Ab Initio Indications for Giant Magnetoelectric Effects Driven by Structural Softness

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(Received 19 April 2010; published 16 July 2010)

We show that inducing *structural softness* in regular magnetoelectric (ME) multiferroics—i.e., tuning the materials to make their structure strongly reactive to applied fields—makes it possible to obtain very large ME effects. We present illustrative first-principles results for $BiFeO_3$ thin films.

DOI: 10.1103/PhysRevLett.105.037208 PACS numbers: 75.80.+q, 71.15.Mb, 77.55.Nv, 77.80.B−

Magnetoelectric (ME) multiferroics present coupled electric and magnetic orders [1], which could lead to novel devices. However, finding multiferroic compounds that display large ME effects at room temperature (T_r) is proving a major challenge, and so far we know only one candidate: the perovskite $BiFeO_3$ (BFO) [2]. The difficulties begin with the scarcity of ferroelectrics (FEs) magnetically ordered at T_r [3]. Moreover, the desired materials must present large ME couplings and be good insulators, as needed for many envisioned applications. Here we propose a general and robust design strategy to satisfy all such requirements. Our approach—i.e., inducing *structural softness* to obtain strong ME effects—is illustrated with first-principles results for BFO films.

Materials-design strategies.—As recently shown in Ref. [4], the linear ME tensor $\boldsymbol{\alpha}$ can be written as

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^{\rm el} + \Omega_0^{-1}\boldsymbol{Z}^T\boldsymbol{K}^{-1}\boldsymbol{\zeta} + \boldsymbol{e}\boldsymbol{C}^{-1}\boldsymbol{h}, \tag{1}$$

where Ω_0 is the cell volume and contributions from both spin and orbital magnetism are in principle considered. Thus, $\boldsymbol{\alpha}$ comprises purely electronic effects ($\boldsymbol{\alpha}^{\rm el}$) and contributions resulting from field-induced lattice distortions. Such a lattice-mediated part can be split in frozen-cell ($\Omega_0^{-1}\boldsymbol{Z}^T\boldsymbol{K}^{-1}\boldsymbol{\zeta}$) and strain-mediated ($\boldsymbol{e}\boldsymbol{C}^{-1}\boldsymbol{h}$) terms. (The latter occurs at the linear level in piezoelectric piezomagnets [4].) Let us discuss how to engineer them.

The mechanisms contributing to $\boldsymbol{\alpha}^{\rm el}$ share the basic feature that the energy cost for polarizing the electrons is roughly given by the band gap. Hence, having a relatively small gap seems necessary to obtain very large effects, but this is detrimental to the insulating character of the material. Electronic FEs like $LuFe_2O_4$ [5] seem to fit this description, and will probably display the largest effects achievable based on electronic mechanisms.

The lattice-mediated part of the response is proportional to the fundamental electro- and magneto-structural couplings, i.e., to the changes of polarization and magnetization caused by atomic displacements (quantified, respectively, by the Born effective charges $\boldsymbol{Z}$ and the *magnetic strengths* $\boldsymbol{\zeta}$) or strain (quantified, respectively, by the piezoelectric and piezomagnetic stress tensors $\boldsymbol{e}$ and $\boldsymbol{h}$). The possibility to enhance the electro-structural couplings $\boldsymbol{Z}$ and $\boldsymbol{e}$ seems unpromising, as their magnitude is basically controlled by the nominal ionization charges and they are already anomalously large in most FE perovskites [3,6,7]. To increase the magneto-structural couplings $\boldsymbol{\zeta}$ or $\boldsymbol{h}$, one would typically need to use heavy magnetic species presenting strong spin-orbit effects. However, transition metals with relatively extended $4d$ and $5d$ orbitals tend to result in metallic states [8]. The insulating character can be obtained by using lanthanides, but at the expense of weak magnetic interactions associated with the localized $4f$ orbitals. Note that exchange-striction mechanisms have also been studied [9], but the ME couplings obtained so far are relatively small. Finally, a large orbital contribution to the ME response will typically require strong spin-orbit effects and *unquenched* magnetic moments, which seems generally incompatible with a robust insulating character [10]; we thus seem restricted to spin magnetism.

