# Magnetoelectric Response of Multiferroic BiFeO$_3$ and Related Materials from First-Principles Calculations

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(Received 30 July 2009; published 31 December 2009)

We present a first-principles scheme for computing the magnetoelectric response of multiferroics. We apply our method to BiFeO$_3$ (BFO) and related compounds in which Fe is substituted by other magnetic species. We show that under certain relevant conditions—i.e., in the absence of incommensurate spin modulation, as in BFO thin films and some BFO-based solid solutions—these materials display a large linear magnetoelectric response. Our calculations reveal the atomistic origin of the coupling and allow us to identify the most promising strategies to enhance it.

DOI: 10.1103/PhysRevLett.103.267205 PACS numbers: 75.80.+q, 71.15.Mb

Magnetoelectric (ME) multiferroics present coupled electric and magnetic orders [1], which may allow the development of a variety of magnetic devices whose behavior would be *switchable* by application of a voltage. The experimental search for robust room-temperature ($T_{\text{room}}$) multiferroics is proving to be a major challenge. The first-principles contribution to this effort is quickly increasing, as shown by recent predictions of new materials [2] and novel ME coupling mechanisms [3]. Yet, many key issues remain to be addressed theoretically, as even the ME response of the most promising systems (e.g., BiFeO$_3$ [4]) still needs to be characterized and understood in detail. Here we describe a method for *ab initio* computations of the ME response of multiferroics, tackling the strain-mediated contributions that typically exist in these materials. We apply our method to BiFeO$_3$ and related compounds.

*Methodology.*—The response of a linear magnetoelectric that is not multiferroic—and is thus paraelectric—can be split in two contributions [5]: a purely electronic one and an ionic one. The ionic part accounts for the structural response to an electric (magnetic) field and the resulting change of magnetization (polarization). When the material is also multiferroic—and thus piezoelectric—there may be a third contribution to the linear ME response: it can be shown from symmetry arguments [6] that multiferroics will typically be piezomagnetic, the combination of piezoelectricity and piezomagnetism resulting in a new ME coupling. To model such effects, we have generalized to the ME case the formalism that Wu, Vanderbilt, and Hamann (WVH) [8] introduced for a systematic treatment of the dielectric and piezoelectric responses.

Let us consider the energy per underformed unit cell volume of a multiferroic crystal, $E(u, \eta)$, as a function of the displacements $u_m$ of atoms away from their equilibrium positions and the homogeneous strains $\eta_j$. In the presence of applied electric ($\mathcal{E}_\alpha$) and magnetic ($\mathcal{H}_\mu$) fields, this energy can be Legendre transformed [8,9] into an *electric-magnetic enthalpy* $F(u, \eta; \mathcal{E}, \mathcal{H})$. We write this enthalpy, expanded to second-order around the zero-field equilibrium structure, as

$$\begin{aligned} F = {} & F_0 + A_\alpha \mathcal{E}_\alpha + A_\mu \mathcal{H}_\mu + \tfrac{1}{2} B_{mn} u_m u_n + \tfrac{1}{2} B_{\alpha\beta} \mathcal{E}_\alpha \mathcal{E}_\beta \\ & + \tfrac{1}{2} B_{\mu\nu} \mathcal{H}_\mu \mathcal{H}_\nu + \tfrac{1}{2} B_{jk} \eta_j \eta_k + B_{m\alpha} u_m \mathcal{E}_\alpha \\ & + B_{m\mu} u_m \mathcal{H}_\mu + B_{mj} u_m \eta_j + B_{\alpha\mu} \mathcal{E}_\alpha \mathcal{H}_\mu \\ & + B_{\alpha j} \mathcal{E}_\alpha \eta_j + B_{\mu j} \mathcal{H}_\mu \eta_j, \end{aligned} \tag{1}$$

assuming summation over repeated indices. The equilibrium condition implies that the terms linear in $u_m$ and $\eta_j$ are zero. The term $A_\alpha = -\mathcal{P}^S_\alpha$ ($A_\mu = -\mathcal{M}^S_\mu$) is the spontaneous polarization (magnetization). The second derivatives of Eq. (1) correspond to well-known physical quantities, such as the purely electronic part of the electric (magnetic) susceptibility $\hat{\bar{\chi}}_{\alpha\beta} = -B_{\alpha\beta}$ ($\hat{\bar{\chi}}_{\mu\nu} = -B_{\mu\nu}$), the force constant matrix $K_{mn} = \Omega_0 B_{mn}$, the frozen-ion elastic tensor $\bar{C}_{jk} = B_{jk}$, the Born dynamical effective charges $Z_{m\alpha} = -\Omega_0 B_{m\alpha}$, the force-response internal strain tensor $\Lambda_{mj} = -\Omega_0 B_{mj}$, or the frozen-ion piezoelectric stress tensor $\bar{e}_{\alpha j} = -B_{\alpha j}$; $\Omega_0$ is the unit cell volume and the bar (hat) stands for *frozen ion* (*frozen cell*). Additionally, the purely electronic ME response is

