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Linear magnetoelectricity at room temperature in perovskite superlattices by design

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Discovering materials that display a linear magnetoelectric (ME) effect at room temperature is a challenge. Such materials could facilitate novel devices based on the electric-field control of magnetism. Here we present simple, chemically intuitive design rules to identify a new class of bulk magnetoelectric materials based on the ‘bicolor’ layering of $Pbnm$ ferrite perovskites, e.g., $\text{LaFeO}_3/\text{LnFeO}_3$ superlattices, Ln = lanthanide cation. We use first-principles density-functional theory calculations to confirm these ideas. We elucidate the origin of this effect and show it is a general consequence of the layering of any bicolor, $Pbnm$ perovskite superlattice in which the number of constituent layers are odd (leading to a form of hybrid improper ferroelectricity). Our calculations suggest that the ME effect in these superlattices is larger than that observed in the prototypical magnetoelectric materials Cr_2O_3 and BiFeO_3 . Furthermore, in these proposed materials, the strength of the linear ME coupling increases with the magnitude of the induced spontaneous polarization which is controlled by the La/Ln cation radius mismatch. We use a simple mean field model to show that the proposed materials order magnetically above room temperature.

I. INTRODUCTION

Multiferroics are materials in which ferroelectricity and magnetism coexist [1–3]. Despite recent intense efforts to discover new multiferroics, there are surprisingly few materials that display this property at room temperature. Furthermore, the primary challenge remains to identify materials that have a functional coupling between an electrical polarization and a magnetization at room temperature [4, 5]. Such materials may, for example, facilitate technologically important devices based on the electric-field control of magnetism [6–11].

One way to design such cross-couplings is to start with a paraelectric material that is magnetically ordered and induce a ferroelectric lattice distortion [12]. For example, it was shown [13] how a polar distortion – in an antiferromagnetic–paraelectric (AFM-PE) material displaying linear magnetoelectricity – would induce weak-ferromagnetism in the LiNbO_3 structure, e.g., FeTiO_3 [14] or MnSnO_3 [15], and subsequently allow for the electric-field switching of the magnetization by 180° . Alternatively a ferroelectric distortion in an AFM-PE material that displays weak-ferromagnetism can induce linear magnetoelectricity [5, 12]. In this direction, Bousquet and Spaldin recently realized that the orthorhombic perovskites, with space group $Pnma$, are prime choices and proposed epitaxial strain as a route to induce ferroelectricity [16]. They showed from first-principles that under large strain, $Pnma$ CaMnO_3 indeed becomes ferroelectric. The polar lattice distortions lowers the symmetry to $Pmc2_1$ and induces a linear magnetoelectric (ME) effect.

In the present study, we show how hybrid improper ferroelectricity (HIF), a recently proposed ferroelectric mechanism [17, 18], can be harnessed to induce linear

magnetoelectricity in the ubiquitous $Pnma$ perovskites, whereby the combination of rotations/tilts of the BO_6 octahedra and A-site cation ordering facilitate ferroelectric order [19–21], without the need for applying external strain [16].

We emphasize that the approach discussed here is generalizable to a wide range of materials and different realizations of HIF [22]. Additionally, HIF is no longer just theoretical ideas. For example, in an exciting development, Oh and co-workers recently demonstrated polarization switching in $\text{Ca}_3\text{Ti}_2\text{O}_7$ [23] one of the first predicted hybrid improper ferroelectrics [18]. The polarization in a related compound, the weak ferromagnet $\text{Ca}_3\text{Mn}_2\text{O}_7$, was also predicted to emerge through a hybrid improper mechanism [18]. In addition, the magnetization was shown to be coupled to the polarization such that switching the direction of the polarization also results in a 180° deterministic switching of the magnetization. Although this prediction has not yet been realized experimentally, recent work by Pitcher *et al.* [24] on polar double perovskite $(\text{Ca}_y\text{Sr}_{1-y})_{1.15}\text{Tb}_{1.85}\text{Fe}_2\text{O}_7$ has shown that the polarization and magnetization in this material co-exist at room temperature and that the polarization is induced through a hybrid improper mechanism. Hence, it appears that HIF may be a promising and practical means to design new magnetoelectrics (MEs).

Here, we consider the rare-earth $(\text{La}/\text{Ln})\text{Fe}_2\text{O}_6$ orthoferrite superlattices in which the La and Ln cations ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Tm}, \text{Lu}$ and Y) are ordered in layers along the crystallographic c -axis, where respective supercells have been constructed as $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ (here, a_p is the pseudocubic lattice parameter of $Pbnm$ LaFeO_3). Note that similar results are obtained for $(\text{LaFeO}_3)_n/(\text{LnFeO}_3)_m$ heterostructures of $Pbnm$ materials when both n and m are odd [25, 26]. We choose to focus on orthoferrites because bulk LnFeO_3 materials order magnetically above room temperature, with T_N as high as ~ 740 K for LaFeO_3 [27–30].

We show from first-principles calculations that the

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magnitude of the linear ME tensor in these heterostructures is 2-3 times that of canonical ME materials such as Cr_2O_3 [31–36] and BiFeO_3 . Moreover, the strength of linear ME coupling in $(\text{La}/\text{Ln})\text{Fe}_2\text{O}_6$ superlattices increases with the increase of the magnitude of the polarization. We discuss the microscopic origin of linear ME coupling for these La/Ln superlattices and high magnetic transition temperature. Interestingly, we identify another linear ME meta-stable phase stabilized by a single octahedral rotation. This work provides a practical route to create a new class of multiferroic materials that display a linear ME effect at room temperature whereby octahedral rotations mediate a nontrivial coupling between magnetism and ferroelectricity [18, 20, 37–39].

