This is the accepted manuscript made available via CHORUS. The article has been published as:

Linear magnetoelectricity at room temperature in perovskite superlattices by design
Saurabh Ghosh, Hena Das, and Craig J. Fennie
Phys. Rev. B 92, 184112 — Published 30 November 2015
DOI: 10.1103/PhysRevB.92.184112
Linear magnetoelectricity at room temperature in perovskite superlattices by design

Saurabh Ghosh,* Hena Das, and Craig J. Fennie
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA
(Dated: September 14, 2015)

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., LaFeO$_3$/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$_2$O$_3$ 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-coupling 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–paralectric (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 magnetoelastic (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 magnetoelasticity 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 Ca$_3$Ti$_2$O$_7$ [23] one of the first predicted hybrid improper ferroelectrics [18]. The polarization in a related compound, the weak ferromagnet Ca$_3$Mn$_2$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 (Ca$_{9}$Sr$_{15}$Tb$_{1.15}$Tb$_{0.85}$Fe$_2$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 (La/Ln)Fe$_2$O$_6$ orthoferrite superlattices in which the La and Ln cations (Ln = Ce, Nd, Sm, Gd, Dy, Tb, 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 (LaFeO$_3$)$_n$/(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 $\sim$ 740 K for LaFeO$_3$ [27–30].

We show from first-principles calculations that the
magnitude of the linear ME tensor in these heterostructures is 2-3 times that of canonical ME materials such as Cr$_2$O$_3$ [31–36] and BiFeO$_3$. Moreover, the strength of linear ME coupling in (La/Ln)Fe$_3$O$_8$ 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 multi ferroelectric 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 $F \propto Q_pQ_K^f$ (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, $F = Q_1Q_2Q_p$. 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 $\mu$eV and 0.1meV/Å, respectively. All calculations were performed with a 500 eV energy cutoff and a Γ-centered 6 × 6 × 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

![Diagram](image-url)

**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) $Q_{\text{Rot}}$, in-phase rotation of BO$_6$ octahedra about [001] (irrep. $M_3^+)$, (b) $Q_{\text{Til}}$, tilt of BO$_6$ octahedra about [110] with A-site displacement (irrep. $R_4^+$), (c) $Q_{\text{AFE}}$ anti-ferroelectric A-site displacement (irrep. $X_2^-$). (d) The group-subgroup relation from high-symmetric $Pm\bar{3}m$ to low-symmetric $Pbnm$. (e) Two-dimensional energy surface contour of LaFeO$_3$ with respect to the primary $Q_{\text{Rot}}$ ($a^+a^-c^+$) and $Q_{\text{Til}}$ ($a^-a^-c^+$) 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
The symmetry of this Pbnm structure is established by two symmetry-lowering structural distortions of the cubic Pn3m perovskite structure: an in-phase rotation of the BO₆ octahedra about the cubic [001] axis (transforming like the irreducible representation M₁⁺) and an out-of-phase tilt of the BO₆ octahedra about the cubic [110] axis (transforming like the irreducible representation R₁⁺), 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 X₃⁺) are trilinearly coupled to the two rotation distortions in the free energy of the Pn3m structure [56], \( F = Q_{\text{AFE}} Q_{\text{Tilt}} Q_{\text{Rot}}, \) where \( Q_{\text{AFE}} \), \( Q_{\text{Tilt}} \), and \( Q_{\text{Rot}} \) 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, \( Q_{\text{AFE}} \). 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 \( Q_{\text{Tilt}} \) distortion in Pbnm and hence the sense of this particular rotation and the direction of the canting 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’)B₂O₆ double perovskites, as shown in Figure 2a. A simple picture [20] that elucidates the mechanism is the following: the two rotation distortions, \( Q_{\text{Rot}} \) and \( Q_{\text{Tilt}} \), break inversion symmetry at the A-site of the cubic Pn3m 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, \( Q_{\text{Tilt}} \), will switch the sense of one of the rotations. If it is \( Q_{\text{Tilt}} \) that switches, then the direction of the canted mo-

