga} , and E_{Mn} are the total energies of the corresponding bulk materials, E_{N} and E_{O} are half the total energies of N₂ and O₂ molecules, respectively. As is evident from Table III, all the interfaces have negative formation energies, which implies that they are energetically stable. We find, however, that the formation energy for the NMn₂/TiO₂ interface is

TABLE V. Calculated magnetic moments (in μ_B) of Mn atoms in the supercell of $4\text{GaNMn}_3 \cdot \text{NMn}_2/4\text{ATiO}_3 \cdot \text{TiO}_2$ ($A = \text{Sr}, \text{Ba}$) with the NMn₂/TiO₂ interface and the Γ_{5g} magnetic structure shown in Fig. 7(a).

	GaNMn ₃ /SrTiO ₃				GaNMn ₃ /BaTiO ₃			
	m_x	m_y	m_z	m_{total}	m_x	m_y	m_z	m_{total}
Mn2	0.299	−1.927	−2.227	2.960	−0.732	1.575	2.306	2.887
Mn2	−1.929	0.298	2.225	2.960	1.576	−0.732	−2.306	2.887
Mn1	1.659	1.658	0.001	2.345	−1.746	−1.744	0.002	2.468
Mn2	0.183	−1.753	−1.936	2.618	−0.153	1.788	1.940	2.643
Mn2	−1.754	0.182	1.935	2.618	1.786	−0.157	−1.942	2.643
Mn1	1.814	1.814	0.001	2.565	−1.839	−1.837	0.002	2.599
Mn2	0.033	−1.854	−1.887	2.646	−0.063	1.832	1.894	2.636
Mn2	−1.854	0.033	1.887	2.646	1.830	−0.066	−1.896	2.636
Mn1	1.814	1.814	0.000	2.565	−1.785	−1.784	0.001	2.524
Mn2	0.183	−1.754	−1.936	2.619	−0.181	1.748	1.929	2.609
Mn2	−1.753	0.182	1.936	2.618	1.747	−0.184	−1.930	2.610
Mn1	1.659	1.659	0.000	2.346	−1.684	−1.684	0.001	2.382
Mn2	0.300	−1.927	−2.226	2.959	−0.026	2.112	2.137	3.005
Mn2	−1.926	0.301	2.227	2.960	2.111	−0.028	−2.138	3.005

FIG. 7. Different initial magnetic configurations at the $\text{GaNMn}_3/\text{ATiO}_3$ interface: (a) IF1, where the Mn2 moments are the continuation of the bulk Γ_{5g} phase; (b) IF2, where the Mn2 moments are antiparallel to the neighboring Mn1 moments; (c) IF3, where the Mn2 moments are parallel to Mn2; (d) IF4, where the Mn2 moments are pointing along the z direction.

significantly lower than the formation energies of the other interface terminations. This is due to the strong ionic bonding between Mn cations and O anions at the interface when Mn is located atop of O. In this regard, a stoichiometric $\text{ATiO}_3/\text{GaNMn}_3$ supercell [58] is expected to be energetically unfavorable.

APPENDIX B: ENERGIES OF DIFFERENT MAGNETIC CONFIGURATIONS AT THE $\text{GaNMn}_3/\text{ATiO}_3(001)$ INTERFACE

When investigating the interfacial magnetism of $\text{GaNMn}_3/\text{ATiO}_3$, we tested different interfacial magnetic configurations. Our starting point was the assumption that away from the interface, GaNMn_3 has the antiferromagnetic Γ_{5g} phase, which is the lowest-energy magnetic structure in the bulk. The two interfacial layers involving Mn1 and Mn2 atoms (Fig. 7) are mostly affected by the perturbation created by the proximity of the perovskite. For these two interfacial layers, we considered four different initial interface magnetic configurations shown in Fig. 7. In all these configurations, we assumed that the Mn1 layer preserves the magnetic ordering of the Γ_{5g} phase. The four magnetic configurations at the interface were therefore distinguished by the orientation of the interfacial Mn2 moments: IF1, where the Mn2 moments are the continuation of the bulk Γ_{5g} phase [Fig. 7(a)]; IF2, where the Mn2 moments are antiparallel to the neighboring Mn1 moments [Fig. 7(b)]; IF3, where the Mn2 moments are parallel to Mn2 [Fig. 7(c)]; and IF4, where the Mn2 moments are pointing along the z direction [Fig. 7(d)]. We found that the IF1 configuration has the lowest energy, while the energies of the other initial magnetic configurations are much higher, as shown in Table IV. This result is not surprising because the stoichiometric interface keeps the sequence of the triangular Kagome lattice, where the