Before we begin, a note on terminology. Prototypical perovskites ferroelectrics, such as BaTiO_3 and PbTiO_3 , display proper ferroelectricity whereby a zone-center polar instability drives the transition to the polar state [40, 41]. This leads to a characteristic energy vs. polarization double well. Prototypical improper ferroelectrics [42] such as the hexagonal manganite YMnO_3 , however, have no polar instability. Instead the polarization, Q_p , is completely controlled by a single unstable oxygen rotation-tilt distortion, Q_K , associated with a non-zero q wave-vector at the zone-boundary [43]. At the phenomenological level, this mechanism can be understood as arising from a term in the free energy of the form $\mathcal{F} \sim Q_p Q_K^f$ (with $f=3$ for YMnO_3). The polarization remains in a single minimum energy well, with the minimum shifted to a non-zero value, analogous to turning on an electric field. The term “hybrid” emphasizes that in this hybrid improper mechanism, two unstable zone-boundary distortions, say Q_1 and Q_2 , couple to a polar zone-center mode Q_p (which need not be unstable like in YMnO_3) via a trilinear coupling, $\mathcal{F} = Q_1 Q_2 Q_p$. The two zone-boundary modes Q_1 and Q_2 together transform like and establish the space group symmetry of the polar ground state, although symmetry arguments alone cannot tell us which of the distortions (or which combinations) actually induce the polar state. However, in most HIFs studied so far Q_1 and Q_2 are assumed to be the primary order parameters. This is in contrast to prototypical improper ferroelectrics (such as YMnO_3 , for example), where the primary order parameter is a single zone-boundary mode. A clear advantage of this hybrid improper mechanism is the additional independent lattice degree of freedom that can potentially be exploited to control the magnetization. Indeed, as discussed above Q_1 and Q_2 may also give rise to weak ferromagnetism and magnetoelectric coupling and this is the focus of the current work.

II. COMPUTATIONAL DETAILS

First-principles calculations were carried out using density functional theory [44] with projector augmented wave (PAW) potentials [45] and within LSDA+U [46], as

implemented in the Vienna ab initio simulation package (VASP) [47]. We used PAW potentials for the Ln^{3+} ions where f -states are treated in the core, eliminating magnetic orderings associated with the f -state magnetism which occurs at low temperature. For Fe^{3+} ions, we have included the on-site $d-d$ Coulomb interaction parameter $U=6.0$ eV, and exchange interaction parameter $J=1.0$ eV. The exchange-correlation part is approximated by the PBEsol functional [48], which improves the structural descriptions over standard LDA or GGA [49]. The total energy and Hellman-Feynman force were converged to $0.1 \mu\text{eV}$ and $0.1\text{meV}/\text{\AA}$, respectively. All calculations were performed with a 500 eV energy cutoff and a Γ -centered $6 \times 6 \times 4$ k -point mesh. We carefully checked convergence with these settings by testing higher energy cutoffs and larger k -meshes. Non-collinear magnetization calculations were performed with L-S coupling [50], and total polarization was calculated with the Berry phase method [51] as implemented in VASP.

III. POLARIZATION, MAGNETIZATION AND SWITCHING

FIG. 1. The ‘orthorhombic’ ABO_3 perovskite, space group $Pbnm$. The structure, Glazer pattern $a^-a^-c^+$, is described by three symmetrize basis modes of cubic $Pm\bar{3}m$: (a) Q_{Rot} , in-phase rotation of BO_6 octahedra about $[001]$ (irrep. M_3^+), (b) Q_{Tilt} , tilt of BO_6 octahedra about $[110]$ with A-site displacement (irrep. R_4^+), (c) Q_{AFE} anti-ferroelectric A-site displacement (irrep. X_5^+). (d) The group-subgroup relation from high-symmetry $Pm\bar{3}m$ to low-symmetry $Pbnm$. (e) Two dimensional energy surface contour of LaFeO_3 with respect to the primary Q_{Rot} ($a^0a^0c^+$) and Q_{Tilt} ($a^-a^-c^0$) distortions.

We start with a brief discussion of notation. The space group designation of the orthorhombic $Pnma$ (space group number 62), the structure adopted by most perovskites [52, 53], is that in the standard crystallographic setting. Throughout this paper we use the equivalent

$Pbnm$ setting, the difference being a reflection of the orientation of the orthorhombic a , b , and c axes to that of the real space axes (See, Figure 1 (a), (b), and (c)).

The symmetry of this $Pbnm$ structure is established by two symmetry-lowering structural distortions of the cubic $Pm\bar{3}m$ perovskite structure: an in-phase rotation of the BO_6 octahedra about the cubic $[001]$ axis (transforming like the irreducible representation M_3^+) and an out-of-phase tilt of the BO_6 octahedra about the cubic $[110]$ axis (transforming like the irreducible representation R_4^+), as shown in Figure 1a and Figure 1b, respectively. Together these two distortions produce the Glazer rotation pattern $a^-a^-c^+$. Other kinds of structural distortions are also allowed by symmetry in the $Pbnm$ structure. In particular, recent work has shown that anti-polar displacements of the A-site cations, which are equal in magnitude but in opposite directions in adjacent AO planes, as shown in Figure 1c, – play a crucial role in stabilizing the structures of $Pbnm$ perovskites [54, 55]. These anti-polar displacements (transforming like the irrep X_5^+) are trilinearly coupled to the two rotation distortions in the free energy of the $Pm\bar{3}m$ structure [56], $\mathcal{F} = Q_{AFE} Q_{Tilt} Q_{Rot}$, where Q_{AFE} , Q_{Tilt} , and Q_{Rot} are the amplitudes of the anti-polar distortion, tilt and rotation, respectively. Hence, reversing the sense of either tilt or rotation will therefore reverse the direction of the anti-polar displacements, Q_{AFE} . In $Pbnm$ orthoferrites, the Fe spins typically order in a G-type antiferromagnetic ordering pattern with weak ferromagnetism (wFM) along the $Pbnm$ orthorhombic c -axis. This wFM is in fact induced by the Q_{Tilt} distortion in $Pbnm$ and hence the sense of this particular rotation and the direction of the canted magnetic moment are naturally coupled in a non-trivial way. These ideas are summarized in Figures 1d and e.