We are thus left with the tensors that quantify the energy cost associated to structural distortions, be it atomic displacements (the force-constant matrix $\boldsymbol{K}$) or cell strains (the relaxed-ion elastic constant tensor $\boldsymbol{C}$). Interestingly, many structural phase transitions are associated with the *softening* of the lattice, i.e., with a vanishingly small eigenvalue of $\boldsymbol{K}$ or $\boldsymbol{C}$. This is the case of soft-mode FEs, for which many strategies to tune the materials properties—by means of epitaxial strain [11], chemical substitution [12,13], etc.—have been demonstrated. Such property tuning usually implies controlling $\boldsymbol{K}$ or $\boldsymbol{C}$: For example, the large piezoelectric-strain response ($\boldsymbol{d} = \boldsymbol{e}\boldsymbol{C}^{-1}$) of $PbZr_{1-x}Ti_xO_3$ (PZT) results from the softening of $\boldsymbol{C}$; in $SrTiO_3$, the softness of $\boldsymbol{K}$ results in a large dielectric response ($\chi \sim \boldsymbol{Z}^T\boldsymbol{K}^{-1}\boldsymbol{Z}$). According to Eq. (1), structural softness will also result in large values of $\boldsymbol{\alpha}$ [14]. This is the strategy we explored.

Test case: $BiFeO_3$ *films.*—BFO is ideal to test this design strategy. Recent studies [11,15] show that under compressive epitaxial strain (001)-BFO films undergo a structural transition involving two FE phases. This suggests there is strain range within which BFO films might be structurally soft, thus having the potential to display large responses.

For our simulations we used the so-called "LDA + U" approach to density functional theory as implemented in the VASP package [16], the details being as in Ref. [4]. We used a 10-atom cell given in a Cartesian setting by: $\boldsymbol{a}_1 = (\delta_2, a+\delta_1, c)$, $\boldsymbol{a}_2 = (a+\delta_1, \delta_2, c)$, and $\boldsymbol{a}_3 = (a, a, 0)$. This cell is compatible with the atomic structure of the two FE phases of interest [11]: an "*R* phase" that is similar to the rhombohedral *R*3*c* phase of bulk BFO, and a "*T* phase" that resembles the tetragonal *P*4*mm* phase of $BiCoO_3$. More precisely, this cell allows for general FE and antiferrodistortive (AFD) distortions associated, respectively, to the Γ_4^- and R_4^+ representations of the reference space group $Pm\bar{3}m$. Because of the epitaxial mismatch in the $(001)_c$ Cartesian plane, these distortions will typically split into out-of-plane ($\Gamma_{4,z}^-$ and $R_{4,z}^+$) and in-plane ($\Gamma_{4,x}^- = \Gamma_{4,y}^-$ and $R_{4,x}^+ = R_{4,y}^+$) components, reflecting a monoclinic *Cc* symmetry. Note that the AFD distortions correspond to the O_6 octahedra *rotations* around $[001]_c$ ($R_{4,z}^+$) and *tilts* around $[110]_c$ ($R_{4,x}^+ = R_{4,y}^+$) usually discussed in the literature. Finally, the chosen cell is compatible with the magnetic order of both FE phases, which we checked to be *G*-type antiferromagnetic (G-AFM) in the strain range of interest [17]. For each value of the epitaxial strain ϵ [18], we ran constrained relaxations to find the equilibrium structure, determined the magnetic easy axis, and computed the response properties as in Ref. [4].

Figure 1 shows the computed $E(\epsilon)$ curves for the *R* and *T* phases. At variance with the study of Ref. [11], we were able to track the two phases up to their (meta)stability limits, thus locating the boundaries of the region within which they can coexist. We found that the *R* phase can occur up to an epitaxial compression of about -6%, and the *T* phase is predicted to occur for compressions above -3%. Beyond its (meta)stability limit, the *R* (*T*) phase relaxes into the *T* (*R*) phase in our simulations. We thus confirm the prediction of a first-order isosymmetric transition between the *R* and *T* phases [11], with an ideal transition point at $\epsilon \approx -4.4\%$ and an hysteretic behavior confined within the -6% to -3% region.

Our simulations allowed us to monitor the softening of the structural modes that result in the destabilization of the FE phases. Interestingly, both soft modes (sketched in Fig. 1) have a strong AFD character [19]: For the *T* phase, 93% of the mode eigenvector is AFD in nature (83% rotation and 10% tilt), and this mode accounts for 75% of the *T*-to-*R* transformation. For the *R* phase, 67% of the mode eigenvector is AFD (41% rotation and 26% tilt) and the FE component reaches 18% (12% and 6% of out-of-plane and in-plane distortions, respectively); this mode accounts for 97% of the *R*-to-*T* transition. Our results show that, while it is correct to describe the $R \leftrightarrow T$ transitions as FE-to-FE, the primary order parameter for them is actually AFD in nature. Note that this is consistent with the fact that the strongest structural instabilities of bulk BFO are AFD type.