FIG. 8. Comparative study of $\text{GaNMn}_3/\text{vacuum}$ and $\text{GaNMn}_3/\text{SrTiO}_3$ heterostructures. (a) Local DOS of the surface and interfacial Mn1 atoms. (b) Local DOS of the surface and interfacial Mn2 atoms.

antiferromagnetic coupling between the nearest-neighbor Mn magnetic moments preserves the bulk Γ_{5g} phase, which is somewhat distorted at the interface.

APPENDIX C: CALCULATED MAGNETIC MOMENTS IN THE $\text{GaNMn}_3/\text{ATiO}_3(001)$ SUPERCELLS

The calculated magnetic moments on the Mn atoms in the supercell of $4\text{GaNMn}_3 \cdot \text{NMn}_2/4\text{ATiO}_3 \cdot \text{TiO}_2$ ($A = \text{Sr, Ba}$) with the $\text{NMn}_2/\text{TiO}_2$ interface and the Γ_{5g} magnetic structure shown in Fig. 7(a) are listed in Table V, corresponding to the magnetic moments presented in Figs. 3(a) and 3(b) in the main text.

APPENDIX D: DENSITY OF STATES ON SURFACE Mn ATOMS

The electronic structure of the $\text{GaNMn}_3/\text{vacuum}$ supercell was calculated and compared to that of the $\text{GaNMn}_3/\text{SrTiO}_3$ supercell. The $\text{GaNMn}_3/\text{vacuum}$ structure was created by replacing SrTiO_3 in the $\text{GaNMn}_3/\text{SrTiO}_3$ structure by vacuum. Figure 8 shows the calculated local density of states on Mn1 [Fig. 8(a)] and Mn2 [Fig. 8(b)] atoms on the surface of the GaNMn_3 slab (solid lines) and at the $\text{GaNMn}_3/\text{SrTiO}_3$ interface (dashed lines). It is seen that for both Mn atoms the local DOS on the surface and at the interface are similar, indicating that the hybridization between atomic orbitals in the TiO_2 plane and NMn_2 plane in the $\text{GaNMn}_3/\text{SrTiO}_3$ heterostructure does not have a strong effect on the local Mn-projected DOS at the interface.

- [1] F. Matsukura, Y. Tokura, and H. Ohno, *Nat. Nanotechnol.* **10**, 209 (2015).
 [2] E. Y. Tsybal, *Nat. Mater.* **11**, 12 (2012).

- [3] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, *Nature (London)* **408**, 944 (2000).