The $Pbnm$ perovskites are thus a system in which octahedral rotations mediate a non-trivial coupling between antiferroelectricity and magnetism. The recently developed theory of hybrid improper ferroelectricity has shown how antiferroelectricity in $Pbnm$ perovskites can give rise to ferri-electricity in perovskite heterostructures, [21] such as $(A/A')B_2O_6$ double perovskites, as shown in Figure 2a. A simple picture [20] that elucidates the mechanism is the following: the two rotation distortions, Q_{Rot} and Q_{Tilt} , break inversion symmetry at the A-site of the cubic $Pm\bar{3}m$ structure whereas the A/A' cation ordering breaks B-site inversion symmetry. As a result, the A-site displacements depicted in Figure 1c are no longer equal in magnitude and opposite but instead give rise to a macroscopic polarization, as shown in Figures 2b (in other words, this A-site displacement mode becomes a zone-center polar mode in the cation ordered unit cell, which has $P4/mmm$ symmetry in the absence of any rotations, Figure 2a). The key is that since the (now polar) A-site displacements are coupled to the rotations as described above, switching the direction of the polarization, Q_P , will switch the sense of one of the rotations. If it is Q_{Tilt} that switches, then the direction of the canted mo-

FIG. 2. Structural and ferroelectric properties of $(La/Ln)Fe_2O_6$ superlattices. (a) $(La/Y)Fe_2O_6$ superlattice in high-symmetry $P4/mmm$ structure, (b) lowest energy $Pb2_1m$ structure with rotation and tilt of FeO_6 octahedra, (c) Group-subgroup relation from $P4/mmm$ to other lower energy structures, (d) Two dimensional energy surface contours for $(La/Y)Fe_2O_6$ superlattice with respect to the primary Q_{Rot} ($a^0a^0c^+$, irrep. M_3^+) and Q_{Tilt} ($a^-a^-c^0$, irrep. M_5^-) distortions. In contour, Black dots represents the possible minimum structures, each corresponding to different sense of FeO_6 octahedra rotations, Green triangles (down) indicate to the $P4/mbm$ structures where Q_{Tilt} is zero and Orange triangles (up) indicate to the $Pbmm$ structure where Q_{Rot} is zero. Variation of (e) Polarization P and (f) Switching barriers along Rotation (ΔE_{Rot}) with respect to $(1-\tau_{avg})$ and $(1-\tau_{avg})^2$, respectively.

ment will also switch, resulting in electric-field control of the magnetization. These facts are summarized in Figure 2c and d (it is highly instructive to compare Figures 1d and 2c.)

We have used first-principles total energy calculations to consider the complete manifold of possible lower symmetry structures for this class of compounds and have identified the structure shown in Figure 2b as the lowest in energy. This structure has polar $Pb2_1m$ space group symmetry and displays both ferroelectricity (with a polarization along the orthorhombic y axis, P_y) and weak ferromagnetism (with a net magnetization along the z -axis, M_z). The resulting magnetic configuration has magnetic point group $m'm'2'$ and consists of G-type AFM ordering with the easy axis along x , A-type AFM ordering along the y -axis and a FM canting of spins along the z -axis (G_x , F_z) [27–30, 57–62].

Since, the origin of the polarization in our (La/Ln)Fe₂O₆ materials is a non-cancellation of the LaO and LnO layer polarizations. A simple way to increase this non-cancellation and hence the polarization is to choose a Ln cation whose tendency to off-center from the ideal perovskite A-site differs greatly from that of La. This is accomplished by choosing a Ln cation that is much smaller than La. In Figure 2e, we show that the magnitude of P_y monotonically increases as the Ln cation becomes smaller, from 2.2 $\mu\text{C}/\text{cm}^2$ for Ln=Ce to 11.6 $\mu\text{C}/\text{cm}^2$ for Ln=Lu. In other words, as the average tolerance factor τ_{avg} decreases, the polarization increases (note, $\tau_{\text{ABO}_3} = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ and $\tau_{\text{avg}} = (\tau_{\text{ABO}_3} + \tau_{\text{A}'\text{BO}_3})/2$), where r_A ($r_{A'}$), r_B and r_O , are ionic radii of A (A'), B and O atoms respectively. As discussed by Mulder et al. [21], such a simple behavior is only true when one of the two A-site cations is the same for all compounds, which is also found to be in agreement with a recent study based on R₂NiMnO₆/La₂NiMnO₆ superlattices [63]. Additionally, there is a small increase in M_z , 0.06–0.07 $\mu_B/\text{f.u.}$, as τ_{avg} decreases.

The direction of the polarization can in principle be switched 180° between symmetry equivalent states with the application of an electric-field. In this process the sense of either Q_{Rot} or Q_{Tilt} will switch. The question as to which distortion would actually switch is a challenging, dynamical problem, one for which today we still do not have a satisfactory answer (please see Ref. [39] for a nice discussion) and beyond the scope of this paper. We know, however, that switching does depend in some way on the energy barriers between the energy minima displayed in Figure 2d. Understanding how to control any of the energy barriers is useful information, even if the precise path is not known. Within this limited sense we briefly discuss the naive switching paths.

We found that the barrier height along Q_{Rot} , $\Delta E_{\text{Rot}} = E_{Pb2_1m} - E_{Pbmm}$, is about three times smaller than the barrier height along Q_{Tilt} , $\Delta E_{\text{Tilt}} = E_{Pb2_1m} - E_{P4/mbm}$ for all the compounds we considered. From this we conclude that it is more likely that Q_{Rot} would switch when the polarization switches. Since M_z switches only if Q_{Tilt}

switches, the (La/Ln)Fe₂O₆ systems do not appear to be likely candidates to pursue the electric-field switching of the magnetization. Furthermore, examination of Figure 2e shows that the ideal energy barrier to switch the polarization, $\Delta E_P \equiv \Delta E_{\text{Rot}}$, increases dramatically as τ_{avg} decreases, as expected from the design rules of Ref. [21]. In fact, it is not likely that the polarization in the majority of these materials could ever be switched under realistic electric-field strengths, other than perhaps (La/Ce)Fe₂O₆, which has the lowest switching barrier (63 meV/f.u. along the $a^0a^0c^+$ rotation path).