---

**FIG. 2.** Structural and ferroelectric properties of (La/Ln)Fe₂O₆ superlattices. (a) (La/Y)Fe₂O₆ superlattice in high-symmetry P4/mmm structure, (b) lowest energy Pb₂m structure with rotation and tilt of FeO₆ octahedra, (c) Group-subgroup relation from P4/mmm to other lower energy structures, (d) Two dimensional energy surface contours for (La/Y)Fe₂O₆ superlattice with respect to the primary \( Q_{\text{Rot}} \) \((a^0b^0c^+\) irrep. \( M_{1}^{+} \)) and \( Q_{\text{Tilt}} \) \((a^-a^-c^+\) irrep. \( M_{5}^{-}\)) distortions. In contour, Black dots represents the the possible minimum structures, each corresponding to different sense of FeO₆ octahedra rotations, Green triangles (down) indicate to the P4/mmb structure where \( Q_{\text{Tilt}} \) is zero and Orange triangles (up) indicate to the Pbnm structure where \( Q_{\text{Tilt}} \) is zero. Variation of (e) Polarization P and (f) Switching barriers along Rotation (\( \Delta E_{\text{Rot}} \)) with respect to \((1-\tau_{\text{avg}})^2\) and \((1-\tau_{\text{avg}})^2\), 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 Pb2m 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′′ 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 μC/cm² for Ln=Ce to 11.6 μC/cm² for Ln=Lu. In other words, as the average tolerance factor τavg decreases, the polarization increases (note, τABO3 = (r A + r O)/√(r B + r O) and τavg = (τABO3 + τA′B03)/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, 0.06-0.07μB/f.u, as τavg 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 QRot or QTilt 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 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 QRot, ΔE ROT = EPb2m - EPbm, is about three times smaller than the barrier height along QTilt, ΔE Tilt = EPb2m - EP4/mbm for all the compounds considered. From this we conclude that it is more likely that QRot would switch when the polarization switches. Since M z switches only if QTilt 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, ΔE P ≡ ΔE 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′′′d′′′ 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),

$$\Delta M_i = \Sigma_{\alpha} E_j$$

$$\Delta P_i = \Sigma_{\alpha} H_j,$$

where $\Delta M_i$ ($\Delta P_i$) is the induced magnetization (polarization) along the ith direction due to an electric (magnetic) field applied along the jth direction. The magnetic point group of all (La/Ln)Fe2O6 compounds is m′′′m′, therefore, the only non-zero components of the linear ME tensor are,

$$\alpha = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \alpha_{yz} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

where $\alpha_{yz} \neq \alpha_{xy}$ (the ME processes associated with these components are schematically shown in Figure 3(a)). The design strategy guarantees the existence of $\alpha$, but what is its magnitude? Here, we used the method described in Ref. [31] to calculate the lattice contribution to $\alpha$ (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 Pb2m crystal (U) under an applied electric-field($\vec{E}$) is given by,

$$U(\vec{q}_n, \vec{E}) = U_0 + \frac{1}{2} \sum C_n q_n^2 - \sum q_n \vec{p}_n \cdot \vec{E}$$

where, $q_n$, C n, and $\vec{p}_n$ are the amplitude, force constant, and dielectric polariy of the n-th infrared (IR) active force constant eigenvector, $\vec{q}_n$, respectively. The dielectric polarity $\vec{p}_n$ of the n-th-IR active mode can be calculated as, $\vec{p}_n = \partial F_n / \partial q_n$, where F n is the polarization (note that
Subsequently, the linear ME tensor, \( \vec{u} \), displacements, can be calculated by freezing in the total induced atomic polarization along the \( y \), \( z \), and \( x \) directions, respectively. By symmetry, the \( \Gamma_4 \) modes do not mediate a Linear ME effect. This is why \( \alpha_{ij} \) 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 \( E \dot{y} \), symmetry dictates that only the \( \Gamma_1 \) modes respond, i.e., \( \vec{p}_n \cdot \vec{E} = \vec{p}_n \cdot \dot{y}E \neq 0 \) for \( n \in \Gamma_1 \). The induced atomic displacements

\[
\vec{u}_{\Gamma_1} = \sum_{n \in \Gamma_1} \frac{1}{C_n} p_n E_y q_n, \tag{6}
\]

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 \( \alpha_{zy} \). We find that the magnitude of \( \alpha_{zy} \) is 3.54x10\(^{-4}\) g.u. (= 9.41x10\(^{-7}\) C/T m\(^2\)), which is 2-3 times larger than the transverse linear ME response of the prototype ME compound Cr\(_2\)O\(_3\) [31, 36] at 0 K.

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

\[
\vec{u}_{\Gamma_3} = \sum_{n \in \Gamma_3} \frac{1}{C_n} p_n E_z q_n, \tag{7}
\]

can be calculated. Here we find that the corresponding magnitude of linear ME response (see Figure 3(b)), measured by the component \( \alpha_{yz} \) is equal to 0.72x10\(^{-4}\) g.u. (= 1.91x10\(^{-7}\) C/T m\(^2\)), much weaker than \( \alpha_{zy} \).

