Effects of Magnetoelectric Ordering Due to Interfacial Symmetry Breaking

J. T. Haraldsen$^{a,b,*}$ and A. V. Balatsky$^{a,b,c}$

$^a$Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; $^b$Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; $^c$NORDITA, Roslagstullsbacken 23, 106 91 Stockholm, Sweden

(Received 8 November 2012; final version received 3 January 2013)

We examine the effects of interfacial symmetry breaking between ferroelectric and ferromagnetic (FM) materials. Using a standard Ginzburg-Landau formalism, we show that the presence of a linear coupling between electric polarization and magnetization produces spatial modulations of the ordered states. This coupling can also induce interfacial order from a non-ordered state. In the case of the paramagnetic state, this coupling produces a shift of the transition temperature and can drive the system from non-ordered to ordered at the interface. For the paraelectric state, an induced interfacial polarization emerges due to the FM state in the adjacent material.

Keywords: Magnetoelectric coupling, Multiferroic, Ferroelectric, Complex oxide interfaces

Multifunctional materials are of great interest to the scientific community due to the possibilities of technological advances through the ability of controlling multiple degrees of freedom (i.e. magnetic, electronic, orbital, etc. [1–3]). Of these materials, multiferroic materials are typically investigated because of the complex coupling of multiple ferroic order parameters including ferromagnetism, ferroelectricity, and ferroelasticity [4–11]. While ferroelasticity is an increasing area of interest, multiferroic materials that couple magnetic and ferroelectric (FE) orders have attracted a great deal of attention, since the effects of magnetoelectric coupling allows one to control electric polarization with magnetic field and/or magnetization with electric field (illustrated in Figure 1 [4–8]). Therefore, magnetoelectric materials exhibit both an electric polarization with distinct magnetic order.

Magnetoelectric coupling can be found in a variety of materials including bulk structures, thin-film heterostructures, and nanoparticles [10–14]. The various mechanisms and symmetries involved in magnetoelectric materials are often competing and producing magnetic and lattice frustration [6]. In proper magnetoelectrics, the FE state prefers to have fully occupied $d$ orbitals. This will help in shifting the atomic positions and produce an overall dipole moment. However, magnetic moments typically require unpaired electrons and thus partially filled $d$ orbitals [4]. This makes coupling of electric polarization and magnetic order difficult and in many ways incompatible, which weakens the magnetoelectric coupling in many bulk multiferroic materials (i.e. BaTiO$_3$, HoMnO$_3$, BiMnO$_3$), [15–17] even though a large electric polarization exists. This is similar for lone pair and charge ordered [18] multiferroics. In improper magnetoelectrics, a FE polarization is produced through a strong coupling to a magnetic spiral (i.e. Ni$_3$V$_2$O$_8$, TbMnO$_3$, and CuFeO$_2$) [19–21]. Here, incommensurate magnetic order breaks inversion symmetry of the lattice and produces an electric polarization through an inverse Dzyloshinskii–Moriya interaction [19,20]. The issue here is that the net polarization is typically an order of magnitude lower than proper magnetoelectrics. Therefore, there is a strong desire to produce materials that have the best of both cases: large electric polarization and strong magnetoelectric coupling.

This endeavor has led many toward the investigation of composite multiferroic materials and magnetoelectric interfaces [6]. While this can be described as FM material is deposited on a FE material, or vice versa [22,23] these interfaces can also be accomplished using piezoelectric and magnetostrictive materials [24,25]. In this

*Corresponding author. Email: jasonh@lanl.gov

© 2013 J. T. Haraldsen, A. V. Balatsky
situation, the magnetoelectric coupling may be produced through the material interface via the electronic reconstruction, strain, or interlayer mixing [26]. This type of configuration allows for the easy manipulation and possible tuneability of the magnetoelectric coupling through applied strain or external fields, and may produce effects not accessible in the bulk compounds.