IV. LINEAR MAGNETOELECTRIC COUPLING (LME)

Although electric-field assisted switching of magnetization is not plausible in (La/Ln)Fe₂O₆ ferrites, the structural distortions associated with the spontaneous polarization however induce by design a linear magnetoelectric effect (which does not require switching of either the polarization or the magnetization),

$$\Delta M_i = \Sigma \alpha_{ij} E_j \quad (1)$$

$$\Delta P_i = \Sigma \alpha_{ij} H_j, \quad (2)$$

where ΔM_i (ΔP_i) is the induced magnetization (polarization) along the i th direction due to an electric (magnetic) field applied along the j th direction. The magnetic point group of all (La/Ln)Fe₂O₆ compounds is $m'2'm$, therefore, the only non-zero components of the linear ME tensor are,

$$\alpha = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{bmatrix} \quad (3)$$

where $\alpha_{yz} \neq \alpha_{zy}$ (the ME processes associated with these components are schematically shown in Figure 3(a)). The design strategy guarantees the existence of α , but what is its magnitude? Here, we used the method described in Ref. [31] to calculate the lattice contribution to α (although the linear ME response can have both lattice and electronic contributions, [12, 31] the method of Ref. [31] should give a reasonable order of magnitude estimate).

A brief description of this method is the following: considering only the lattice contribution to the energy, the energy of the $Pb2_1m$ crystal ($\mathcal{U}$) under an applied electric-field($\vec{E}$) is given by,

$$\mathcal{U}(\vec{q}_n, \vec{E}) = \mathcal{U}_0 + \frac{1}{2} \sum_n C_n q_n^2 - \sum_n q_n \vec{p}_n \cdot \vec{E} \quad (4)$$

where, q_n , C_n , and $\vec{p}_n$ are the amplitude, force constant, and dielectric polarity of the n^{th} infrared (IR) active force constant eigenvector, $\hat{q}_n$, respectively. The dielectric polarity $\vec{p}_n$ of the n^{th} -IR active mode can be calculated as, $\vec{p}_n = \partial \vec{P}_n / \partial q_n$, where $\vec{P}_n$ is the polarization (note that

FIG. 3. Linear Magnetolectric response of (La/Y)Fe₂O₆ superlattice. (a) Superlattice with La/Y cation ordering along z -direction which is the crystallographic c -axis. The spontaneous HIF polarization is along y -direction and net magnetization M in the system along z -direction (P_y^s, M_z^s). The ME tensor has two non-zero components. First, α_{zy} , change in polarization along y -direction (ΔP_y) changes the magnetization along z -direction (ΔM_z) and second α_{yz} , change in polarization along z -direction (ΔP_z) changes the magnetization along y -direction (ΔM_y), (b) Change in magnetization (with respect to the saturation magnetization) subject to the variation of electric-field ($\vec{E}$). Linear magnetolectric components α_{zy} and α_{yz} are obtained from the slope of M_z vs. E_y and M_y vs. E_z curve, respectively. The magnitude of α_{zy} and α_{yz} are given in Gaussian units (g.u.).

the force constants and dielectric polarity are routinely calculated from first principles [31, 64]). Therefore, for a given electric-field it is straightforward to calculate the induced atomic displacements associated with each force constant eigenvector, $\vec{q}_n = q_n \hat{q}_n$, where $q_n = \frac{1}{C_n} \vec{p}_n \cdot \vec{E}$. Subsequently, the linear ME tensor,

$$\alpha_{ij} = \partial M_i / \partial E_j, \quad (5)$$

can be calculated by freezing in the total induced atomic displacements, $\vec{u} = \sum_n q_n \hat{q}_n$, then recalculating the net magnetization.

A. (La/Y) Fe₂O₆: a prototype example

As an example let us first discuss the calculation of the linear ME response for (La/Y)Fe₂O₆ ($P_y^s = 9.0 \mu\text{C}/\text{cm}^2$ and $P_x = P_z = 0$; $M_z^s = 0.13 \mu_B$ and $M_x = M_y = 0$). It is useful to keep in mind that in $Pb2_1m$ the IR modes transform as irreducible representations Γ_1, Γ_3 , or Γ_4 , each leading to a polarization along the y, z , and x directions, respectively. By symmetry, the Γ_4 modes do not mediate a Linear ME effect. This is why α_{ij} for any i or $j = x$ is zero by symmetry. For the purpose of the calculation, we imagine the experiment in which an electric-field is applied and the resulting change in magnetization is measured.

With the application of an electric-field along the y direction $E\hat{y}$, symmetry dictates that only the Γ_1 modes respond, i.e., $\vec{p}_n \cdot \vec{E} = \vec{p}_n \cdot \hat{y}E \neq 0$ for $n \in \Gamma_1$. The induced atomic displacements

$$\vec{u}_{\Gamma_1} = \sum_{n \in \Gamma_1} \frac{1}{C_n} p_n E_y \hat{q}_n, \quad (6)$$

were frozen into the equilibrium structure and the change in magnetization, which by symmetry is along the z direction, was calculated from first-principles. This procedure was repeated for various magnitudes of the applied electric field. These results are shown in Figure 3(b)), the slope of which gives the linear ME coupling α_{zy} . We find that the magnitude of α_{zy} is 3.54×10^{-4} g.u. ($= 9.41 \times 10^{-7} \text{ C/T m}^2$), which is 2-3 times larger than the transverse linear ME response of the prototype ME compound Cr₂O₃ [31, 36] at 0 K.

With the application of an electric-field along the z direction, symmetry dictates that only the Γ_3 modes respond, i.e., $\vec{p}_n \cdot \vec{E} = \vec{p}_n \cdot \hat{z}E \neq 0$ for $n \in \Gamma_3$. The induced atomic displacements

$$\vec{u}_{\Gamma_3} = \sum_{n \in \Gamma_3} \frac{1}{C_n} p_n E_z \hat{q}_n. \quad (7)$$

can be calculated. Here we find that the corresponding magnitude of linear ME response (see Figure 3(b)), measured by the component α_{yz} is equal to 0.72×10^{-4} g.u. ($= 1.91 \times 10^{-7} \text{ C/T m}^2$), much weaker than α_{zy} .