- [4] D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, and H. Ohno, *Nature (London)* **455**, 515 (2008).
- [5] M. Weisheit, S. Fähler, A. Marty, Y. Souche, C. Poinsignon, and D. Givord, *Science* **315**, 349 (2007).
- [6] Y. Shiota, T. Nozaki, F. Bonell, S. Murakami, T. Shinjo, and Y. Suzuki, *Nat. Mater.* **11**, 39 (2012).
- [7] W.-G. Wang, M. Li, S. Hageman, and C. L. Chien, *Nat. Mater.* **11**, 64 (2012).
- [8] 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).
- [9] Y. Takahashi, R. Shimano, Y. Kaneko, H. Murakawa, and Y. Tokura, *Nat. Phys.* **8**, 121 (2012).
- [10] 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).
- [11] S. Zhang, *Phys. Rev. Lett.* **83**, 640 (1999).
- [12] J. M. Rondinelli, M. Stengel, and N. A. Spaldin, *Nat. Nanotechnol.* **3**, 46 (2008).
- [13] C.-G. Duan, J. P. Velev, R. F. Sabirianov, Z. Zhu, J. Chu, S. S. Jaswal, and E. Y. Tsymlal, *Phys. Rev. Lett.* **101**, 137201 (2008).
- [14] T. Maruyama, Y. Shiota, T. Nozaki, K. Ohta, N. Toda, M. Mizuguchi, A. A. Tulapurkar, T. Shinjo, M. Shiraishi, S. Mizukami, Y. Ando, and Y. Suzuki, *Nat. Nanotechnol.* **4**, 158 (2009).
- [15] J. Zhang, P. V. Lukashev, S. S. Jaswal, and E. Y. Tsymlal, *Phys. Rev. B* **96**, 014435 (2017).
- [16] C. J. Fennie and K. M. Rabe, *Phys. Rev. Lett.* **97**, 267602 (2006).
- [17] M. Ye, Zhuravlev, S. Maekawa, and E. Y. Tsymlal, *Phys. Rev. B* **81**, 104419 (2010).
- [18] Y. W. Yin, J. D. Burton, Y.-M. Kim, A. Y. Borisevich, S. J. Pennycook, S. M. Yang, T. W. Noh, A. Gruverman, X. G. Li, E. Y. Tsymlal, and Q. Li, *Nat. Mater.* **12**, 397 (2013).
- [19] C. A. F. Vaz, J. Hoffman, C. H. Ahn, and R. Ramesh, *Adv. Mater.* **22**, 2900 (2010).
- [20] C.-G. Duan, S. S. Jaswal, and E. Y. Tsymlal, *Phys. Rev. Lett.* **97**, 047201 (2006).
- [21] K. Yamauchi, B. Sanyal, and S. Picozzi, *Appl. Phys. Lett.* **91**, 062506 (2007).
- [22] M. Fechner, I. V. Maznichenko, S. Ostanin, A. Ernst, J. Henk, P. Bruno, and I. Mertig, *Phys. Rev. B* **78**, 212406 (2008).
- [23] H. J. A. Molegraaf, J. Hoffman, C. A. F. Vaz, S. Gariglio, D. van der Marel, C. H. Ahn, and J.-M. Triscone, *Adv. Mater.* **21**, 3470 (2009).
- [24] H. Lu, T. A. George, Y. Wang, I. Ketsman, J. D. Burton, C.-W. Bark, S. Ryu, D. J. Kim, J. Wang, C. Binek, P. A. Dowben, A. Sokolov, C.-B. Eom, E. Y. Tsymlal, and A. Gruverman, *Appl. Phys. Lett.* **100**, 232904 (2012).
- [25] S. Dong and E. Dagotto, *Phys. Rev. B* **88**, 140404(R) (2013).
- [26] G. Radaelli, D. Petti, E. Plekhanov, I. Fina, P. Torelli, B. R. Salles, M. Cantoni, C. Rinaldi, D. Gutiérrez, G. Panaccione, M. Varela, S. Picozzi, J. Fontcuberta, and R. Bertacco, *Nat. Commun.* **5**, 3404 (2014).
- [27] T. T. Nguyen, K. Yamauchi, T. Oguchi, and N. N. Hoang, *J. Electron. Mater.* **46**, 3808 (2017).
- [28] X. Hong, A. Posadas, A. Lin, and C. H. Ahn, *Phys. Rev. B* **68**, 134415 (2003).
- [29] D. Chiba, S. Fukami, K. Shimamura, N. Ishiwata, K. Kobayashi, and T. Ono, *Nat. Mater.* **10**, 853 (2011).
