Theory of spin-orbit enhanced electric-field control of magnetism in multiferroic BiFeO$_3$

Rogério de Sousa and Marc Allen

Department of Physics and Astronomy, University of Victoria, Victoria, B.C., V8W 3P6, Canada

Maximilien Cazayous

Laboratoire Matériaux et Phénomènes Quantiques (UMR 7162 CNRS), Université Paris Diderot-Paris 7, 75205 Paris cedex 13, France

(Dated: May 22, 2014)

We present a microscopic theory that shows the importance of spin-orbit coupling in perovskite compounds with heavy ions. In BiFeO$_3$ (BFO) the spin-orbit coupling at the bismuth ion sites results in a special kind of magnetic anisotropy that is linear in the applied electric field. This interaction can convert the cycloid ground state into a homogeneous antiferromagnet, with a weak ferromagnetic moment whose orientation can be controlled by the electric field direction. Remarkably, the E-field control of magnetism occurs without poling the ferroelectric moment, providing a pathway for reduced energy dissipation in spin-based devices made of insulators.

PACS numbers: 75.85.+t, 71.70.Ej, 75.30.Gw, 77.80.Fm

The ability to control magnetism using electric fields is of great fundamental and practical interest. It may allow the development of ideal magnetic memories with electric write and magnetic read capabilities [1]. The traditional mechanism of E-field control of magnetism is based on the dependence of magnetic anisotropy on the filling of $d$-orbitals. This allows E-field control of magnetism in metallic materials such as magnetic semiconductors [2] and ferromagnetic thin films [3], but not in insulators.

A method to influence magnetism using E-fields in insulators is desirable because it would not generate electric currents, potentially allowing the design of spin-based devices with much lower energy dissipation [4].

In insulators, the interactions that couple spin to electric degrees of freedom, the so-called magnetoelectric interactions, are usually too weak to induce qualitative changes to magnetic states. A remarkable exception occurs in the presence of the linear magnetoelectric effect (LME), an interaction that couples spin and charge linearly in either the external electric field $E$ or the internal electric polarization $P$ of the material. Multiferroic insulators with coexisting magnetic and ferroelectric phases have emerged as the natural physical system to search for LME and enhanced cross correlation between electricity and magnetism [5]. In a large class of multiferroic materials, the dominant form of LME was found to be due to the spin-current effect [6], that couples localized spins according to $H_{SC} = \sum_{i<j} J_{SC} (P \times R_{ij}) \cdot (S_i \times S_j)$, with $R_{ij}$ the vector linking the atomic location of spin $S_i$ to the atomic location of spin $S_j$. In manganese-based multiferroics, the spin-current interaction leads to magnetic induced ferroelectricity and thus allows magnetic field control of ferroelectricity [5].

For E-field control of magnetism, research has been centered instead on iron-based multiferroics, with bismuth ferrite [BiFeO$_3$ or BFO] being the most notable example [8]. At temperatures below 1143 K, BFO develops a strong electric polarization $P = 100 \, \mu C/cm^2$ that points along one of the eight cube diagonals of its unit cell [Fig. 1(a)]. It becomes an antiferromagnet below 643 K with Fe spins forming a spiral of the cycloid type, described by antiferromagnetic Néel vector $\hat{L} = \sin(q \cdot r)\hat{q} + \cos(q \cdot r)\hat{P}$. The microscopic origin of the cycloid can also be understood as arising from the spin-current interaction [8]. Plugging the cycloid $\hat{L}$ into

FIG. 1: (color online) (a) Conventional unit cell for BFO. The simple cubic axes $\hat{x}$, $\hat{y}$, $\hat{z}$ are denoted by grey vectors. The ferroelectric polarization $P$ is shown pointing along $[111]$, arising mostly from the displacement of Bi ions with respect to the oxygens. The directions $\hat{X}$ and $\hat{Y}$ denoted by black vectors describe the plane perpendicular to $P$. (b) Energy level diagram for Fe$^{3+} = [\text{Ar}]3d^6$ and Bi$^{3+} = [\text{Pt}]6s^2$ orbitals in BFO; the Fermi level lies between $E_{3d}$ and $E_{6p}$.