It is important to note that \( \alpha_{zy} \) component is the same order of magnitude as that of the most studied multiferroic BiFeO\(_3\) [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 \( \alpha_{zy} \) varies with the composition of the ferrite superlattices, which we discuss next.

### A. (La/Y) Fe\(_2\)O\(_3\): a prototype example

As an example let us first discuss the calculation of the linear ME response for (La/Y)Fe\(_2\)O\(_3\) (\( P_y^* = 9.0\) µC/cm\(^2\) and \( P_x^* = P_z^* = 0 \)); \( M_y^* = 0.13\) µB and \( M_z = M_y = 0\) ). It is useful to keep in mind that in \( P0\) the IR modes transform as irreducible representations \( \Gamma_1 \), \( \Gamma_3 \), or \( \Gamma_4 \), each leading to a polarization along the \( y \), \( z \), and \( x \) directions, respectively. With the application of an electric-field along the \( y \) direction \( E \dot{y} \), symmetry dictates that only the \( \Gamma_1 \) modes respond, i.e., \( \vec{p}_n \cdot \vec{E} = \vec{p}_n \cdot \dot{y}E \neq 0 \) for \( n \in \Gamma_1 \). The induced atomic displacements

\[
\vec{u}_{\Gamma_1} = \sum_{n \in \Gamma_1} \frac{1}{C_n} p_n E_y q_n, \tag{6}
\]

can be calculated. Here we find that the corresponding magnitude of linear ME response (see Figure 3(b)), measured by the component \( \alpha_{xz} \) is equal to 0.72x10\(^{-4}\) g.u. (= 1.91x10\(^{-7}\) C/T m\(^2\)), much weaker than \( \alpha_{zy} \).

It is important to note that \( \alpha_{zy} \) component is the same order of magnitude as that of the most studied multiferroic BiFeO\(_3\) [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 \( \alpha_{zy} \) varies with the composition of the ferrite superlattices, which we discuss next.

### B. (La/Ln)Fe\(_2\)O\(_3\) series

In Figure 4 we show the composition dependence of \( \alpha_{zy} \) obtained using the first-principles method described above. Because \( \alpha_{yz} \) is order of magnitude weaker than
In (La/Y)Fe$_2$O$_6$, we calculate the $\alpha_{zy}$ component only for other compositions. Interestingly, $\alpha_{zy}$ increases almost linearly with the increase of $(1 - \tau_{\text{avg}})$, 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 ($Q_{\text{Rot}}$) 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 $\alpha_{yz}$ and $\alpha_{zy}$, which is exactly the same as in the ground state $Pb2_1m$ structure. On the other hand, $Q_{\text{Tilt}}$ induces wFM, but forbids linear ME coupling. Therefore, while $Q_{\text{Tilt}}$ induces wFM, linear ME coupling is driven by $Q_{\text{Rot}}$ (illustrated in 2c); we establish this by considering a phenomenological model below.

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

$$M_z \sim \gamma_1 L_0 + \frac{1}{2} \gamma_2 L_0 Q_{\text{Rot}}^2$$

where, $L_0$ is the antiferromagnetic order parameter which is even under space inversion, and $\gamma_1$ denotes the magnitude of the magnetization in the $Pbmmm$ structure and varies with odd powers of $Q_{\text{Tilt}}$. Therefore the change in magnetization $M_z$ induced by the applied electric-field along the $y$ direction is given by,

$$\Delta M_z \sim \gamma_2 L_0 Q_{\text{Rot}} \Delta Q_{\text{Rot}}$$

It is important to note that we consider change of $\gamma_1(Q_{\text{Tilt}})$ 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,

$$F = \frac{1}{2} a_R Q_{\text{Rot}}^2 + \frac{1}{2} a_T Q_{\text{Tilt}}^2 + \frac{1}{2} a_P P_y^2 + \xi Q_{\text{Rot}} Q_{\text{Tilt}} P_y$$

$$+ \ldots - E_y P_y$$

we find that,

$$\Delta Q_{\text{Rot}} \sim -\frac{\xi}{a_P a_R} \Delta E_y$$

Which gives rise to,

$$\alpha_{zy} \sim -\frac{\gamma_2 \xi}{a_P a_R} L_0 Q_{\text{Rot}}$$

Note that this expression is similar to that derived for the Ruddlesden-Popper system Ca$_3$B$_2$O$_7$, where B= Ti and Mn [18].

