Ferroelectrically Induced Weak Ferromagnetism by Design

Craig J. Fennie

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA
(Received 19 December 2007; published 22 April 2008)

We present a strategy to design structures for which a polar lattice distortion induces weak ferromagnetism. We identify a large class of multiferroic oxides as potential realizations and use density-functional theory to screen several promising candidates. By elucidating the interplay between the polarization and the Dzyaloshinskii-Moriya vector, we show how the direction of the magnetization can be switched between 180° symmetry equivalent states with an applied electric field.

The rational design of new materials with emergent properties is a challenge today in materials physics. It begins with understanding a mechanism to control the interplay between diverse microscopic degrees of freedom in order to create targeted macroscopic phenomena and ends with the discovery or design of new material realizations. When combined with first-principles density-functional theory, this approach provides an efficient strategy to survey the vast space of possible materials to target for synthesis. For example, new multiferroics in which magnetism coexists with ferroelectricity have been discovered where magnetic order itself induces ferroelectricity. Through this specific spin-lattice interaction, it is readily possible to control the direction of the electrical polarization with a magnetic-field [1,2]. An equally fundamental but technologically more relevant problem that has received far less study is the electric-field control of magnetism [3–6]. In particular, the electric-field switching of a magnetization between 180° symmetry equivalent states has yet to be demonstrated. The most promising direction to achieve this in single-phase materials involves a ferroelectric distortion inducing weak-ferromagnetism [7–10]. Discovering a prototypical structure for which this approach might be realized, however, has remained elusive.

Weak ferromagnetism (wFM) is the phenomenon whereby the predominantly collinear spins of an antiferromagnet cant in such a way as to produce a residual magnetization (**M**). It can arise as a spin-orbit correction to Anderson's superexchange, i.e., the Dzyaloshinskii-Moriya (DM) interaction [11,12], $E_{DM} = D_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j$ where D is the Dzyaloshinskii vector. A ferroelectric (FE) distortion can induce wFM when the phenomenological invariant $E_{PLM} \sim \mathbf{P} \cdot (\mathbf{L} \times \mathbf{M})$ is allowed in the energy of the antiferromagnetic-paraelectric (AFM-PE) phase, where **P** and **L** are the polarization and AFM vector, respectively. In such AFM-PE's, at the FE transition, i.e., once **P** becomes finite, the system can lower its energy via E_{PLM} by simultaneously generating a finite **M**. Note that for fixed **L** the sign of **M** is correlated with the sign of **P**. The magnetization can therefore be switched by reversing the direction of the polarization with an applied electric field. It is important to realize that a FE can still exhibit

wFM without the FE distortion *per se* causing the wFM, i.e., without E_{PLM} in the corresponding PE phase. For example, although $BiFeO_3$ (the most widely studied multiferroic) can display wFM, such an invariant does not exist as previously shown from explicit first-principles calculations [13] and as we argue below from symmetry. The challenge then is understanding how to start with the microscopic properties of E_{DM} and build a material capturing the macroscopic physics of E_{PLM}. In this Letter we present for the first time design criteria that facilitate this process. In general the criteria target a structure for which wFM is symmetry forbidden in the PE phase but symmetry allowed in the FE phase [4,13]. Below we use this to identify a class of multiferroic oxides as potential realizations and use density-functional theory to screen several promising candidates. One complication arises in magnetic systems with broken spatial inversion such as a FE; a symmetry allowed interaction [14] may in some cases generate a long-wavelength magnetic spiral canceling the net **M**, e.g., as in (bulk) $BiFeO_3$. Here we consider the situation where this inhomogeneous state is suppressed, e.g., when single-ion anisotropy is large [15].