In recent years, multiferroic interfaces have been widely studied, where some multiferroic heterostructures include La_{0.7}Sr_{0.3}MnO_3/BiFeO_3 [22,26], La_{0.7}Sr_{0.3}MnO_3/BaTiO_3 [27], Fe_3O_4/BaTiO_3 [23,28], and Pb(Zr,Ti)O_3/(Tb,Dy)Fe_2 [29] to name a few. There have also been a number of theoretical investigations of the microscopic role of strain and lattice distortions in the magnetoelectric coupling at the interface [30,31]. In an effort to help to identify these types of materials, our investigation is to examine the effects of magnetoelectric coupling arising from interfacial symmetry breaking.

Magnetism and ferroelectricity have different symmetry breaking mechanisms [4]. Due to inversion symmetry breaking at the interface (\(z \neq -z\)), the electric polarization \(P\) will couple linearly to the magnetization squared \(M^2\). This produces an interaction that we denote as \(\lambda PM^2\). As shown in Figure 2, we consider a material interface consisting of FE and FM materials. Here, we assume that there exists an interaction region, through either orbital reconstruction or interlayer mixing, that extends into the bulk materials by lengths \(\xi_P\) and \(\xi_M\). A similar investigation by Cai et al. [32] on a FM/FE/metal tri-composite demonstrated an induced magnetization at the interface. This has also been examined for PE/superconducting interfaces, where it was shown that the coupling produced an electric polarization in the PE state [33].

In this letter, we examine the Ginzburg-Landau free energy for the magnetoelectric interface and show that an ordered FE or FM state will produce spatial modulations in the adjacent ordered state due to the linear \(P\) coupling. Also, it is determined that if a non-ordered state is coupled to an ordered state, then it is possible to induced interface magnetization or polarization from the non-ordered state. This presents a basic mechanism to help to identify and possibly quantify the magnetoelectric coupling in multiferroic heterostructures.

The symmetry breaking at the interface of heterostructures due to the directionality of the electric polarization produces a coupling that is linear with respect to the \(z\)-direction, where \(P = (0,0,P_z)\). At the interface, the total free energy can be described as

\[
E_{\text{tot}} = \int_{-\xi_P}^{-\xi_M} E(z)_{B,P} \, dz + \int_{-\xi_P}^{0} (E(z)_{I,P} + E(z)_{I,int}) \, dz \\
+ \int_{\xi_P}^{\xi_M} (E(z)_{I,M} + E(z)_{I,int}) \, dz + \int_{\xi_M}^{L} E(z)_{B,M} \, dz,
\]

where the total energy is integrate over the bulk (\(B\)) and interface (\(I\)) spaces of a heterostructure of length \(2L\), and

Figure 1. Multiferroicity is the coexistence of multiple ferroic forms of ordering (ferromagnetism, ferroelectricity, ferroelasticity, etc.) through a coupling of multiple degrees of freedom. In a magnetoelectric multiferroic (shown above), a magnetic field \(H\) is able to control the electric polarization \(P\) or an electric field is able to control the magnetization \(M\) through coupling of spin and charge degrees of freedom. Other order parameters (i.e. strain, orbital, or lattice) may also play a role in the coupling.

Figure 2. The top panel illustrates the interface magnetoelectric interaction of \(\lambda PM^2\) between FE and ferromagnetic (FM) materials. The interfacial (lighter color) area is a relatively small region from \(-\xi_P\) to \(\xi_M\). The bulk (darker color) region is that volume that is essentially unaffected by the interface interactions. The bottom panel details the effect of the magnetoelectric interaction. The general effect of an ordered interacting with an ordered state produces a modulation of the corresponding order parameter, which has been normalized. The overall effect will produce different levels of modulation to each order parameter. When an ordered state interacts with a non-ordered state, the ordered state induces an interfacial ordering. This produces a feedback modulation to the corresponding ordered state. Therefore, the FM state will produce a modulation of the FE state or an induction of an interfacial polarization from the paraelectric (PE) state or vice versa. It should be noted that PE/paramagnetic (PM) interface will not produce any effect. The only interactions are FE/FM (A), PE/FM (B), and FE/PM (C).
the interface regions are defined by correlation lengths of $\xi_P$ and $\xi_M$. The bulk and interface coexist up to the Thomas-Fermi screening length $\xi_T$, which is considered to be much smaller than the interaction correlation lengths. From this, the depth-dependent free energy for the bulk and interface is given by