...
arises in the fourth order of our total Hamiltonian, i.e., orbit interaction \[15\]. In our case the largest contribution to be dominated by the heaviest ion of the lattice, and \(\ell \leq H\). The electric-field has three contributions, that was by the direction of the applied homogeneous magnetic state with its orientation tunable capable of switching the cycloidal spin state of BFO into a \(E\)−field control of magnetism in multiferroics published application of an external interaction is not the only LME present in BFO. The zero, with potential applications to electrically-written spin-orbit coupling. Our predicted LME explains the orientation tunable induced magnetic anisotropy, and argue that it can provide Eq. (2) by taking as Bi orbitals the states \(|6p_{x}\rangle\), \(|6p_{y}\rangle\), \(|6p_{z}\rangle\), and as Fe orbitals the \(e_{g}\) states \(|3d_{x^{2}−z^{2}}\rangle\) and \(|3d_{x^{2}−y^{2}}\rangle\), written with respect to the cubic axes \(\hat{x}, \hat{y}, \hat{z}\) of BFO’s parent perovskite lattice. The Fe \(t_{2g}\) states are not considered here because they are about 2 eV lower in energy \[13\], and thus only give a small correction to Eq. (1).

We now turn to an explicit evaluation of the matrix elements appearing in Eq. (2). The spin-orbit matrix element is given by

\[\langle 6p_{n'}|\zeta\ell|6p_{n}\rangle = −i\eta \hat{n}' × \hat{n},\]  

with \(\eta = 0.86\) eV chosen to match the spin-orbit splitting measured in isolated Bi ions \[16\]. Using symmetry, all lattice matrix elements \(|3d_{m}|H_{\text{latt}}|6p_{n'}\rangle\) can be expressed in terms of the direction cosines of \(R_{Bi}\) plus only two parameters: \(V_{pd\sigma} = (3d_{3z^{2}−r^{2}}|H_{\text{latt}}|6p_{\sigma})\) and \(V_{pd\pi} = (3d_{x^{2}−y^{2}}|H_{\text{latt}}|6p_{\pi})\), with \(\sigma\) pointing along \(R_{Bi}\). A similar procedure can be applied to the electronic matrix elements \(|3d_{m}|H_{\text{elec}}|6p_{n'}\rangle\), reducing them to expressions that depend on the direction cosines of \(R_{Bi}\) plus matrix elements like \(|3d_{x^{2}−y^{2}}|z'|6p_{\pi}\rangle\), etc.

In order to compute the vectors in Eq. (2), we need to sum over all Bi neighbors forming a distorted cube around each Fe. We do this by converting the sum into an angular integral,

\[\sum_{R_{Bi}}\langle 3d_{m}|H_{\text{latt}, \text{elec}}|6p_{n'}\rangle \approx \frac{8}{4\pi} \int d\Omega_{R} [1 + \delta R \cdot \nabla_{R}] \times (3d_{m}|H_{\text{latt, elec}}|6p_{n'}),\]  

with \(\delta R = (R_{||} \hat{P} + u_{||} E_{||})\) denoting the deviation of the Bi ions from the perfect cube. This includes Bi displacement along \(\hat{P}\) causing ferroelectricity; the displacement is given by \(R_{||} = 0.116 R_{Bi}\) with \(R_{Bi} = 4.88\) Å \[17\]. The component of \(E\) along \(\hat{P}\) can be neglected (it can not compete with the internal field generated by ferroelectricity), so we write the external \(E\)-field as \(E_{\perp} = E_{\perp}[\cos(\psi)\hat{X} + \sin(\psi)\hat{Y}]\), with the rhombohedral axes \(\hat{X}\) and \(\hat{Y}\) defined in \[18\] and shown in Fig. (a). This perpendicular component induces additional lattice displacement \(u_{\perp} E_{\perp}\); an estimate based on infrared spectroscopy \[19\] yields \(u_{\perp} E_{\perp}/R_{Bi} = 2.4 \times 10^{-4} E_{\perp}/(10^5\text{V/cm})\).