Our strategy is to formulate the problem in terms of a structural-chemical criterion and a magnetic criterion. A synopsis of the structural-chemical criterion is as follows: start with a PE structure, decorate the lattice with spins such that the midpoint between two spins coincides with a site having inversion (I) symmetry (so that $D = 0$ by symmetry, i.e., Moriya's first rule [12]), place a FE-active ion at an I-site. Compounds which satisfy this criterion are quite intriguing because if there are no other symmetry elements that would forbid wFM—the magnetic criterion—all that is required to induce a nonzero D and wFM is to remove the I center by controlling the off centering of the FE-active ion either by temperature, pressure, or electric-field. The magnetic criterion is primarily a question of how the spins order and of their direction with respect to the crystallographic axes. Notice our microscopic based criteria implies that **L** is odd under I, which is precisely what is required considering macroscopic phenomenology, i.e., E_{PLM}. These criteria facilitate evaluating known compounds or when combined with crystal chem-

istry principles designing new prototypes. For example, using PE BiFeO$_3$ as a starting point, we apply them to design a novel structure.

In PE BiFeO$_3$, crystallographic space group $R\bar{3}c$ (a summary of the relevant symmetry properties of $R\bar{3}c$ is shown in Fig. 1(a)], the Bi ions occupy the A site, Wyckoff position 2a, with local site symmetry 32, while the magnetic Fe-ion occupies a site with inversion symmetry, the B-site, position 2b, site symmetry $\bar{3}$. The Fe-spins order ferromagnetically within antiferromagnetically coupled (111) planes with the magnetic easy axis perpendicular to [111]. Although PE BiFeO$_3$ satisfies the magnetic criterion, I transforms each Fe sublattice onto itself, $I\mathbf{L} = I(S_1 - S_2) = \mathbf{L}$, as can be seen in Fig. 1(b). In this case of B-site magnetism the structural-chemical criterion is not met and the invariant E_{PLM} is forbidden by symmetry (the PE point group is $2'/m'$ or $2/m$ for which wFM is allowed). In contrast, consider the case where the magnetic ion is on the A site and similarly ordered so that the magnetic criterion is still satisfied, Fig. 1(c). Now, in this case of A-site magnetism, $I\mathbf{L} = -\mathbf{L}$. Placing a FE-active ion such as Ti^{4+} on the B site would then satisfy the structural-chemical criterion. The PE magnetic point group is now $2/m'$ ($2'/m$) in which wFM is forbidden and *by design* a FE distortion, via E_{PLM}, would lower the symmetry to m' (m) thereby inducing wFM. The question remaining is whether compounds in our rationalized structure can be synthesized? As we discuss next, several already exist.

The mineral Ilmenite FeTiO$_3$ is one member of a family of compounds [16] that include the titanantes A^{2+}Ti^{4+}O$_3$ with $A = $ Mn-Ni. They are all AFM insulators with ordering temperatures $T_N \sim 40$ K–100 K. At atmospheric pres-

sure they form in the Ilmenite structure, space group $R\bar{3}$. Ilmenite can be thought of as an ordered corundum structure. At high-pressure both MnTiO$_3$ and FeTiO$_3$ have been found to form a quenchable metastable LiNbO$_3$ LBO-phase, space group $R3c$ [17,18]. Note this LBO-phase is structurally isomorphic to BiFeO$_3$ except the magnetic and FE atom positions are reversed: for example, MnTiO$_3 \rightarrow$ BiFeO$_3$ implies Mn $\rightarrow$ Bi and Ti $\rightarrow$ Fe. This is precisely the structural-chemical criterion outlined above. The remaining question is to identify the magnetic ground state in the FE phase to determine if the magnetic criterion is satisfied. In the remainder of this Letter we present a first-principles study of the FE and magnetic properties of the LBO-phase of MnTiO$_3$, FeTiO$_3$, and NiTiO$_3$. We demonstrate that these are realizations of the design criteria and provide a novel simple picture of how the interplay of D and **P** leads to electric-field control of wFM.