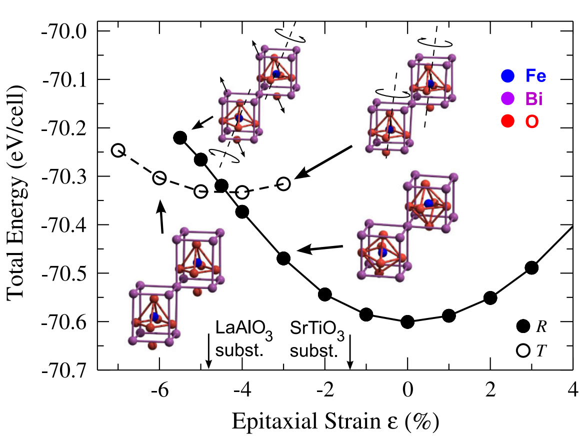

FIG. 1 (color online). Energy vs epitaxial strain for the *R* and *T* phases. Computed soft modes are sketched (see text).

Figure 2 summarizes how the properties of the *R* and *T* phases change as a function of ϵ. The results for the structure [panels (a) and (b)] and polarization [(panel (c)] show a tetragonalization of both phases as the epitaxial compression grows. The main differences between them are apparent: The *R* phase presents much stronger O_6 rotations and the *T* phase is characterized by a very large out-of-plane polar distortion. We can compare our results at $\epsilon = -4.8\%$ ($LaAlO_3$ substrate) with the experimental characterization of the *T* phase. The values measured at T_r are [15]: $c/a = 1.23$, $\mathcal{P}_z^s = 0.75\ \mathrm{C/m^2}$, and $d_{\mathrm{eff}} = 30$ pC/N. We obtained $c/a = 1.23$, $\mathcal{P}_z^s = 1.5\ \mathrm{C/m^2}$, and $d_{33} = 18$ pC/N for the *T* phase, and $c/a = 1.14$, $\mathcal{P}_z^s = 0.8\ \mathrm{C/m^2}$, and $d_{33} = 87$ pC/N for the *R* phase. As noted

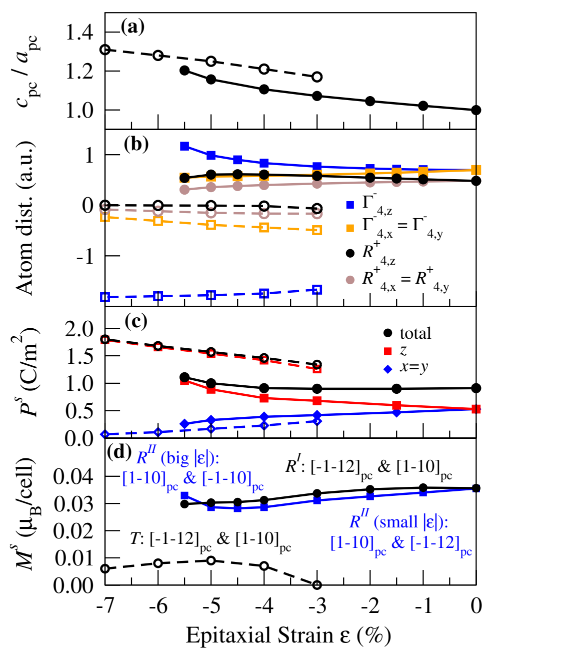

FIG. 2 (color online). Properties of the *R* (filled symbols, solid lines) and *T* (open, dashed) phases. Panel (a): Aspect ratio of the pseudocubic (pc) cell associated with relaxed structures. Panel (b): Atomic structure given as a set of distortions (in arbitrary units) of prototype $Pm\bar{3}m$ phase as obtained with the ISODISPLACE software [27]; data condensed by adding up contributions from isosymmetric modes; small contributions not associated with Γ_4^- or R_4^+ not shown; for clarity, *T*-phase results were chosen to be negative. Panels (c) and (d): Spontaneous polarization and magnetization. Easy axis and $\mathcal{M}^s$ directions indicated in (d); note that two *R* phases were considered (see text).

before [15], the measured $\mathcal{P}_z^s$ is surprisingly small; additionally, we found it is in (probably fortuitous) agreement with our result for the R phase.

Figure 2(d) summarizes our results for the magnetic structure [20]. We found that the magnetic ground state of the R phase changes from R^I to R^{II} [notation from Fig. 2(d)] for compressions above -5%. The computed spontaneous magnetization $\mathcal{M}^s$, which stems from the canting of the G-AFM spin structure, is significant only for the R phases, and tends to decrease for increasing compression. This probably reflects the fact that the AFD distortion—which tends to diminish with increasing compression for the R phases and is small for the T phase—is necessary for the spin canting to exist in the kind of G-AFM ground states we obtained [22].