\[\text{FIG. 4. Variation of magnitude of the linear ME coefficient, }\alpha_{zy} \text{ (in g.u.) as a function of } (1 - \tau_{\text{avg}}) \text{ for (La/Ln)}\text{Fe}_2\text{O}_6 \text{ superlattices, where Ln= Ce, Nd, Sm, Gd, Dy, Tm, Lu and Y. We follow the method described in section-IVA to calculate the value of the off-diagonal component } \alpha_{zy}.\]

In (La/Ln)Fe$_2$O$_6$ series we found that $Q_{\text{Rot}}$ increases linearly with $(1 - \tau_{\text{avg}})$. Therefore,

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

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

Finally, as $P_y \propto (1 - \tau_{\text{avg}})$, in other words, the strength of linear ME coupling in (La/Ln)Fe$_2$O$_6$ superlattices grows with the increase of the induced spontaneous polarization. Within the (La/Ln)Fe$_2$O$_6$ superlattices, the highest predicted magnitude of $\alpha_{zy}$ is 4.25 $\times 10^{-4}$ g.u. for (La/Ln)Fe$_2$O$_6$. This is larger than the linear ME coefficients reported for the most studied magnetoelectrics, Cr$_2$O$_3$ and BiFeO$_3$ [31, 65] at 0 K.

C. \((\text{La/Ln})_{m,n}\text{Fe}_{(m+n)}\text{O}_{3(m+n)}\) 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 \(\langle 2'/m' \rangle\) 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,

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

where, $P_y(1, 1)$ denotes the induced polarization of the 1/1 superlattice. The calculated polarizations of the (La/Y)$_{2,2}$Fe$_4$O$_{12}$, (La/Y)$_{3,3}$Fe$_6$O$_{18}$, \(\text{(La/Y)}_{1,3}\text{Fe}_6\text{O}_{18}\) and (La/Y)$_{1,5}$Fe$_8$O$_{18}$ 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 $P_y(1,1) = 9.0 \mu C/cm^2$. 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 $\alpha_{zy}$ for the (La/Y)$_{3.1}$Fe$_2$O$_{12}$ superlattice is $2.01 \times 10^{-4}$ g.u., which is close to the value, $1.77 \times 10^{-4}$ g.u., estimated from Equation 15 (where we used $\alpha_{zy}(1, 1) = 3.54 \times 10^{-4}$ g.u., computed using first-principles method). This shows that the magnitude of $\alpha_{zy}$ decreases with increasing layer thickness. However, it is important to note that, for the (La/Y)$_{5.5}$ superlattice (as experimentally grown [25]) the expected magnitude of $\alpha_{zy}$ is $\sim 0.71 \times 10^{-4}$ g.u., close to that reported for Cr$_2$O$_3$[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 $P4/mmm$ ($a^d a^e c^0$) and $P4/mmm$ ($a^d a^e c^+)$ phases forbid the anti-symmetric 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 $P\bar{6}21m$ 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)).

![Figure 5(a)](image)

(a) Six $nn$ DM interactions acting on Fe$_1$ in $P\bar{6}21m$ structure are shown. Four inequivalent DM vectors acting via $Fe_1 - O_{ap} - Fe_4$, $Fe_1 - O_{ap}' - Fe_4$, $Fe_1 - O_p - Fe_2$ and $Fe_1 - O_p' - Fe_2$ 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 $\vec{D}_{12}' (0, D_y^{ap'}, D_z^{ap'})$, respectively. (b) Response of the in-plane DM interactions under the application of electric-field along $y$ axis. $E_y$ changes in-plane $D_y$ interactions, such that $\Delta D_y = \Delta D_y^p$ which lead to linear change in $m_y(-\hat{z})$. 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 $(0, SD^o_x, -SD^o_y)$, $(0, SD^o_x, SD^o_y)$, $(0, -SD^o_x, S\bar{D}^o_y)$, $(0, -SD^o_x, SD^o_y)$, respectively. Where $SD^o_x$ and $SD^o_y$ 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 $\vec{D}_y^o$ 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, $\vec{D}_z^o$, adopt a $\Lambda$-type AFM order, so $M_y = 0$. Considering that the magnitude of the canting spin components along the $y$ and $z$ axes to be same (as we explicitly have observed in first-principles results) we find,
\[ m_y = m_z \sim \frac{1}{\sqrt{2}} m_s \sin \Theta \]  