Method.—We performed density-functional calculations using PAW potentials within LSDA + U [19] as implemented in VASP [20,21]. The wave functions were expanded in plane waves up to a cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a $6 \times 6 \times 6$ Γ-centered k-point mesh. Phonon frequencies and eigendisplacements were calculated from finite differences of forces were each ion was moved approximately 0.01 Å. Where noted, noncollinear calculations with L-S coupling were performed. For all ATiO$_3$ compounds we used $U = 4.5$ eV and $J_H = 0.9$ eV for the A-ion on-site Coulomb and exchange parameters respectively [22]. It should be noted that the presented results do not qualitatively change for reasonable variations of U.

Ferroelectricity.—In the soft-mode theory of ferroelectricity, the PE to FE transition is associated with the softening of a single unstable infrared-active phonon. In the $R\bar{3}c \rightarrow R3c$ transition, this is a PE phonon polarized along [111] of symmetry type A_{2u}. We calculated the frequencies of these A_{2u} phonons at $T = 0$ and found one highly unstable mode, e.g., in MnTiO$_3$, $\omega_{\mathrm{soft}} \approx i150$ cm^{-1}. The character of this soft mode consists of A-ion and Ti displacements moving against oxygen, similar to other $R3c$ FEs such as BiFeO$_3$ and LiNbO$_3$.

Next we broke inversion symmetry and performed a full structural optimization within the $R3c$ space group. The calculated lattice constants at $T = 0$ are found to be in excellent agreement with those observed at room temperature for MnTiO$_3$ [17] and FeTiO$_3$ [18] ($R3c$ NiTiO$_3$ has not yet been synthesized.) The distortion leading from the PE to the FE structure can be decomposed entirely in terms of the soft mode. The atomic displacements are almost equal in magnitude to those in LiNbO$_3$, meeting Abraham's structural criteria for switchable ferroelectricity [23]. Based on Abraham's empirically derived formula relating the magnitude of these distortions to the FE transition temperature [23], we estimate FE $T_C \sim$ 1500–2000 K. Finally, using the modern theory of polar-

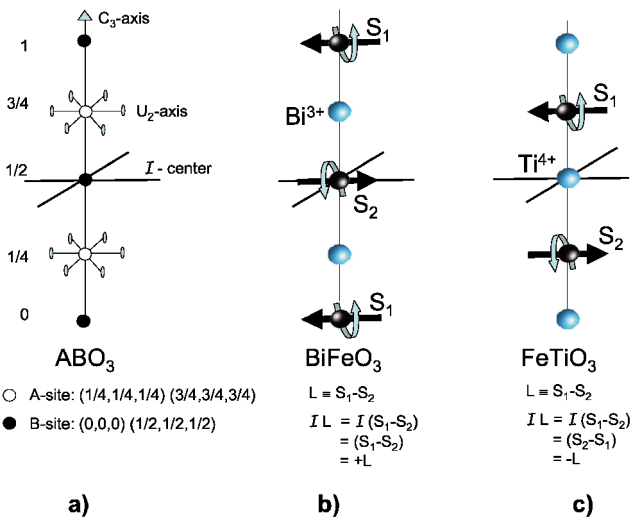FIG. 1 (color online). Paraelectric ABO_3, space group, $R\bar{3}c$. A-site: Wyckoff position 2a, site symmetry 32. B-site: Wyckoff position 2b, site symmetry $\bar{3}$. Oxygen-site (not shown): Wyckoff position 6d, site symmetry $\bar{1}$. Note, the unique point symmetries of the A and B sites are due to their location with respect to the O site.

ization [24] we calculated a large $\mathbf{P} \approx 80$–$100 \ \mu C/cm^2$ comparable to that of $BiFeO_3$.