After computing the averages over all matrix elements

\[\mathcal{H}_{SC}, \text{ one finds that the lowest energy state is always achieved when the cycloid wavevector } \mathbf{q} \text{ is perpendicular to } \mathbf{P}. \text{ Hence the spins are pinned to the plane formed by } \mathbf{P} \text{ and } \mathbf{q}. \text{ This fact} \]
Eq. (1) yields
\[ \mathcal{H}_a = -\frac{a}{2} \left( \mathbf{S} \cdot \hat{\mathbf{P}} \right)^2, \]  
(5)
\[ \mathcal{H}_E = \frac{\xi E_\perp}{2} \left[ \cos (\psi) S^2_x + \cos \left( \psi - \frac{2\pi}{3} \right) S^2_y \right. 
\+ \cos \left( \psi - \frac{4\pi}{3} \right) S^2_z \left. \right]. \]  
(6)
Equation (6) depends linearly on \( E_\perp \), i.e., it gives rise to the LME.

Even in the absence of an external \( E \)-field, we find a magnetic anisotropy,
\[ a = \frac{1792\eta^2}{9(2S)^2} \frac{V_{\parallel}^2}{(E_{\parallel p} - E_{3d})^3}, \]  
(7)
while the lattice LME is
\[ \xi_{\text{latt}} = \frac{4\sqrt{2}}{7} \left( \frac{a}{V_{\parallel}} \right) \left( V_{\parallel p} + V_{\text{pde}} \right) \left( \frac{u_{\perp}}{R_B} \right). \]  
(9)
Note how these are physically distinct mechanisms: The lattice mechanism is proportional to \( u_\perp E_\perp \), i.e., it arises from \( E \)-field induced lattice displacement contained in \( \xi_{\text{latt}} \). Plugging the tabulated values for \( V_{\parallel p} \) and \( V_{\text{pde}} \) we get \( \xi_{\text{latt}} = -5 \times 10^{-2} \mu \text{eV}/(10^5 \text{V/cm}) \). The electronic mechanism is instead related to \( E \)-field induced atomic orbital admixture, and its matrix elements are not tabulated. Assuming \( \langle 3d_{\parallel 3}\rangle \sim R_B \) we get an order of magnitude estimate of \( \xi_{\text{elec}} \sim +30 \mu \text{eV}/(10^5 \text{V/cm}) \).

Comparison to experiments.—The experiment in Ref. [4] discovered a strong dependence of magnon frequencies on the external \( E \)-field, and used group theory to fit two kinds of \( E \)-field induced anisotropy: \( F_1 = \langle \xi/4 \rangle (E_\perp \cdot \mathbf{S}) (\mathbf{S} \cdot \hat{\mathbf{P}}) \), and \( F_2 = \langle \xi/4 \rangle (E_\perp \cdot [(S^2_x - S^2_y) \hat{\mathbf{X}} + (2S_X S_Y) \hat{\mathbf{Y}}]). \) It was shown that only \( F_2 \) would give rise to the observed linear in \( E_\perp \) magnon shift, and a fit of \( \xi_{\text{exp}} = +55 \mu \text{eV}/(10^5 \text{V/cm}) \) with \( a = 0 \) was established at \( T = 300 \text{ K} \). To compare this result to our theory, we write our Eq. (6) in the rhombohedral basis and get that it is equal to \( F_2 + 2\sqrt{2} F_1 \). Thus our Eq. (6) can be expressed as a function of the two anisotropy terms of Ref. [4] and explains the origin of the interaction leading to electrical control of magnons in BFO.

Our calculations are also supported by the good agreement between our calculated zero-field anisotropy energy \( a = 32 \mu \text{eV} \) and the value of \( a \sim 10 \mu \text{eV} \) extracted from neutron diffraction experiments [22].

We find that Eq. (4) will dominate over other known magnetoelastic couplings in BFO for \( E \)-fields in the practical range (\( E_\perp < 10^7 \text{ V/cm} \)), this is shown in the supplemental material section [23].