and,

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

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. \( J_{nn} \) and \( J_{ap} \) 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, as tabulated in Table-I for (La/Ce)Fe

\[ \text{TABLE I. Magnitude of Dzyaloshinskii-Moriya (DM) vectors (} \hat{D}_{14}, \hat{D}_{14}, \hat{D}_{12} \text{ and } \hat{D}_{12}, \text{ corresponding symmetric interaction (Heisenberg type, } J_{nn} \text{) and weak magnetization per Fe (} m_z \text{)} \text{ have been tabulated for (La/Fe)}_2 \text{O}_6, \text{ we estimate } m_z = 0.0365 \mu_B/\text{Fe}. \text{ This value is in good agreement with the value calculated in the Pb}_2\text{m structure, } m_z = 0.0295 \mu_B/\text{Fe}. \]  

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 outlined in section IV. We observe that changes in \( J_{nn} \) and \( J_{ap} \) 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 Fe spins connected via \( O_p \) (0, \( D^0_y - \Delta D^0_y, D^0 - \Delta D^0 \)), and increases it for the Fe spins connected via \( O'_p \) (0, \( D^0_y + \Delta D^0_y, D^0 + \Delta D^0 \)). However, whereas \( \Delta D^0_y = \Delta D^0 \), we observe \( \Delta D^0 > \Delta D^0 \), which induces a net change in canted moment \( \Delta m_z \) along \( (-\hat{z}) \), and in turn the linear magnetoelectric coupling \( \alpha_{zy} \). The net change in \( m_z \) (per Fe) due to application of an electric field \( (E_{y\hat{y}}) \) is given by,

\[ \Delta m_z \propto \sin(\Delta \Theta/2) m_x \]  

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 know 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.

\[ \begin{array}{cccccc}
\text{Interactions} & D_x & D_y & D_z & J_{nn} & m_z \text{ (} \mu_B/\text{Fe}\text{) } \\
(\mu\text{eV}) & (\mu\text{eV}) & (\mu\text{eV}) & (\text{meV}) & \text{Computed} & \text{Eqn. 17} \\
1-O_p' & -2 & 0 & 115 & -101 & -6.36 \\
1-O_p' & -2 & 0 & 115 & -123 & -6.25 \\
1-O_{ap} & -4 & -28 & 89 & 0 & -6.63 \\
1-O_{ap} & -4 & -28 & 90 & 0 & -5.98 \\
\end{array} \]

\[ \begin{array}{cccc}
\text{System} & J_{nn} & J_{ap} & J_{ap} \text{ (} \mu\text{eV}\text{) } \\
& & & \text{Computed} \text{ [Experiment]} \\
\text{LaFeO}_3 & 5.81 & 5.20 & 5.61 & 1139 & 740 \text{ [28]} \\
\text{YFeO}_3 & 5.20 & 4.51 & 4.97 & 1009 & 655 \text{ [28]} \\
(La/Y)\text{Fe}_2\text{O}_6 & 5.60 & 5.30 & 5.50 & 1117 & - \\
\end{array} \]
Table III, shows the calculated values of $T_N$ for LaFeO$_3$, YFeO$_3$, and the (La/Y)Fe$_2$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 ($J_{nn}^{\alpha \alpha}$) of (La/Y)Fe$_2$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 $T_N^{LaFeO_3}$ and $T_N^{YFeO_3}$ is in good agreement with the ratio of the measured values. Given this fact, the $T_N$ of (La/Y)Fe$_2$O$_6$ superlattice is expected to be close to the magnetic transition temperature of LaFeO$_3$ ($\sim 740K$). 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 3$d^5$ electronic state of the Fe$^{+3}$ ions, as we discuss below.

VII. ELECTRONIC STRUCTURE

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., (La/Y)Fe$_2$O$_6$ in $P6_2m$ 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., (La/Y)Fe$_2$O$_6$ in $P6_2m$ 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 (La/Ln)Fe$_2$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 |
|-------------------------|----------------------|------------------------------|
| $A_xG_yC_z$             | m2m                 | $\alpha_{xz}, \alpha_{yz}$   |
| $F_xC_yG_z$             | m2$'$m$'$            | $\alpha_{xy}, \alpha_{yz}$   |
| $G_zA_yF_x$             | m2$'$m$'$            | $\alpha_{xy}$               |
| $C_yF_yA_z$             | m2$'$m$'$            | $\alpha_{xz}, \alpha_{yz}, \alpha_{yy}$ |