$$E(z)_B = E(z)_{B,p} + E(z)_{B,int} = \alpha_B |M_{zB}|^2 + \frac{\beta_B}{2} |M_{zB}|^4 + \gamma_B |P_{zB}|^2 + \frac{\eta_B}{2} |P_{zB}|^4$$

and

$$E(z)_I = E(z)_{I,p} + E(z)_{I,int},$$

where

$$E(z)_{I,p} = \alpha_I |M_{zI}|^2 + \beta_I |M_{zI}|^4 + g_M(\nabla|M_{zI}|)^2,$$

$$E(z)_{I,int} = \gamma_I |P_{zI}|^2 + \eta_I |P_{zI}|^4 + g_P(\nabla|P_{zI}|)^2,$$

$$E(z)_{I,int} = \lambda |P_{z|zI}|^2.$$  \hspace{1cm} (4)

Here, $\alpha = \alpha(T - T_c)$ describes the FM state when $\alpha < 0$, since the free energy will produce a non-zero minimum value. Similarly, $\gamma$ defines the FE state when $\gamma < 0$ [34,35]. The overall free energy can increase or decrease depending on positive or negative $P_z$ at the interface, respectively. Here, $g$ is considered to be a positive constant and introduces the gradient terms, which defines the interface limits at $z = 0$.

The general effect of the magnetoelectric coupling can be easily understood by looking at the free energy plots for each order parameter (shown in Figure 3). Since the electric polarization is linear with respect to $P$, the FE and PE states are shifted. This produces a preferred polarization in the FE Figure 3(a) and establishes a bound polarization from the PE state (Figure 3(b)). This is different from the magnetization. The interaction term is still quadratic for the magnetization because it has to be invariant under time-reversal symmetry breaking ($M \rightarrow -M$). Therefore, the interaction produces a larger magnetization near the interface for the FM state (Figure 3(c)). In the case of the PM state, the interaction may drive the system into a FM state by affecting the overall quadratic term (Figure 3(d) and discussed in more detail below). This shows that the interface of the heterostructure should produce changes to the order parameters at the interface.

To investigate this further, we examine the effects of magnetoelectric coupling through this linear interaction. Higher order terms are assumed to be negligible due to the small perturbation produced by the linear term. However, with large polarization or magnetization, they will become more relevant. To proceed, we minimize the energy and determine the equations of motion for $P_z$ and $M_{zI}$ through a Fourier transform that which produce the following conditions

$$\gamma_I + g_P k_z^2 P_{k_i} + \beta_I M_0^2 = 0$$  \hspace{1cm} (5) and

$$\alpha_I + g_M k_z^2 M_{k_i} + 2\lambda P_0 M_0 = 0,$$  \hspace{1cm} (6)

where $P_0$ and $M_0$ are the effective order parameters at the interface ($z = 0$), which is considered to be a finite thickness integrated over the Thomas-Fermi screening length. For convenience, $\beta_I$ and $\eta_I$ are ignored, since we are in the small limit polarization and magnetization limit. Here, $k$ is produced through the standard Fourier transform of the spatial gradient. Therefore, there are three main possibilities at the interface; FE/FM (A), FE/PM (B), or PE/FM (C).

Two ordered interfaces (A)—In the case of FE/FM interfaces, $\gamma$ and $\alpha$ are less than zero, which define the ordered states. By solving the equations of motion for $P_{k_i}$ and $M_{k_i}$ and through a Fourier transform into real space, the interface dependence of the order parameters can be determined. For completeness, the electric polarization needs to be written as a sum of the bulk and interface components $P_z = P_{zB} + P_{zI}$ for $z < 0$ (as shown in Figure 2). The polarization is written as

$$P_z = \frac{\lambda M_0^2}{|\gamma_I|\xi_P} \sin \left( \frac{|z|}{\xi_P} \right) e^{i\xi_P} + P_{zI}$$  \hspace{1cm} (7)
Table 1. \( P_z \) and \( M_z \) as a function of \( z \) for magnetoelectric coupling through the interface.