Electric-field control of magnetism.—To find out whether our effect can be used to control magnetism using an external \( E \)-field, we incorporate Eq. (6) into the usual continuum free energy model for BFO [24 26],
\[ \mathcal{F} = \int d^3x \left\{ -\frac{m'}{2} L^2 \right. 
\+ \left. \sum_{\gamma=x,y,z} |\nabla L_\gamma|^2 \right. 
\- \alpha' \mathbf{P} \cdot [L (\nabla \cdot \mathbf{L}) + \mathbf{L} \times (\nabla \times \mathbf{L})] \right. 
\+ \left. \frac{\xi E_\perp}{2} \left[ \cos (\psi) L^2_x + \cos \left( \psi - \frac{2\pi}{3} \right) L^2_y \right. 
\+ \left. \cos \left( \psi - \frac{4\pi}{3} \right) L^2_z \right] \right\}. \]  
(10)
Here \( \mathbf{L} \) is the Néel vector, and the first and second terms inside the brackets of Eq. (10) arise from the exchange interaction between spins; the third term arises from the continuum limit of the spin-current coupling, leading to \( \alpha' = J_{SC}(\Omega_0/2)^{5/3}/(2S\mu_B)^2 \), with \( \Omega_0 = 124.32 \text{ Å}^3 \) the unit cell volume in BFO. This term explains the origin of the cycloid in BFO when \( \mathbf{q}'q^2 \sim 1 \) [24 26]. The
Using \( \xi \)\(^{30,31} \). Using a phenomenological theory, Bai et al.\(^{30} \) showed that the strain in films can destroy the cycloid state. Our theory establishes a microscopic mechanism for destroying the cycloid in films that is unrelated to strain. In our model, the heterostructure inversion asymmetry leads to an internal \( E \)-field. A sufficiently large value of this field will induce homogeneous magnetic order.

The ability to switch from cycloidal to homogeneous spin order without poling \( P \) is a pathway for \( E \)-field control of magnetism that avoids charge displacement and energy dissipation associated to the relaxation of \( P \) into another direction\(^{32} \). In BFO, the weak magnetization \( M \propto \mathbf{Z} \times \mathbf{L} \) is tied to \( \mathbf{L} \). Thus our mechanism allows the electrical switching of \( M \) from a sinusoidal state with zero spatial average to a homogeneous state with non-zero \( \langle M \rangle \). This effect converts an \( E \)-field pulse into a magnetic pulse. By combining BFO with another magnetic material (as done in \(^{11} \)), one can envision the writing of data in a magnetic memory element using an \( E \)-field pulse in an insulator instead of the usual current pulse in a metal.

**Conclusions.**—We presented a microscopic theory of...
E-field induced magnetic anisotropy, and showed how it gives rise to an additional linear magnetoelectric effect (LME) in insulators. The origin of this special kind of LME is based on the combination of two factors: The presence of a non-magnetic ion with large spin-orbit coupling, and a significant amount of inversion asymmetry (induced e.g. by ferroelectricity). For BFO, the presence of this additional LME implies that its magnetic cycloid can be converted into a homogeneous state under the application of a practical external E-field without the need for poling \( P \); and that the additional ferromagnetic degree of freedom \( M \) will be fully controllable by \( E \) and will not average out to zero over large length scales. Thus, it shows that E-field control of magnetism at room temperature can happen even without poling the ferroelectric polarization \( P \) into another direction, and can be done with much less energy dissipation than what has been demonstrated so far.

Our research was supported by the NSERC Discovery program. The authors would like to thank D. Colson, I. Souza, and I. Žutić for helpful discussions.