- [30] M. Fechner, P. Zahn, S. Ostanin, M. Bibes, and I. Mertig, *Phys. Rev. Lett.* **108**, 197206 (2012).
- [31] J. D. Burton and E. Y. Tsymlal, *Phys. Rev. B* **80**, 174406 (2009).
- [32] C. A. F. Vaz, J. Hoffman, Y. Segal, J. W. Reiner, R. D. Grober, Z. Zhang, C. H. Ahn, and F. J. Walker, *Phys. Rev. Lett.* **104**, 127202 (2010).
- [33] R. O. Cherifi, V. Ivanovskaya, L. C. Phillips, A. Zobelli, I. C. Infante, E. Jacquet, V. Garcia, S. Fusil, P. R. Briddon, N. Guiblin, A. Mougin, A. A. Ünal, F. Kronast, S. Valencia, B. Dkhil, A. Barthélémy, and M. Bibes, *Nat. Mater.* **13**, 345 (2014).
- [34] P. Tong, B.-S. Wang, and Y.-P. Sun, *Chin. Phys. B* **22**, 067501 (2013).
- [35] D. Fruchart and E. F. Bertaut, *J. Phys. Soc. Jpn.* **44**, 781 (1978).
- [36] C. X. Quintela, K. Song, D.-F. Shao, L. Xie, T. R. Paudel, N. Campbell, M. S. Rzchowski, E. Y. Tsymlal, S.-Y. Choi, and C.-B. Eom (unpublished).
- [37] T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, and R. J. Cava, *Nature (London)* **411**, 54 (2001).
- [38] K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, T. Sasaki, and T. Kanomata, *Phys. Rev. B* **63**, 024426 (2000).
- [39] K. Takenaka, M. Ichigo, T. Hamada, A. Ozawa, T. Shibayama, T. Inagaki, and K. Asano, *Sci. Technol. Adv. Mater.* **15**, 015009 (2014).
- [40] B. S. Wang, P. Tong, Y. P. Sun, X. Luo, X. B. Zhu, G. Li, X. D. Zhu, S. B. Zhang, Z. R. Yang, and W. H. Song, *Europhys. Lett.* **85**, 47004 (2009).
- [41] D. Matsunami, A. Fujita, K. Takenaka, and M. Kano, *Nat. Mater.* **14**, 73 (2015).
- [42] E. F. Bertaut, D. Fruchart, J. P. Bouchaud, and R. Fruchart, *Solid State Commun.* **6**, 251 (1968).
- [43] K. Shi, Y. Sun, J. Yan, S. Deng, L. Wang, H. Wu, P. Hu, H. Lu, M. I. Malik, Q. Huang, and C. Wang, *Adv. Mater.* **28**, 3761 (2016).
- [44] P. Lukashev, R. F. Sabirianov, and K. Belashchenko, *Phys. Rev. B* **78**, 184414 (2008).
- [45] J. Zemen, Z. Gercsi, and K. G. Sandeman, *Phys. Rev. B* **96**, 024451 (2017).
- [46] P. Lukashev and R. F. Sabirianov, *Phys. Rev. B* **82**, 094417 (2010).
- [47] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [48] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [49] D. Hobbs, G. Kresse, and J. Hafner, *Phys. Rev. B* **62**, 11556 (2000).
- [50] D. Hobbs, J. Hafner, and D. Špiřák, *Phys. Rev. B* **68**, 014407 (2003).
- [51] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [52] G. Gurung, D.-F. Shao, T. R. Paudel, and E. Y. Tsymlal, *arXiv:1901.05040*.
- [53] J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, Cambridge, England, 2010).

- [54] N. E. Christensen, O. Gunnarsson, O. Jepsen, and O. K. Andersen, *J. Phys. Colloques* **49**, C8-17 (1988).
- [55] G. D. Samolyuk, B. P. T. Fokwa, R. Dronskowski, and G. J. Miller, *Phys. Rev. B* **76**, 094404 (2007).
- [56] K. Momma and F. Izumi, *J. Appl. Cryst.* **44**, 1272 (2011).
- [57] M. A. Caprio, *Comput. Phys. Commun.* **171**, 107 (2005).
- [58] P. Lukashev, K. D. Belashchenko, and R. F. Sabirianov, *Phys. Rev. B* **84**, 134420 (2011).