Finally, Fig. 3 shows two representative responses: piezoelectric (d_{33}) and magnetoelectric ($\alpha_{\max}$, as defined in the figure caption). For all phases, the responses increase as we approach the stability limit. We explicitly checked this enhancement is driven by structural softness: a mode-by-mode decomposition [4] of the frozen-cell ME response showed that the instability modes become dominant near the correspnding coexistence boundary. This is most apparent in the frozen-cell ME response of the R phases at $\epsilon = -6\%$ [23], which displays a large enhancement associated to a very soft $\boldsymbol{K}$ eigenvalue of 0.3 eV/Å^2 (to be compared with a lowest-lying $\boldsymbol{K}$ eigenvalue of 3.2 eV/Å^2 for bulk BFO). Note that a significant part of the total response is strain-mediated, especially in the case of R^{II}.

The dominant AFD character of the soft modes is key to understand the computed responses. First, the weakly polar soft modes couple weakly with an applied electric field.

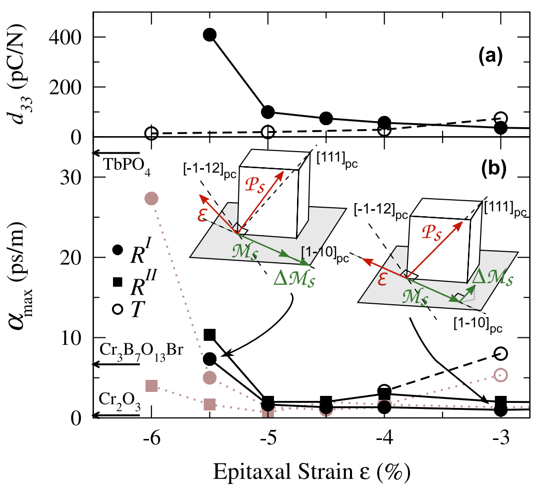

FIG. 3 (color online). Piezoelectric (a) and ME (b) responses of the R (filled symbols, solid lines) and T (open, dashed) phases. Panel (b): $\alpha_{\max}$ is the square root of the largest eigenvalue of the quartic form $\boldsymbol{\alpha}^T\boldsymbol{\alpha}$. Frozen-cell (light colored) and full (dark) lattice responses are given. Insets sketch $\alpha_{\max}$ response of R^I (see text) at small and strong epitaxial compression. $\alpha_{\max}$ for three representative MEs are indicated (data taken from Ref. [21]; note 1 ps/m $= 3 \times 10^{-4}$ Gaussian units).

Hence, the instability modes need to become very soft to dominate the responses, and the softness-driven enhancement (strictly speaking, *divergence*) is confined to relatively narrow regions of epitaxial strain close to the coexistence boundaries. To better appreciate this weakly polar nature, note that the electric polarity [24] of the R phase soft mode has a largest component of about 2.2$|e|$, e being the electron charge, while strongly polar modes for the same state reach values of 7.4$|e|$. For the T phase, the largest component of the soft-mode electric polarity barely reaches 1$|e|$.

Second, the marked AFD character of the soft mode of the R phase determines the nature of the strongest ME effects obtained, which correspond to R^I. The results are sketched in Fig. 3(b): For small compressions, $\alpha_{\max}$ is associated to the development of a magnetization $\Delta\mathcal{M}$ perpendicular to $\mathcal{M}^s$, as in bulk BFO [4]; the dominant modes do not present any AFD component. For strong compressions, $\alpha_{\max}$ corresponds to a change in the magnitude (not direction) of $\mathcal{M}^s$. That response is dominated by a weakly polar soft mode with a large AFD component; its effect in the magnitude of the canted magnetic moment is thus natural, as such a canting was shown to be proportional to the amplitude of the O_6 rotations [22]. Finally, note that the computed soft modes do not display particularly large magnetic polarities $\boldsymbol{p}^m$ [24]: a largest value of 2×10^{-3} Bohr magnetons (μ_B) was obtained for R^I, while values of about $6 \times 10^{-3}\mu_B$ were obtained for the more magnetically active modes. We observed the largest $\boldsymbol{p}^m$'s tend to correspond to modes characterized by Fe displacements.