It is important to note that α_{zy} component is the same order of magnitude as that of the most studied multiferroic BiFeO₃ [65, 66], which clearly shows (La/Ln) ferrite superlattices can be an alternative in search of room temperature linear magnetoelectric material. Therefore it is important to investigate how α_{zy} varies with the composition of the ferrite superlattices, which we discuss next.

B. (La/Ln)Fe₂O₆ series

In Figure 4 we show the composition dependence of α_{zy} obtained using the first-principles method described above. Because α_{yz} is order of magnitude weaker than

α_{zy} in (La/Y)Fe₂O₆, we calculate the α_{zy} component only for other compositions. Interestingly, α_{zy} increases almost linearly with the increase of $(1 - \tau_{avg})$, similar to P_y . In order to understand this trend we first analyze the magnetic symmetry of the G-type AFM order with easy axis along x in the paraelectric high symmetry phases. The paraelectric $P4/mmm$ ($a^0a^0c^0$) phase neither allows weak ferromagnetism nor linear ME coupling. Introduction of in-phase rotation (Q_{Rot}) does not lead to weak ferromagnetism, but the underlying magnetic point group $m'mm$ of G-type AFM order with easy axis along x allows a linear ME coupling. It is important to note that the non-zero components of the linear ME susceptibility tensor are α_{yz} and α_{zy} , which is exactly the same as in the ground state $Pb2_1m$ structure. On the other hand, Q_{Tilt} induces wFM, but forbids linear ME coupling. Therefore, while Q_{Tilt} induces wFM, linear ME coupling is driven by Q_{Rot} (illustrated in 2c); we establish this by considering a phenomenological model below.

Around the paraelectric–weak ferromagnetic $Pbmm$ ($Q_{Tilt} \neq 0$, $Q_{Rot}=0$) structure, the net magnetization M_z couples with even powers of Q_{Rot} . Considering up to the 2nd order term,

$$M_z \sim \gamma_1 L_0 + \frac{1}{2} \gamma_2 L_0 Q_{Rot}^2 \quad (8)$$

where, L_0 is the antiferromagnetic order parameter which is even under space inversion, and γ_1 denotes the magnitude of the magnetization in the $Pbmm$ structure and varies with odd powers of Q_{Tilt} . Therefore the change in magnetization M_z induced by the applied electric-field along the y direction is given by,

$$\Delta M_z \sim \gamma_2 L_0 Q_{Rot} \Delta Q_{Rot} \quad (9)$$

It is important to note that we consider change of $\gamma_1(Q_{Tilt})$ as a function of applied electric-field is negligible. Although the change in polarization under applied electric-field modulates the tilt distortion, within the linear range of atomic response the change in magnetization is negligible.

Considering the free energy expression,

$$\mathcal{F} = \frac{1}{2} a_R Q_{Rot}^2 + \frac{1}{2} a_T Q_{Tilt}^2 + \frac{1}{2} a_P P_y^2 + \xi Q_{Rot} Q_{Tilt} P_y + \dots - E_y P_y \quad (10)$$

we find that,

$$\Delta Q_{Rot} \sim -\frac{\xi}{a_P a_R} \Delta E_y \quad (11)$$

Which gives rise to,

$$\alpha_{zy} \sim -\frac{\gamma_2 \xi}{a_P a_R} L_0 Q_{Rot} \quad (12)$$

Note that this expression is similar to that derived for the Ruddlesden-Popper system $Ca_3B_2O_7$, where B= Ti and Mn [18].

FIG. 4. Variation of magnitude of the linear ME coefficient, $|\alpha_{zy}|$ (in g.u.) as a function of $(1 - \tau_{avg})$ for (La/Ln)Fe₄O₆ superlattices, where Ln= Ce, Nd, Sm, Gd, Dy, Tm, Lu and Y. We follow the method described in section-IVA to calculate the value of the off-diagonal component α_{zy} .

In (La/Ln)Fe₂O₆ series we found that Q_{Rot} increases linearly with $(1 - \tau_{avg})$. Therefore,

$$\alpha_{zy}(\tau_{avg}) \propto (1 - \tau_{avg}) \quad (13)$$

Equation 13, clearly explains the first-principles results presented in Figure 4.

Finally, as $P_y \propto (1 - \tau_{avg})$, in other words, the strength of linear ME coupling in (La/Ln)Fe₂O₆ superlattices grows with the increase of the induced spontaneous polarization. Within the (La/Ln)Fe₂O₆ superlattices, the highest predicted magnitude of α_{zy} is 4.25×10^{-4} g.u. for (La/Lu)Fe₂O₆. This is larger than the linear ME coefficients reported for the most studied magnetoelectrics, Cr₂O₃ and BiFeO₃ [31, 65] at 0 K.

C. (La/Ln)_{m,n}Fe_(m+n)O_{3(m+n)} series

A linear ME response is also allowed for higher order (La/Ln)_{m,n}Fe_(m+n)O_{3(m+n)} superlattices, if both m and n are odd. With even m and n the system adopts a centrosymmetric $P2_1/c$ structure, which does not allow any polarization. Moreover, the magnetic point group ($2'/m'$) associated with G-type AFM order with the easy axis along x forbids linear ME coupling.

The polarization as a function of layer thicknesses m and n is given by,

$$P_y(m, n) = \frac{2P_y(1, 1)}{m + n} \quad (14)$$

where, $P_y(1, 1)$ denotes the induced polarization of the 1/1 superlattice. The calculated polarizations of the (La/Y)_{2,2}Fe₄O₁₂, (La/Y)_{3,3}Fe₆O₁₈, (La/Y)_{1,3}Fe₄O₁₂ and (La/Y)_{1,5}Fe₆O₁₈ superlattices are found to be 0, 3.05 $\mu C/cm^2$, 4.52 $\mu C/cm^2$ and 3.01 $\mu C/cm^2$, respectively.