* rlesousa@uvic.ca

[1] J.F. Scott, Nature Mater. 6, 256 (2007).
[2] D. Chiba et al., Nature 455, 515 (2008).
[3] Y. Shiota et al., Nature Mater. 11, 39 (2012).
[4] P. Rovillain et al., Nature Mater. 9, 975 (2010).
[5] See e.g. N.A. Spaldin, S.-W. Cheong, and R. Ramesh, Phys. Today 63, 38 (2010); S.-W. Chong and M. Mostovoy, Nature Mater. 6, 13 (2007).
[6] H. Katsura, N. Nagaosa, and A.V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
[7] T. Kimura et al., Nature 426, 55 (2003).
[8] G. Catalan and J.F. Scott, Adv. Mater. 21, 2463, (2009); A.M. Kadamseva, A.K. Zvezdin, Yu.F. Popov, A.P. Pyatakov, and G.P. Vorob'ev, JETP Lett. 79, 571 (2004).
[9] D. Rahmedov, D. Wang, J. Iñiguez, and L. Bellaiche, Phys. Rev. Lett. 109, 037207 (2012).
[10] D. Lebeugle et al., Phys. Rev. Lett. 100, 227602 (2008); T. Zhao et al., Nature Mater. 5, 823 (2006).
[11] J.T. Heron et al., Phys. Rev. Lett. 107, 217202 (2011); M. Fiebig, Physics 4, 95 (2011).
[12] C. Ederer and N.A. Spaldin, Phys. Rev. B 71, 060401(R) (2005).
[13] R. de Sousa and J.E. Moore, Phys. Rev. Lett. 102, 249701 (2009).
[14] M. Ramazanoglu et al., Phys. Rev. Lett. 107, 207206 (2011).
[15] See A. Abragam and B. Bleaney, Electron paramagnetic resonance of transition metal ions (Clarendon Press, Oxford, U.K., 1970), Chapters 7 and 19.
[16] The spin-orbit interaction splits the 6p manifold into \( j = 3/2 \) and \( j = 1/2 \) levels, with splitting given by \( 3\eta \). Spectroscopy measurements yield \( 3\eta = 2.58 \) eV. See the first excited state of Bi III in the NIST atomic spectra database, [http://physics.nist.gov/asd](http://physics.nist.gov/asd).
[17] F. Kubel and H. Schmid, Acta Crystallogr. Sect. B: Struct. Sci 46, 698 (1990).
[18] We used the definition \( \vec{X} = (-2\hat{x} + \hat{y} + \hat{z})/\sqrt{6} \) and \( \vec{Y} = (-\hat{y} + \hat{z})/\sqrt{2} \) as new rhombohedral axes perpendicular to \( \vec{P} = \vec{Z} = (\hat{x} + \hat{y} + \hat{z})/\sqrt{3} \).
[19] R.P.S.M. Lobo, R.L. Moreira, D. Lebeugle, and D. Colson, Phys. Rev. B 76, 172105 (2007).
[20] A. Kumar et al., Appl. Phys. Lett. 92, 121915 (2008).
[21] W.A. Harrison, Elementary electronic structure (World Scientific, Singapore, 2004). The method to calculate matrix elements between localized atomic orbitals is described in p. 546, with tabulated values shown at the end of the book “solid-state table”.
[22] M. Ramazanoglu et al., Phys. Rev. B 83, 174434 (2011); M. Matsuda et al., Phys. Rev. Lett. 109, 067205 (2012).
[23] See Supplemental Material at [http://link.aps.org/supplemental/10.1103/PhysRevLett.000.000000](http://link.aps.org/supplemental/10.1103/PhysRevLett.000.000000) for a comparison of our predicted LME [Eq. (6)] to other known magnetoelectric couplings.
[24] A. Sparavigna, A. Strigazzi, and A. Zvezdin, Phys. Rev. B 50, 2953 (1994).
[25] R. de Sousa and J.E. Moore, Phys. Rev. B 77, 012406 (2008).
[26] I. Sosnowska and A.L. Zvezdin, J. Magn. Magn. Mater. 140-144, 167 (1995).
[27] The E-field necessary to flip the cycloid \( q \) out of one of its three degenerate states (\( q \parallel \{1, -1, 0\} \) and cyclic permutations) is \( E_\perp \approx 0.6J(qR_{Bi})^2/\xi \approx 10^2 \) V/cm.
[28] R. de Sousa and J.E. Moore, Appl. Phys. Lett. 92, 022514 (2008).
[29] M. Cazayous et al., Phys. Rev. Lett. 101, 037601 (2008).
[30] F. Bai et al., Appl. Phys. Lett. 86, 032511 (2005).
[31] H. Béa et al., Philos. Mag. Lett. 87, 165 (2007).
[32] K. Ashraf, S. Smith, and S. Salalhuddin, Proceedings of the Electron Devices Meeting (IEDM), 2012 IEEE International, p. 26.5.1 (2012).