We have thus shown that structural softness results in a large enhancement of the ME response of the BFO films, even if the somewhat inappropriate character of the observed soft modes (i.e., their relatively small electric and magnetic polarities) is detrimental to the effect. To put our results in perspective, we have indicated in Fig. 3(b) the measured ME response of several representative materials (see Table 1.5.8.2 of Ref. [21]): $TbPO_4$ (strongest single-phase magnetoelectric), $Co_3B_7O_{13}Br$ (strongest transition-metal magnetoelectric), and Cr_2O_3 (a material with typically small $\boldsymbol{\alpha}$). Note that the indicated α's correspond to temperatures slightly below the magnetic ordering transition, where the ME effect is strongly enhanced. Remarkably, the responses of the R and T phases of BFO films, which we computed at $T = 0$ K, are comparable to these largest of α's for a significant range of epitaxial strains.

As to the practical implications of our results for BFO, one should first note that, for any value of ϵ, the predicted stable phase is not soft enough to have a strong ME response. Nevertheless, as regards the real BFO films at T_r, the large reactivity to electric fields observed by Zeches *et al.* [11] in the samples presenting a *mixed R-T* state is clearly suggestive of the structural softness discussed here, and might thus be accompanied by large ME effects. Additionally, note that BFO-based solid solutions may provide a more convenient alternative to soften the BFO lattice. Indeed, enhanced electromechanical responses have been observed in compounds in which a rare earth substitutes for Bi [13], and the substitution of Fe by Co [25] has been shown to result in a monoclinic phase that acts as a *structural bridge* between $BiCoO_3$'s T and $BiFeO_3$'s R phases, as in strong piezoelectric PZT [12]. Our results clearly suggest that such compounds will present very large ME respones.

Let us stress that none of BFO's peculiarities (e.g., the occurrence of AFD distortions or spin canting) seems essential for the softness-driven enhancement. Thus, for example, a ME response based on nonrelativistic exchange-strictive mechanisms [9] will be enhanced if the lattice softens. Further, collinear ferromagnetic phases like those predicted to occur in strain-engineered $SrMnO_3$ films [26] seem good candidates to display a large ME response driven by soft lattice distortions.

In summary, we have shown that inducing structural softness constitutes a promising and general strategy to obtain very large ME responses. We hope our results will motivate the experimental exploration of this strategy.

Work funded by the EC-FP6 (Grant No. STREP_FP6-03321) and the Spanish DGI (Grant No. FIS2006-12117-C04-01 and No. CSD2007-00041). We used the BSC-CNS and CESGA Supercomputing Centers. We thank J. Fontcuberta and F. Sánchez for useful discussions.

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[18] We constrained the cell in-plane area by imposing $a(a + \delta_1 - \delta_2) = [a_0(1 + \epsilon)]^2$, where a_0 is the computed pseudocubic lattice constant of the $R3c$ phase of bulk BFO. Thus, an in-plane skewing of the cell was allowed, but this distortion was found to be small. The epitaxial constraint was imposed in the response calculations by setting to infinity the corresponding elastic constants. The relaxed structures, as well as the $\boldsymbol{K}$, $\boldsymbol{C}$, $\boldsymbol{Z}$, $\boldsymbol{e}$ tensors and their derived quantities, were found to be essentially independent of the magnetic easy axis orientation.

[19] The obtained soft modes are fully symmetric, i.e., they preserve the Cc symmetry of the R and T phases as compatible with isosymmetric $R \leftrightarrow T$ transitions. To analyze their character, we expressed them in the basis of the eigenmodes of $\boldsymbol{K}$ for cubic $Pm\bar{3}m$ BFO, where the FE (Γ_4^-) and AFD (R_4^+) components are distinct by symmetry. For these manipulations, and for the analysis of the character of the $R \leftrightarrow T$ transitions, we worked with relative atomic positions, thus ignoring cell changes.

[20] We checked that the computed $\mathcal{M}^s$'s lie along directions compatible with the magnetic class [21]. In the case of R^{II}, the easy axis is $[1\bar{1}0]_{pc}$ (i.e., perpendicular to the symmetry plane of Cc) and the magnetic class m', implying that $\mathcal{M}^s$ must be within the $(1\bar{1}0)_{pc}$ plane. We found $\mathcal{M}^s$ rotates from $[\bar{1}\,\bar{1}\,2]_{pc}$ to $[\bar{1}\,\bar{1}\,0]_{pc}$ (see Fig. 2).

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[24] If $\boldsymbol{v}_s$ is the normalized soft-mode eigenvector, its dielectric (magnetic) polarity is $\boldsymbol{p}_s^d = \boldsymbol{v}_s \boldsymbol{Z}$ ($\boldsymbol{p}_s^m = \boldsymbol{v}_s \boldsymbol{\zeta}$) [4].

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