These values are in good agreement with the values estimated from Equation 14 using calculated $P_y(1,1) = 9.0 \mu\text{C}/\text{cm}^2$. Therefore one can write,

$$\alpha_{zy}(m,n) \sim \frac{2\alpha_{zy}(1,1)}{m+n} \quad (15)$$

We found that the computed magnitude of α_{zy} for the $(\text{La}/\text{Y})_{3,1}\text{Fe}_4\text{O}_{12}$ superlattice is 2.01×10^{-4} g.u., which is close to the value, 1.77×10^{-4} g.u., estimated from Equation 15 (where we used $\alpha_{yz}(1,1) = 3.54 \times 10^{-4}$ g.u., computed using first-principles method). This shows that the magnitude of α_{zy} decreases with increasing layer thickness. However, it is important to note that, for the $(\text{La}/\text{Y})_{5,5}$ superlattice (as experimentally grown [25]) the expected magnitude of α_{zy} is $\sim 0.71 \times 10^{-4}$ g.u., close to that reported for Cr_2O_3 [31].

V. MICROSCOPIC ORIGIN OF LINEAR MAGNETOELECTRIC COUPLING

To understand the microscopic origin of linear magnetoelectric coupling in ferrite superlattices we considered the bilinear coupling between Fe spins. The corresponding Hamiltonian [67] consists of three terms,

$$\mathcal{H} = \sum_{i,j} J_{ij}(\vec{S}_i \cdot \vec{S}_j) + \sum_{i,j} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) + \sum_i \vec{S}_i \cdot \vec{\Phi}_i \cdot \vec{S}_i \quad (16)$$

The first and second terms are the symmetric (Heisenberg exchange, J_{ij}) and antisymmetric exchange (Dzyaloshinskii-Moriya, DM) interactions between the i^{th} and j^{th} spins, respectively. The third term is the contribution from the single ion anisotropy (SIA), where $\vec{\Phi}_i$ is the SIA tensor of the i^{th} spin. While the symmetric exchange interactions between Fe spins dictate the G-type AFM ordering, the DM interactions and off-diagonal components of the SIA tensor are expected to cant the spins. In the following, however, we continue our discussion based on the symmetric and antisymmetric DM exchange interactions between Fe spins only, as the off-diagonal components of SIA tensor are expected to contribute similar as the DM interactions.

The crystal symmetry of the paraelectric $P4/mmm$ ($a^0a^0c^0$) and $P4/mbm$ ($a^0a^0c^+$) phases forbid the antisymmetric DM interactions between Fe spins, thus no spins are allowed to cant. The octahedral tilt distortion introduces the y-component of the nearest neighbor (nn) DM vectors, further symmetry breaking by in-phase rotations allows the x and z components. The vector form of the nn DM interactions for the lowest energy $Pb2_1m$ structure are given in Figure 5(a) for Fe spin 1 (according to the numbering of the Fe^{+3} spins in Figure 5 (a) and (b)). Corresponding DM vectors around other Fe spins can be found by using crystal symmetry. The net force acting on the i^{th} spin due to six nn DM interactions is given by, $\vec{F}_i = \sum_{j=1,6} \vec{f}_i^j$, where $\vec{f}_i^j = \vec{D}_{ij} \times \vec{S}_j$.

FIG. 5. (a) Six nn DM interactions acting on Fe_1 in $Pb2_1m$ structure are shown. Four inequivalent DM vectors acting via $\text{Fe}_1 - \text{O}_{ap} - \text{Fe}_4$, $\text{Fe}_1 - \text{O}_{ap}' - \text{Fe}_4$, $\text{Fe}_1 - \text{O}_p - \text{Fe}_2$ and $\text{Fe}_1 - \text{O}_p' - \text{Fe}_2$ magnetic paths are $\vec{D}_{14} (D_x^{ap}, D_y^{ap}, 0)$, $\vec{D}_{14}' (D_x^{ap'}, D_y^{ap'}, 0)$, $\vec{D}_{12} (0, D_y^p, D_z^p)$ and $\vec{D}_{12}' (0, D_y^{p'}, D_z^{p'})$, respectively. (b) Response of the in-plane DM interactions under the application of electric-field along y axis. $E\hat{y}$ changes in-plane $D_y\hat{y}$ interactions, such that $\Delta D_y^p > \Delta D_y^{p'}$ which lead to linear change in $m_z(-\hat{z})$. Red arrows indicate direction of major components of the Fe spins.

The force acting on Fe spins 1, 2, 3 and 4, aligned along the x axis, are given by $(0, S\bar{D}_z^0, S\bar{D}_y^0)$, $(0, S\bar{D}_z^0, S\bar{D}_y^0)$, $(0, -S\bar{D}_z^0, S\bar{D}_y^0)$, $(0, -S\bar{D}_z^0, S\bar{D}_y^0)$, respectively. Where $\bar{D}_y^0$ and $\bar{D}_z^0$ are the averaged nn DM component along y and z directions, respectively. Here, zero represents the state without application of the external electric-field. Thus, the y-component of the nn DM vectors i.e. $\bar{D}_y^0$ orders the Fe spins in FM pattern along z direction, giving rise to a net magnetization M_z . Therefore intermediate phase $Pbmm$ is also wFM. On the other hand the y-component of the Fe spins, driven by the z component of the nn DM vectors, i.e. $\bar{D}_z^0$, adopt a A-type AFM order, so $M_y = 0$. Considering that the magnitude of the canted spin components along the y and z axes to be same (as we explicitly have observed in first-principles results) we find,

$$m_y = m_z \sim \frac{1}{\sqrt{2}} m_s \sin \Theta \quad (17)$$

and,

$$\Theta = \frac{1}{2} \tan^{-1} \left[\frac{\sqrt{2}(3\bar{D}_y^0 - 2\bar{D}_z^0)}{4J_p^{0,nn} + J_{ap}^{0,nn}} \right] \quad (18)$$

where $m_s = \sqrt{(m_x^2 + m_y^2 + m_z^2)}$, m_y and m_z are magnetic moment per Fe canted along y and z , respectively. $J_p^{0,nn}$ and $J_{ap}^{0,nn}$ represent first nn interaction mediated through planar and apical oxygens, respectively.