| System     | \( P_z \)                                      | \( M_z \)                                      |
|------------|-----------------------------------------------|-----------------------------------------------|
| FE/FM      | \( \frac{\lambda M^2_z}{|\gamma|\xi_p} \sin \left( \frac{|z|}{\xi_p} \right) e^{-|z|/\xi_p} + P_{zB} \) | \( \frac{2\lambda P_{0} M^2_z}{|\alpha|\xi_M} \sin \left( \frac{|z|}{\xi_M} \right) e^{-|z|/\xi_M} + M_{zB} \) |
| PE/PM      | \( \frac{\lambda M^2_{zB}}{|\gamma|\xi_p} e^{-2|z|/\xi_p} \)                                       | \( \frac{2\lambda^2 M^3_z}{|\alpha|\xi_M |\gamma|\xi_p} \sin \left( \frac{|z|}{\xi_M} \right) e^{-|z|/\xi_M} + M_{zB} \) |

where \( P_{zB} \) is the bulk electric polarization. For the magnetization, we define \( M_z = M_{zB} + M_{zB} \). Using the same Fourier transformation for \( z > 0 \), where the solution is given by

\[
M_z = \frac{2\lambda P_{0} M_0}{|\alpha|\xi_M} \sin \left( \frac{|z|}{\xi_M} \right) e^{\xi_z/\xi_M} + M_{zB},
\]  

(8)

where \( M_{zB} \) is the bulk magnetization. In this scenario, the interaction between the two ordered state produces a modulation of the order parameters. This modulation will have a specific decay length on the order of the \( \xi_p = \sqrt{g_{\alpha}/|\gamma|} \) (for the electric polarization) and \( \xi_M = \sqrt{g_{\alpha}/|\alpha|} \) (for the magnetization). Since both states are ordered, the interface constraints are \( P_0 = P_{zB} \) and \( M_0 = M_{zB} \), which means that the interface boundary conditions are equal to the bulk parameters. This is illustrated in Figure 2, and is an artifact of the mean-field approach of this letter. Higher order terms and microscopic interactions not considered here may alter these boundary conditions.

Ordered and non-ordered interfaces (B and C) —

In the case of PE/FM or FE/PM interfaces, one state is ordered, while the second in the non-ordered state (\( \gamma \) or \( \alpha \) less than zero). For the case of a PE/FM interface, it is found that the inclusion of the linear interaction term produces an induced interfacial polarization at \( z = 0 \), which will also have an explicit decay length \( \xi_p \). This a similar modulation effect to the one predicted in case PE and superconducting coupling as shown in Ref. [33].

Using the same Fourier transformation for \( z < 0 \), the electric polarization is given by

\[
P_z = \frac{\lambda M^2_{zB}}{|\gamma|\xi_p} e^{-2|z|/\xi_p}.\]

(9)

This produces a net electric polarization at the interface, which decays toward the bulk. Since the bulk has no net polarization, \( P_{zB} = 0 \). Therefore, the interface constraints are different than in the doubly ordered case. Here, \( M_0 = M_{zB} \) and \( P_0 = \lambda M^2_{zB}/|\gamma|\xi_p \). This leads to the induced polarization being dependent on the magnetization and the coupling. As shown in Figure 2, the polarization will have a finite value at \( z = 0 \) and then decay to the bulk. This has a feedback mechanism and produces a modulation of the magnetization.

For the FE/PM case, the interface polarization is equal to that of the bulk (\( P_0 = P_{zB} \)). Therefore, the magnetization transition temperature is given by

\[
\hat{T}_c = \hat{T}_c^0 - \left( \frac{g_{\alpha} k_B}{\alpha M} \right),
\]

(11)

which will shift the magnetic transition temperature depending on the combined effect of fluctuations and electric polarization locally at the interface.

To determine the initial magnetization analytically, we reintroduce the quartic term to the free energy \( \beta M^4 \), and assume the previous solution for the electric polarization. This makes \( M_B = \sqrt{\hat{\alpha}_I/\beta_I} \), which is the standard Ginzburg-Landau solution. Similar to the PE/FM case, the magnetization as a function of \( z \) is given by

\[
M_z = \frac{2\lambda P_{0} M_0}{|\alpha|\xi_M} e^{-2|z|/\xi_M}.
\]

(12)

This provides a constraint to the polarization at \( z = 0 \) of \( P_{zB} = |\alpha_I|\xi_M/2\lambda \) in order to induce a magnetization. A similar feedback produces a modulation of the electric polarization as described in the FE/FM case.