Magnetic structure.—Weak ferromagnetism arises as a small perturbation—caused by the spin-orbit interaction—to a predominately collinear magnetic state, i.e., $|J| \gg |D|$, where J and D are Heisenberg and DM exchange, respectively. This difference in energy scales naturally separates the problem. As such we first identify the collinear state that minimizes the spin-interaction energy without L-S coupling, i.e., $E_H = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. The first four nearest neighbor (n.n.) exchange integrals, J_n, were extracted by mapping first-principles calculations of the total energy for different spin configurations onto E_H. We found the state that minimizes E_H consists of spins aligned ferromagnetically within antiferromagnetically coupled (111) planes, consistent with the magnetic criterion outlined above. This magnetic state arises due to a strong AFM coupling J_1 between n.n. spins in adjacent (111) planes. The Currie-Weiss (Θ_{CW}) and the Néel (T_N) temperatures can be approximated by solving E_H within mean-field theory [25]: $k_B \Theta_{CW} = \frac{2}{3} S(S+1) \sum_n J_n z_n$, where z is the number of n.n.'s, while for the calculated ground state, $T_N = \frac{2}{3} S(S+1)(-J_1 z_1 + J_2 z_2 + J_3 z_3 - J_4 z_4)$. We find $\Theta_{CW} \sim -300$ K for $MnTiO_3$ and $FeTiO_3$ and $\Theta_{CW} \sim -200$ K for $NiTiO_3$ while $T_N \sim 100$ K for $MnTiO_3$ and $NiTiO_3$ and $T_N \sim 250$ K for $FeTiO_3$.

For a uniaxial crystal the orientation of the global spin axis relative to the crystallographic axis is given to lowest order by $E_{ani} = \sum_i K_i \sin^2(\theta)$, where θ is the angle between [111] and $\mathbf{L}$. Depending on the sign of K, the spins lie in a plane perpendicular or parallel to [111], in which case wFM is allowed or forbidden, respectively. To calculate the single-ion anisotropy constant K we first performed a self-consistent density-functional calculation with collinear spins, without L-S coupling. Then, using the charge density and wave functions, we performed a series of non-self-consistent calculations with spin-orbit interaction included. We calculated the total energy for different orientations of the global spin axis which we mapped onto E_{ani} to extract K. We found that the magnetic easy axis lies in the plane perpendicular to [111] with K ranging from -0.03 meV for $MnTiO_3$ and $NiTiO_3$, to -0.7 meV for $FeTiO_3$ (the much large anisotropy for $FeTiO_3$ is associated with the orbital degeneracy). Symmetry then allows an additional contribution to the total energy which can cause the spins to cant: $E_{DM} = \sum_{ij} \tilde{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$, where $\tilde{D}_{ij}$ is the Dzyaloshinskii vector. Phenomenologically this can be described by $E_{DLM} = \mathbf{D} \cdot (\mathbf{L} \times \mathbf{M})$ where $\mathbf{L} = S_1 - S_2$ and $\mathbf{M} = S_1 + S_2$. Symmetry requires $\mathbf{D}$ to point along [111], i.e., parallel or antiparallel to $\mathbf{P}$. Since $\mathbf{L}$ was determined to be in the plane perpendicular to [111] and, subsequently, to $\mathbf{D}$, the induced $\mathbf{M}$ is perpendicular to $\mathbf{P}$. Once the direction of $\mathbf{L}$ is fixed, the sign of $\mathbf{M}$ that minimizes E_{DLM} is determined by the sign of $\mathbf{D}$.

Symmetry allows the spins to cant in the FE phase, but do they and by how much? To address this question we calculated the self-consistent spin-density in the presence of the spin-orbit interaction for the FE structure with for example the polarization pointing down. The spins were initialized in a collinear configuration, e.g., $\mathbf{L}^0 = (2g\mu_B S, 0, 0)$, $\mathbf{M}^0 = (0, 0, 0)$, and then allowed to relax without any symmetry constraints imposed. For $MnTiO_3$ the induced moment was rather weak, $\mathbf{M} = (0, -0.002, 0)\mu_B/f.u.$, although comparable to the canonical weak ferromagnet Fe_2O_3 and still measurable (the smallness of these moments is not too surprising remembering that wFM is a spin-orbit effect and Mn^{2+} and Fe^{3+} are both S states). The induced moment however increased substantially for $FeTiO_3$ and $NiTiO_3$; $\mathbf{M} = (0, -0.03, 0)\mu_B/f.u.$ and $\mathbf{M} = (0, 0.25, 0)\mu_B/f.u.$ respectively, where spin-orbit effects are larger [26].