We used calculated energies of eight collinear and twenty four non-collinear spin configurations to fit the Hamiltonian in order to estimate the strength of the nn exchange interactions. Using the first-principles estimated values of nn exchange interactions, as tabulated in Table-I for (La/Ce)Fe₂O₆, we estimate $m_z = 0.0365 \mu_B/\text{Fe}$. This value is in good agreement with the value calculated in the Pb2₁m structure, $m_z = 0.0295 \mu_B/\text{Fe}$.

In order to understand the microscopic origin of the Linear ME coupling we estimate the values of the exchange interactions under application of the electric field. To simulate this effect we follow the same procedure as we outline in section IV. We observe that changes in J_p^{nn} and J_{ap}^{nn} are negligible. The magnetic g-factor also remains the same under finite electric-field. Therefore the DM couplings are expected to play a major role in driving linear ME coupling in the system at 0 K. Below we propose a mechanism of linear ME coupling in these superlattices based on the response of the DM interactions under applied electric-field.

Figure 5 (b), schematically shows the response of the in-plane DM interactions under the application of electric-field along the y axis. We find that the applied electric-field $E_y \hat{y}$ decreases the interaction between

TABLE I. Magnitude of Dzyaloshinskii-Moriya (DM) vectors ($\bar{D}_{14}$, $\bar{D}'_{14}$, $\bar{D}_{12}$ and $\bar{D}'_{12}$), corresponding symmetric interaction (Heisenberg type, J^{nn}) and weak magnetization per Fe ($m_z \hat{z}$) have been tabulated for (La/Ce)Fe₂O₆ superlattice in lowest energy Pb2₁m structure, in absence of $\vec{E}$. Here, $m = 4.199 \mu_B/\text{Fe}^{3+}$. (Note1, we have reported the data following the method as described in Ref. [68]. We have also cross checked following the other method as described in Ref. [69], in our case, both methods found to give reasonable agreement. Note2: Throughout the text, we have defined M and m, as net magnetization in the cell and magnetic moment per Fe³⁺, respectively.)

Interactions	D_x (μeV)	D_y (μeV)	D_z (μeV)	J^{nn} (meV)	m_z (in μ_B/Fe)	
					Computed	Eq. 17
$1-O_p-2$	0	115	-101	-6.36	0.0295	0.0365
$1-O'_p-2$	0	115	-123	-6.25		
$1-O_{ap}-4$	-28	89	0	-6.03		
$1-O'_{ap}-4$	-28	90	0	-5.98		

Fe spins connected via O_p ($0, D_y^p - \Delta D_y^p, D_z^p - \Delta D_z^p$), and increases it for the Fe spins connected via O'_p ($0, D_y^p + \Delta D_y^p, D_z^p + \Delta D_z^p$). However, whereas $\Delta D_z^p = \Delta D_z'^p$, we observe $\Delta D_y^p > \Delta D_y'^p$, which induces a net change in canted moment (Δm_z) along $(-\hat{z})$, and in turn the linear magnetoelectric coupling α_{zy} . The net change in m_z (per Fe) due to application of an electric field ($E\hat{y}$) is given by,

$$\Delta m_z \propto \sin(\Delta\Theta/2) m_x \quad (19)$$

where m_x is the major component of the Fe spin moment along the x axis and $\sin(\Delta\Theta/2) \propto (\Delta\bar{D}_y - \Delta\bar{D}'_y)$.

The calculated difference between $\Delta\bar{D}_y$ and $\Delta\bar{D}'_y$ is found to be $-2 \mu\text{eV}$ ($+2 \mu\text{eV}$) for La/Ce superlattice under the application of electric-field of $0.02 \text{ V/\AA}$ ($-0.02 \text{ V/\AA}$), which gives rise to $\Delta m_z = -0.0004 \mu_B/\text{Fe}$ ($+0.0004 \mu_B/\text{Fe}$), and a corresponding value of α_{zy} of -1.16×10^{-4} in g.u, which is lower than the value calculated by the method described in section-IVA ($\alpha_{zy} = -2.50 \times 10^{-4}$ in g.u.). The possible origin of this discrepancy is that we have not considered the effect of SIA in the present study. Finally, we find that for La/Lu superlattice, the magnitude of m_x and $(\Delta\bar{D}_y - \Delta\bar{D}'_y)$ both increase compared to that of La/Ce superlattices, which enhances the magnitude of α_{zy} .

VI. ORDERING TEMPERATURE

From previous work, the robustness and universality of the polar linear ME ground state is clear. However, we must address the question of whether or not we expect the spins to order at room temperature. A relatively straightforward mean field approach to calculating the Néel temperature (T_N) involves mapping total energy calculations onto a Heisenberg model, from which the magnetic exchange interactions, J_{ij} , were extracted. Unfortunately, it is well known that the results obtained through this approach depend sensitively on the particular value of Hubbard U . Here we can take advantage of the fact that the experimental values of T_N are known for the perovskite constituents of our superlattices.

TABLE II. Computed super-exchange constants (J_{ij}) and mean field estimated magnetic transition temperatures. J_p^{nn} and J_{ap}^{nn} represent nearest neighbor Fe-Fe interaction mediated via planar and apical oxygen, respectively. The average interaction is given by $J_{avg}^{nn} = (4 \times J_p^{nn} + 2 \times J_{ap}^{nn})/6$. See Figure 5(b)). Note, here, Cartesian (x, y, z) $\rightarrow$ Crystallographic (a, b, c) and superlattice growth axis is along $z(c)$.