Though 3$d^5$ 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 ($G_zA_yF_z$) at 670 K, followed by spin reorientation from $G_zA_yF_z$ to $F_zC_yG_z$ around 480 K. Moreover, $F_zC_yG_z$ is reported to induce ferroelectricity in to the system [70]. Important point to note that, all crystal symmetry allowed magnetic configurations in space group $P6_2m$, admit Linear ME coupling, as tabulated in Table III. Considering the spin-reorientation transitions into account, the form of the linear ME tensor and corresponding strength expected to be change (for example, from ($\alpha_{xy}, \alpha_{yz}$) to ($\alpha_{xy}, \alpha_{yz}$) for $G_zA_yF_z$ to $F_zC_yG_z$ spin-reorientation), which strengthen our investigation more, as that opens a broad compositional space for experimentalist to synthesis new linear ME materials with a possibility of operation with wide rage of temperature. However, in this present communication our main focus is, how La/Ln cation radius mismatch effects the linear ME response of (La/Ln)Fe$_2$O$_6$ superlattice and what it the microscopic origin of such response. Here, to note that for the base building block LaFeO$_3$, magnetic configuration is $G_zA_yF_z$ 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 (La/Ln)Fe$_2$O$_3$ 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 synthesize, even as thin-films, similar results should be observed for any (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.

IX. ACKNOWLEDGEMENT

The authors acknowledge useful discussions with Nicole Benedek, James Rondinelli, Philippe Ghosez, and Darrell Schlom. S.G. and C.J.F. are supported by the Army Research office under grant No. W911NF-10-1-0345, and H.D. is supported by the NSF-MRSEC Center for Nanoscale Science at Penn State, DMR-0820404.

[1] Keiitsiro Aizu, “Possible species of ferromagnetic, ferroelectric, and ferroelastic crystals,” Phys. Rev. B 2, 754–772 (1970).
[2] W Eerenstein, N. D. Mathur, and J. F. Scott, “Multiferroic and magnetoelectric materials,” Nature (London) 442, 759 (2006).
[3] Nicola A. Spaldin and Manfred Fiebig, “The renaissance of magnetoelectric multiferroics,” Science 309, 391–392 (2005).
[4] H. W. Jang, S. H. Baek, D. Ortzi, C. M. Folkman, R. R. Das, Y. H. Chu, P. Shafer, J. X. Zhang, S. Choudhury, V. Vaithyanathan, Y. B. Chen, D. A. Felker, M. D. Bielinski, M. S. Rzchowski, X. Q. Pan, D. G. Schom, L. Q. Chen, R. Ramesh, and C. B. Eom, “Strain-induced polarization rotation in epitaxial (001) BiFeO$_3$ thin films,” Phys. Rev. Lett. 101, 107602 (2008).
[5] James F. Scott, “Room-temperature multiferroic magnetoelectrics,” NPG Asia Mater 5, e72 (2013).
[6] Manuel Bibes and Agnes Barthelemy, “Multiferroics: Towards a magnetoelectric memory,” Nature Mat 7, 425 (2008).
[7] Sadanichi Maekawa, “Rashba spin-orbit anisotropy and the electric field control of magnetism,” Sci. Rep. 4, 4105 (2014).
[8] Martin Weisheit, Sebastian Fhler, Alaint Marty, Yves Souche, Christiane Poisignou, and Dominique Givord, “Electric field-induced modification of magnetism in thin-film ferromagnets,” Science 315, 349–351 (2007), http://www.sciencemag.org/content/315/5810/349.full.pdf.
[9] S. S. P. Parkin, K. P. Roche, M. G. Samant, P. M. Rice, R. B. Beyers, R. E. Scheuerlein, E. J. O’Sullivan, S. L. Brown, J. Buchigiano, D. W. Abraham, Yu Lu, M. Rooks, P. L. Troulloud, R. A. Wanner, and W. J. Gallagher, “Exchange-biased magnetic tunnel junctions and application to nonvolatile magnetic random access memory (invited),” Journal of Applied Physics 85 (1999).
[10] Martin Gajek, Manuel Bibes, Stephane Fusil, Karim Bouzehouane, Josep Fontcuberta, Agnes Barthelemy, and Albert Fert, “Tunnel junctions with multiferroic barriers,” Nat Mater 6, 296–302 (2007).
[11] 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, “Electric-field-induced magnetization reversal in a ferromagnet-multiferroic heterostructure,” Phys. Rev. Lett. 107, 217202 (2011).
[12] Turan Birol, Nicole A. Benedek, Hena Das, Aleksander L. Wysocki, Andrew T. Mulder, Brian M. Abbott, Eva H. Smith, Saurabh Ghosh, and Craig J. Fennie, “The magnetoelectric effect in transition metal oxides: Insights and the rational design of new materials from first principles,” Current Opinion in Solid State and Materials Science 16, 227 – 242 (2012), multiferroics.
[13] Craig J. Fennie, “Ferroelectrically induced weak ferromagnetism by design,” Phys. Rev. Lett. 100, 167203 (2008).
[14] Tamas Varga, Timothy C. Droubay, Mark E. Bowden, Ponnusamy Nachimuthu, Vaithiyalingam Shuththanadan, Trudy B. Bolin, William A. Shelton, and Scott A. Chambers, “Epitaxial growth of NiTiO$_3$ with a distorted ilmenite structure,” Thin Solid Films 520, 5534 – 5541 (2012).
[15] Angel M. Arévalo-López and J. Paul Attfield, “Weak ferromagnetism and domain effects in multiferroic LiNiO$_2$-type MnTiO$_3$,” Phys. Rev. B 88, 104416 (2013).
[16] Eric Bousquet and Nicola Spaldin, “Induced magnetoelectric response in Pnma perovskites,” Phys. Rev. Lett. 107, 197603 (2011).
[17] Eric Bousquet, Matthew Dawber, Nicolas Stucki, Celine Lichtensteifer, Patrick Hermet, Stefano Gariglio, Jean-Marc Triscone, and Philippe Ghosez, “Improper ferroelectricity in perovskite oxide artificial superlattices,” Nature 452, 732 (2008).
[18] N. A. Benedek and C. J. Fennie, “Hybrid improper ferroelectricity: A mechanism for strong polarization-magnetization coupling,” Phys. Rev. Lett. 106, 107204 (2011).
[19] James M. Rondinelli and Craig J. Fennie, “Octahedral rotation-induced ferroelectricity in cation ordered perovskites,” Advanced Materials 24, 1961–1968 (2012).
[20] Nicole A. Benedek, Andrew T. Mulder, and Craig J. Fennie, “Polar octahedral rotations: A path to new multifunctional materials,” Journal of Solid State Chemistry 195, 11–20 (2012).
[21] Andrew T. Mulder, Nicole A. Benedek, James M. Rondinelli, and Craig J. Fennie, “Turning abo3 antifer-
roelectrics into ferroelectrics: Design rules for practical rotation-driven ferroelectricity in double perovskites and a $\beta$-2O7 ruddlesden-popper compounds," Advanced Functional Materials 23, 4810–4820 (2013).