Next we proceed to elucidate the interaction between $\mathbf{M}$ and $\mathbf{P}$. Similar calculations as we just discussed were performed for the PE structure and for the FE structure with $\mathbf{P}$ in the opposite (symmetry equivalent) direction, again relaxing the spin-density without symmetry constraints. In the former $\mathbf{M}$ vanished confirming that the FE distortion is required for the observed wFM while in the latter $\mathbf{M}$ switched sign. These results are consistent with our earlier symmetry arguments for a FE inducing wFM, i.e., for the invariant $E_{PLM} \sim \mathbf{P} \cdot (\mathbf{L} \times \mathbf{M})$ [27] and suggests that the direction of $\mathbf{M}$ can be switched between stable 180° directions by an external electric field that would switch $\mathbf{P}$ thereby switching $\mathbf{M}$. One way to understand this result is to argue that the sign of the DM vector $\mathbf{D}$ depends on the direction of $\mathbf{P}$, i.e., $\mathbf{P} \propto \mathbf{D}$. At first this may seem puzzling considering the fact that D_{ij} is an axial vector. As Ederer and Spaldin pointed out [13], $\mathbf{P}$ would have to change the sense of oxygen rotation in order for D to change sign. In Fig. 2 we compare the S-O-S bonds in the PE and up or down FE states, centering on spin S_2 and its nearest neighbors in adjacent (111) planes. A change in chirality of the S-O-S bonds is clearly visible due to a change in the direction of $\mathbf{P}$. The physics becomes clear by examining the microscopic E_{DM} and realizing that the net Dzyaloshinskii vector $\tilde{D}_{ij} = \sum_\alpha D_{ij}^\alpha$ has to be summed over all distinct S_1-O_α-S_2 pathways. In the PE structure two pathways, a left and right chiral, contribute to $\tilde{D}_{12}$ as we show in Fig. 3. The orientation of the D_{12}^A vector is
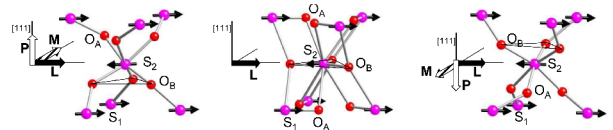

FIG. 2 (color online). Chiral nature of the S_1-O-S_2 bonds; (left) Polarization-up and (right) Polarization-down. (middle) Paraelectric state showing two equivalent *interplanar* pathways, e.g., S_1-O_A-S_2 and S_1-O_B-S_2. Note: $\mathbf{D} \parallel \mathbf{P}$, $\mathbf{L} \perp \mathbf{M} \perp \mathbf{P}$.
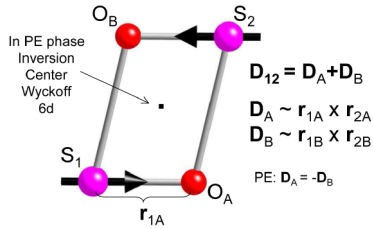
FIG. 3 (color online).   Superexchange pathways, S_1-O_A-S_2 and S_1-O_B-S_2, between nearest neighbor spins. The net Dzyaloshinski-Moriya vector, $\mathbf{D}_{12}$, contains two contributions, $\mathbf{D}_A$ and $\mathbf{D}_B$, that cancel in the paraelectric phase.

given by [28,29] $D_{12}^A \sim r_{1A} \times r_{2A}$ where r_{1A} is the unit vector pointing along the S_1-O_A direction. There is, however, an additional pathway connecting S_1 to S_2 through O_B. In the PE phase D^A and D^B can be shown to have equal magnitude but opposite sign leading to a vanishing net DM interaction. In the FE phase, **P** strengthens or weakens one pathway over the other leading to a finite DM interaction (in Fig. 2 we only show the "strong" S_1-O-S_2 pathway in the FE phase). Therefore the origin of ferroelectrically-induced wFM in this class of materials is a change in the relative contribution of two DM superexchange pathways (with opposite sign) due to a polar lattice distortion.