System	J_p^{nn}	J_{ap}^{nn}	J_{avg}^{nn}	T_N (K)	
				Computed	Experiment
LaFeO ₃	5.81	5.20	5.61	1139	740 [28]
YFeO ₃	5.20	4.51	4.97	1009	655 [28]
(La/Y)Fe ₂ O ₆	5.60	5.30	5.50	1117	—

Table-III, shows the calculated values of T_N for LaFeO_3 , YFeO_3 , and the $(\text{La}/\text{Y})\text{Fe}_2\text{O}_6$ superlattice for a fixed value of U , considering up to the third nearest neighbor exchange interactions. There are a few things to note. We found that the dominant interaction is only between nearest neighbor (nn) spins and the average nn exchange interaction (J_{avg}^{nn}) of $(\text{La}/\text{Y})\text{Fe}_2\text{O}_6$ is almost equal in value to that of LaFeO_3 . Additionally, when compared to the experimental values, our calculations generally overestimated T_N , however, the calculated ratio of $T_N^{\text{LaFeO}_3}$ and $T_N^{\text{YFeO}_3}$ is in good agreement with the ratio of the measured values. Given this fact, the T_N of $(\text{La}/\text{Y})\text{Fe}_2\text{O}_6$ superlattice is expected to be close to the magnetic transition temperature of LaFeO_3 ($\sim 740\text{K}$). For the other (La/Ln) superlattices, we have also calculated the corresponding T_N and found that for all the cases it is around the T_N of LaFeO_3 . This leads us to propose that these superlattices are expected to order magnetically above room temperature. The high magnetic transition temperature and G-type magnetic ground state of the orthoferrites is driven by the $3d^5$ electronic state of the Fe^{+3} ions, as we discuss below.

VII. ELECTRONIC STRUCTURE

FIG. 6. Calculated Density of States (DOS) for (a) LaFeO_3 , (b) YFeO_3 in $Pbnm$ and (c) $(\text{La}/\text{Y})\text{Fe}_2\text{O}_6$ in $Pb2_1m$ symmetry. For Fe^{+3} ions, we have used the on-site $d-d$ Coulomb interaction parameter $U=6.0$ eV and exchange interaction parameter $J=1.0$ eV.

As an example, let us briefly discuss the basic electronic structure of $Pbnm$ LaFeO_3 and YFeO_3 and the superlattice made out of them *i.e.* $(\text{La}/\text{Y})\text{Fe}_2\text{O}_6$ in $Pb2_1m$ symmetry. As shown in Figure 6(a) and (b), both LaFeO_3 and YFeO_3 are charge transfer insulators. The valence band is formed by majority Fe-3d states and O-2p states, while the minority Fe-3d states are completely empty and form the conduction band. Due to the

d^5 electronic configuration only antiferromagnetic super-exchange interactions between Fe^{+3} ions via single O-2p orbitals are allowed. The ferromagnetic contribution involving two perpendicular $2p$ orbitals is negligibly small as the Fe-O-Fe bond angle is close to 180° . Therefore, the G-type AFM configuration and high magnetic transition temperature are commonly observed for LnFeO_3 systems. We have found that the layered arrangement of La/Ln cations results in negligible changes to the basic electronic structure of the energy level positioning and band width (see Figure 6(c)). We therefore expect that the major component of Fe^{3+} spins of the $(\text{La}/\text{Ln})\text{Fe}_2\text{O}_6$ superlattice will order above room temperature.

TABLE III. Magnetic symmetry allowed non-zero coefficients of Linear ME tensor.

Magnetic Configurations	Magnetic Point Group	No-zero Linear ME coefficient
$A_x G_y C_z$	$m2m$	α_{xz}, α_{zx}
$F_x C_y G_z$	$m'2'm'$	α_{xy}, α_{yx}
$G_x A_y F_z$	$m'2'm$	α_{yz}, α_{zy}
$C_x F_y A_z$	$m'2m'$	$\alpha_{xx}, \alpha_{yy}, \alpha_{yy}$

Though $3d^5$ electronic configuration of Fe^{+3} ion ensures G-type AFM ordering, the direction of magnetic anisotropy may change, as has been reported for some of the LnFeO_3 compounds (such as Sm , Dy and Tm) [27, 70]. For example, SmFeO_3 exhibit magnetic transition from paramagnetic to G-type AFM order ($G_x A_y F_z$) at 670 K, followed by spin reorientation from $G_x A_y F_z$ to $F_x C_y G_z$ around 480 K. Moreover, $F_x C_y G_z$ is reported to induce ferroelectricity in the system [70]. Important point to note that, all crystal symmetry allowed magnetic configurations in space group $Pb2_1m$, admit Linear ME coupling, as tabulated in Table-III VII. Considering the spin-reorientation transitions into account, the form of the linear ME tensor and corresponding strength expected to be change (for example, from $(\alpha_{zy}, \alpha_{yz})$ to $(\alpha_{xy}, \alpha_{yx})$ for $G_x A_y F_z$ to $F_x C_y G_z$ spin-reorientation), which strengthen our investigation more, as that opens a broad compositional space for experimentalist to synthesize new linear ME materials with a possibility of operation with wide range of temperature. However, in this present communication our main focus is, how La/Ln cation radius mismatch effects the linear ME response of $(\text{La}/\text{Ln})\text{Fe}_2\text{O}_6$ superlattice and what is the microscopic origin of such response. Here, to note that for the base building block LaFeO_3 , magnetic configuration is $G_x A_y F_z$ with anisotropy axis along x , for a wide temperature range [27], thus we have discussed our results based on this particular spin structure. It will be interesting to investigate the effect of spin-reorientation on the strength of the ME coupling which can be taken in future.

VIII. CONCLUSION

We have used first-principles calculations to identify a family of $(\text{La/Ln})\text{Fe}_2\text{O}_6$ superlattices that may display a strong linear magnetoelectric effect at room temperature. Although the magnetoelectricity is ferroelectrically induced, polarization switching is not required to observe the effects studied here. An advantage of the superlattice approach is the possibility for additional functionality over that of the strain-induced approach due to the natural, non-trivial coupling of the polar, magnetic and rotation domains within the hybrid improper mechanism. Although the $(1/1)$ materials will be challenging to syn-

thesize, even as thin-films, similar results should be observed for any $(\text{La/Ln})_{m,n}$ ferrite superlattice when both n and m are odd. Finally, the microscopic origin of the linear magnetoelectric effect has been discussed based on Dzyaloshinskii-Moriya interaction at 0 K.

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