Therefore, the coupling of an ordered state to a non-ordered state will induce either a polarization or magnetization (depending on which state is ordered). This induced field at the interface will make the corresponding ordered state experience spatial modulations of the order parameter as predicted by the two ordered state scenario. Since we are using a mean-field approach, this technique is not sensitive enough to distinguish between metallic or insulator states. The technique assumes general interactions through the interface. However, it should be noted...
that FE materials are typically insulators and mobile carriers from a magnetic metallic state could increase the microscopic interactions.

In conclusion, we predict interface effects for multiferroic heterostructures using a Ginzburg-Landau formalism (detailed in Table 1). We show that the presence of two ordered states will modulate the order parameters at the interface. In the case of a non-ordered state being present, an ordered state may induce a finite ordered component near the interface. These effects are arising solely due to the breaking of inversion symmetry at the interface, which produces a linear coupling of the electric polarization to the magnetization. This modulation and linear dependence will occur for any combination of order parameters that experience a breaking spatial symmetry due to an interface. These predicted effects are local to the interface and may be observed through nonlinear optics measurements (i.e. pump-probe) or local polarized neutron scattering experiments, where the local moment or electric polarization can be probed directly at the interface.

Acknowledgements We thank T. Das, J. She, M. Graf, and S. Trugman for their helpful discussions. JTH and AVB acknowledge the support by the Center for Integrated Nanotechnologies, a US Department of Energy, Office of Basic Energy Sciences user facility. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Energy Sciences program. JTH also acknowledges the support by the Center for Integrated Nanotechnologies. AVB also acknowledges the support by the Center for Integrated Nanotechnologies, a US Department of Energy, Office of Basic Energy Sciences user facility. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Energy Sciences program.