[22] Joshua Young and James M. Rondinelli, “Atomic scale design of polar perovskite oxides without second-order jahn-teller ions,” Chemistry of Materials 25, 4545–4550 (2013), http://dx.doi.org/10.1021/cm402550q.

[23] Yoon Seok Oh, Xuan Luo, Fei-Ting Huang, Yazhong Wang, and Sang-Wook Cheong, “Experimental demonstration of hybrid improper ferroelectricity and the presence of abundant charged walls in (La,Sr)$_3$Ti$_2$O$_7$ crystals,” Nat Mater 14, 407–413 (2015).

[24] Michael J. Pitcher, Pranab Mandal, Matthew S. Dyer, Jonathan Alaria, Pavel Borisov, Hongjun Niu, John B. Claridge, and Matthew J. Rosseinsky, “Tilt engineering of spontaneous polarization and magnetization above 300 k in a bulk layered perovskite,” Science 347, 420–424 (2015), http://www.sciencemag.org/content/347/6220/420.full.pdf.

[25] J. Alaria, P. Borisov, M. S. Dyer, T. D. Manning, S. Lepidge, and M. J. Rosseinsky, “Engineered spatial inversion symmetry breaking in an oxide heterostructure built from isosymmetric room-temperature orthoferrites,” Acta Crystallographica Section B 53, 32–43 (1997).

[26] Zeila Zanolli, Jorge Iñiguez, and M. J. Rosseinsky, “Tilt engineering of spontaneous polarization and magnetization above 300 k in a bulk layered perovskite,” Science 347, 407–413 (2015).

[27] Ayato Iyama and Tsuyoshi Kimura, “Magnetoelectric transition in YMnO$_3$ from first principles,” Phys. Rev. B 72, 100103 (2005).

[28] Joshua Young and James M. Rondinelli, “Atomic scale design of polar perovskite oxides without second-order jahn-teller ions,” Chemistry of Materials 25, 4545–4550 (2013), http://dx.doi.org/10.1021/cm402550q.