Today, the challenge in multiferroics has shifted from finding new magnetic ferroelectrics to identifying materials in which the polarization and the magnetization are strongly coupled. In this work we have presented criteria that have the potential to advance the discovery of such complex materials. These electrically controlled switchable magnets provide fertile ground for additional studies of how spin and lattice degrees of freedom interact and also hold promise for application in magnetic devices.

[1] S. -W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).
[2] T. Kimura, Annu. Rev. Mater. Res. **37**, 387 (2007).
[3] T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature (London) **430**, 541 (2004).
[4] C. Ederer and N. A. Spaldin, Phys. Rev. B **74**, 020401(R) (2006).
[5] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, Nat. Mater. **5**, 823 (2006).
[6] Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arima, and Y. Tokura, Phys. Rev. Lett. **98**, 147204 (2007).
[7] D. L. Fox and J. F. Scott, J. Phys. C **10**, L329 (1977).
[8] R. Ramesh and N. A. Spaldin, Nat. Mater. **6**, 21 (2007).
[9] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[10] J. F. Scott, Science **315**, 954 (2007).
[11] I. Dzyaloshinskii, J. Phys. Chem. Solids **4**, 241 (1958).
[12] T. Moriya, Phys. Rev. **120**, 91 (1960).
[13] C. Ederer and N. A. Spaldin, Phys. Rev. B **71**, 060401(R) (2005).
[14] I. Dzyaloshinskii, Sov. Phys. JETP **19**, 960 (1964).
[15] More generally, a spiral may be "unwound" [9] by doping, high magnetic fields, or strain. See for example: F. Bai, J. Wanf, M. Wuttig, J. Lie, N. Wang, A. P. Pyatakov, A. K. Zvezdin, L. E. Cross, and D. Viehland, Appl. Phys. Lett. **86**, 032511 (2005).
[16] J. B. Goodenough and J. J. Stickler, Phys. Rev. **164**, 768 (1967).
[17] J. Ko and C. T. Prewitt, Phys. Chem. Miner. **15**, 355 (1988).
[18] L. C. Ming, Y.-H. Kim, T. Uchida, Y. Wang, and M. Rivers, Am. Mineral. **91**, 120 (2006).
[19] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).
[20] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); G. Kresse and J. Furthmüller, *ibid.* **54**, 11 169 (1996).
[21] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).
[22] To find appropriate values of on-site Coulomb U and exchange J_H parameters we calculated the Curie-Weiss temperature (see text for definition) as a function of U for $MnTiO_3$, $FeTiO_3$, and $NiTiO_3$ in the *ground state Ilmenite structure*, space group $R\bar{3}$.
[23] S. C. Abrahams, S. K. Kurtz, and P. B. Jamieson, Phys. Rev. **172**, 551 (1968).
[24] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, R1651 (1993).
[25] J. Samuel Smart, *Effective Field Theories of Magnetism* (Saunders Company, Philadelphia, 1966).
[26] The trend is also consistent with $\mathbf{D} \sim \Delta g J$, where Δg is the change in the g-factor. See Refs. [12,16].
[27] We performed further calculations with **L** and **P** initialized in several directions, all results are consistent with the symmetry of this interaction, i.e., $P_z(L_x M_y - L_y M_x)$.
[28] F. Keffer, Phys. Rev. **126**, 896 (1962).
[29] A. S. Moskvin, J. Exp. Theor. Phys. **104**, 913 (2007).