References

[1] Dagotto E. Complexity in strongly correlated electronic systems. Science 2005;309(5732):257–262.
[2] Bibes M, Villegas JE, Barthelemy A. Ultrathin oxide films and interfaces for electronics and spintronics. Adv. Phys. 2011;60(1):5–84.
[3] Zubko P, Gariglio S, Gabay M, Ghosez P, Triscone J-M. Interface physics in complex oxide heterostructures. Annu. Rev. Conden. Matter Phys. 2011;2(1):141–165.
[4] Eerenstein W, Mathur ND, Scott JF. Multiferroic and magnetoelectric materials. Nature (London). 2006;442(7104):759–765.
[5] Fiebig MJ. Revival of the magnetoelectric effect. Phys. D. 2005;38(8):R123–R152.
[6] Spaldin NA, Fiebig M. The renaissance of magnetoelectric multiferroics. Science 2005;309(5733):391–392.
[7] Kimura T, Goto T, Ishizaka K, Arima T, Tokura Y. Magnetic control of ferroelectric polarization. Nature. 2005;436(7054):1136–1138.
[8] Park T-J, Papaefthymiou GC, Viscas AJ, Moodenbaugh AR, Wong SS. Size-dependent magnetic properties of single-crystalline multiferroic BiFeO3 nanoparticles. NanoLetters 2009;9(7):766–772.
[9] Srivastava T, Kondalaiya DC, Gosavi SW, Kulkami SK, Venkatesan T, Ogale SB, Urban J, Park S, Cheong S-W. Multiferroic TbMnO3 nanoparticles. Solid State Comm. 2006;138(8):395–398.
[10] Spaldin NA. Why are there so few magnetic ferroelectrics. J. Phys. Chem. B. 2000;104(29):6694–6709.
[11] Neaton JB, Ederer C, Waghmare UV, Spaldin NA, Rabe KM. First-principles study of spontaneous polarization in multiferroic BiFeO3. Phys. Rev. B. 2005;71(1):014113.
[12] Seshadri R, Hill NA. Visualizing the role of Bi 6s lone pairs in the off-center distortion in ferromagnetic BiMnO3. Chem. Mater. 2001;13(9):2892–2899.
[13] Ikeda N, Ohsumi H, Ohwada K, Ishii K, Inami T, Kaka rai K, Murakami Y, Yoshi K, Mori S, Horibe Y, Kiti H. Ferroelectricity from iron valence ordering in the charge-frustrated system LuFe2O4. Nature. 2005;436(7054):1136–1138.
[14] Katsura H, Nagaosa N, Balatsky AV. Spin current and magnetoelectric effect in noncollinear magnets. Phys. Rev. Lett. 2005;95(5):057205.
[15] Sergienko IA. Dagotto E. Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites. Phys. Rev. B. 2006;73(9):094434.
[16] Arima T. Ferroelectricity induced by proper-screw type magnetic order. J. Phys. Soc. Jpn. 2007;76(7):073702.
[17] Eerenstein W, Wiora M, Prieto JL, Scott JF, Mathur ND. Giant sharp and persistent converse magnetoelectric effects in multiferroic epitaxial heterostructures. Nature Mater. 2007;6(5):348–351.
[18] Tian HF, Qu TL, Luo LB, Yang JJ, Guo SM, Zhang HY, Zhao YG, Li JQ. Strain induced magnetoelectric coupling between magnetite and BaTiO3. Appl. Phys. Lett. 2008;92(6):063507.
[19] Filipov DA, Bichurin MI, Nan CW, Liu JM. Magnetoelectric effect in hybrid magnetostri ctive-piezoelectric composites in the electromechanical resonance region. J. Appl. Phys. 2005;97(11):113910.
[20] Bichurin MI. Petrov VM. Magnetoelectric effect in magnetostri ction-piezoelectric multiferroics. Low Temp. Phys. 2010;36(6):544–549.
[21] Yu P, Lee J-S, Okamoto S, Rossell MD, Huijben M, Yang C-H, He Q, Zhang JX, Yang SY, Lee MJ, Ramasse QM, Erni R, Chu Y-H, Arenu DA, Kao C-C, Martin W, Ramesh R. Interface ferromagnetism and orbital reconstruction in BiFeO3-LuO2-5Sr2O3-3MnO3 heterostructures. Phys. Rev. Lett. 2010;105(12):027201.
[22] Wang CC, He M, Yang F, Wen J, Liu GZ, Lu HB. Enhanced tunability due to interfacial polarization in La0.7Sr0.3MnO3/BaTiO3 multilayers. Appl. Phys. Lett. 2007;90(19):192904.
[23] Niranjan MK, Velev JP, Duan C-G, Jaswal SS, Tsymbal EY. Magnetoelectric effect at the Fe3O4/BaTiO3 (001) interface: a first-principles study. Phys. Rev. B. 2008;78(10):104405.
[29] Shi Z, Ma J, Lin Y, Nan C-W. Magnetoelectric resonance behavior of simple bilayered Pb(Zr,Ti)O_{3}(Tb,Dy)Fe_{2}/epoxy composites. J. Appl. Phys. 2007;101(4):043902.

[30] Duan C-G, Jaswal SS, Tsymbal EY. Predicted magnetoelectric effect in Fe/BaTiO_{3} multilayers: ferroelectric control of magnetism. Phys. Rev. Lett. 2006;97(4):047201.

[31] Rondinelli JM, Stengel M, Spaldin NA. Carrier-mediated magnetoelectricity in complex oxide heterostructures. Nat. Nanotechnol. 2008;3(1):46–50.

[32] Cai T, Ju S, Lee J, Sai N, Demkov AA, Niu Q, Li Z, Shi J, Wang E. Magnetoelectric coupling and electric control of magnetization in ferromagnet/ferroelectric/normal-metal superlattices. Phys. Rev. B 2009;80(14):140415(R).

[33] Haraldsen JT, Trugman SA, Balatsky AV. Induced polarization at a paraelectric/superconducting interface. Phys. Rev. B 2011;84(2):020103(R).

[34] Jona F, Shirane G. Ferroelectric crystals. New York, NY: Pergamon; 1962.

[35] Rabe K, Ahn C-H, Triscone J-M, editors. Physics of ferroelectrics: a modern perspective. New York, NY: Springer; 2007.