[29] Yoon Seok Oh, Xuan Luo, Fei-Ting Huang, Yazhong Wang, and Sang-Wook Cheong, “Experimental demonstration of hybrid improper ferroelectricity and the presence of abundant charged walls in (La,Sr)$_3$Ti$_2$O$_7$ crystals,” Nat Mater 14, 407–413 (2015).

[30] Kris T. Delaney, Maxim Mostovoy, and Nicola A. Spaldin, “Superexchange-driven magnetoelectricity in magnetic vortices,” Phys. Rev. Lett. 102, 157203 (2009).

[31] Sai Mu, A. L. Wysocki, and K. D. Belashchenko, “First-principles microscopic model of exchange-driven magnetoelectric response with application to $\delta$2O3,” Phys. Rev. B 89, 174413 (2014).

[32] Graham King and Patrick M. Woodward, “Cation or-
http://pubs.acs.org/doi/pdf/10.1021/jp402046t.

[56] Safari Amisi, Eric Bousquet, Karume Katcho, and Philippe Ghosez, “First-principles study of structural and vibrational properties of srzro3,” Phys. Rev. B 85, 064112 (2012).

[57] M. Robbins, G.K. Wertheim, A. Menth, and R.C. Sherwood, “Preparation and properties of polycrystalline cerium orthoferrite (cefeo3),” Journal of Physics and Chemistry of Solids 30, 1823 – 1825 (1969).

[58] E. N. Maslen, V. A. Streletsov, and N. Ishizawa, “A synchrotron X-ray study of the electron density in SmFeO3,” Acta Crystallographica Section B 52, 406–413 (1996).

[59] Mingyu Shang, Chenyang Zhang, Tingsong Zhang, Lin Yuan, Lei Ge, Hongming Yuan, and Shouhua Feng, “The multiferroic perovskite yfeo3,” Applied Physics Letters 102, 062903 (2013).

[60] D. Treves, “Studies on orthoferrites at the weizmann institute of science,” Journal of Applied Physics 36 (1965).

[61] L Bellaiche, Zhigang Gui, and Igor A Kornev, “A simple law governing coupled magnetic orders in perovskites,” Journal of Physics: Condensed Matter 24, 312201 (2012).

[62] Hong Jian Zhao, Wei Ren, Yurong Yang, Xiang Ming Chen, and L Bellaiche, “Effect of chemical and hydrostatic pressures on structural and magnetic properties of rare-earth orthoferrites: a first-principles study,” Journal of Physics: Condensed Matter 25, 466002 (2013).

[63] Hong Jian Zhao, Wei Ren, Jorge Íñiguez, Yurong Yang, Xiang Ming Chen, and L. Bellaiche, “Near-room-temperature multiferroic materials with tunable ferromagnetic and electrical properties,” Nat Commun 5, 4021 (2014).

[64] Hena Das, Yanan Wysocki, Aleksander L and Geng, Weida Wu, and Craig J. Fennie, “Bulk magnetoelectricity in the hexagonal manganites and ferrites,” Nat Commun 5, 2998 (2013).

[65] D. Albrecht, S. Lisenkov, Wei Ren, D. Rahmedov, Igor A. Kornev, and L. Bellaiche, “Ferromagnetism in multiferroic bifeo3 films: A first-principles-based study,” Phys. Rev. B 81, 140401 (2010).

[66] J.-P. Rivera and H. Schmid, “On the birefringence of magnetoelectric bifeo3,” Ferroelectrics 204, 23–33 (1997).

[67] E. F. Bertaut, Magnetism (Academic Press Inc) 3, p.146 (1963).

[68] C. Weingart, N. Spaldin, and E. Bousquet, “Non-collinear magnetism and single-ion anisotropy in multiferroic perovskites,” Phys. Rev. B 86, 094413 (2012), arXiv:1206.0718 [cond-mat.mtrl-sci].

[69] H. Xiang, E. Kan, Su-Huai Wei, M.-H. Whangbo, and X. Gong, “Predicting the spin-lattice order of frustrated systems from first principles,” Phys. Rev. B 84, 224429 (2011).

[70] Jung-Hoon Lee, Young Kyu Jeong, Jung Hwan Park, Min-Ae Oak, Hyun Myung Jang, Jong Yeog Son, and James F. Scott, “Spin-canting-induced improper ferroelectricity and spontaneous magnetization reversal in SmFeO3,” Phys. Rev. Lett. 107, 117201 (2011).