$$\hat{\bar{\alpha}}_{\alpha\mu} = -\frac{\partial^2 F}{\partial \mathcal{E}_\alpha \partial \mathcal{H}_\mu}\bigg|_{u,\eta} = \frac{\partial \mathcal{P}_\alpha}{\partial \mathcal{H}_\mu}\bigg|_{u,\eta} = -B_{\alpha\mu}, \tag{2}$$

and the frozen-ion piezomagnetic stress tensor is

$$\bar{h}_{\mu j} = -\frac{\partial^2 F}{\partial \mathcal{H}_\mu \partial \eta_j}\bigg|_{u,\mathcal{E}} = \frac{\partial \mathcal{M}_\mu}{\partial \eta_j}\bigg|_{u,\mathcal{E}} = -B_{\mu j}. \tag{3}$$

Lastly, the magnetization change driven by an atomic displacement is

$$\zeta_{m\mu} = -\Omega_0 \frac{\partial^2 F}{\partial u_m \partial \mathcal{H}_\mu}\bigg|_{\eta,\mathcal{E}} = -\Omega_0 B_{m\mu}. \tag{4}$$

The tensors describing the response to static fields should account for the field-induced ionic relaxation. To compute such *relaxed-ion* quantities, we introduce the functional $\tilde{F}(\eta; \mathcal{E}, \mathcal{H}) = \min_u F(u, \eta; \mathcal{E}, \mathcal{H})$, which is obtained from Eq. (1) by replacing

$$u_m = -(B)^{-1}_{mn}(B_{n\alpha}\mathcal{E}_\alpha + B_{n\mu}H_\mu + B_{nj}\eta_j). \tag{5}$$

$\tilde F$ can be written in a form analogous to Eq. (1) with $\tilde B$ coefficients that are combinations of the original $B$'s. We can then obtain, for example, the piezomagnetic stress tensor

$$\begin{aligned} h_{\mu j} &= -\frac{\partial^2 \tilde F}{\partial \mathcal{H}_\mu \partial \eta_j}\bigg|_{\mathcal{E}} = -\tilde B_{\mu j} = -B_{\mu j} + B_{m\mu}(B)^{-1}_{mn}B_{nj} \\ &= \bar h_{\mu j} + \Omega_0^{-1}\zeta_{m\mu}(K^{-1})_{mn}\Lambda_{nj} \end{aligned} \tag{6}$$

or the frozen-cell ME tensor

$$\hat\alpha_{\alpha\mu} = -\frac{\partial^2 \tilde F}{\partial \mathcal{E}_\alpha \partial \mathcal{H}_\mu}\bigg|_{\eta} = \hat{\hat\alpha}_{\alpha\mu} + \Omega_0^{-1}Z_{m\alpha}(K^{-1})_{mn}\zeta_{n\mu}. \tag{7}$$

Finally, in order to compute the full ME response, we go one step beyond WVH and introduce $\mathcal{F}(\mathcal{E}, \mathcal{H}) = \min_\eta \tilde F(\eta; \mathcal{E}, \mathcal{H})$, from which we derive our main result:

$$\begin{aligned} \alpha_{\alpha\mu} &= -\frac{\partial^2 \mathcal{F}}{\partial \mathcal{E}_\alpha \partial \mathcal{H}_\mu} \\ &= \hat{\hat\alpha}_{\alpha\mu} + \Omega_0^{-1}Z_{m\alpha}(K^{-1})_{mn}\zeta_{n\mu} + e_{\alpha j}(C^{-1})_{jk}h_{\mu k}. \end{aligned} \tag{8}$$

We would like our theory to describe the so-called *proper* piezoelectric effects. WVH dealt with this issue by introducing suitably rescaled electric fields and polarizations [8], an approach that has been further developed in Ref. [9]. Equivalently, the desired result is obtained if the $B_{\alpha j}$ coefficients of Eq. (1) are computed by finite differences as described in Ref. [10]. Interestingly, the proper versus improper distinction applies to the piezomagnetic case too, a fact that has seemingly passed unnoticed so far. Indeed, we want our proper $B_{\mu j}$ coefficients to be such that (i) $\mathcal{H}$-induced rotations of the sample do not contribute to the response and (ii) a mere change in the unit cell volume has no magnetic effect. The former requirement is easily accomplished by working only with the symmetric part of the strain tensor, and we comply with the latter by computing the $B_{\mu j}$ coefficients from strain-induced changes in the magnetic moment *per* cell, as opposed to changes in the magnetization [11].

*Application to* $BiFeO_3$ *and related materials.*—We applied our method to $BiFeO_3$ (BFO), arguably the most promising multiferroic. We simulated BFO with the magnetic structure of the systems that are most relevant for applications, i.e., BFO thin films and solid solutions in which Bi is partly substituted by a lanthanide to improve the dielectric properties. In such cases, BFO loses the spin cycloid that occurs in bulk samples [12–14] and presents a canted $G$-type antiferromagnetic (AFM) spin arrangement. The magnetic easy axis lies within the plane perpendicular to the polar direction [$xy$ in Fig. 1(a), $z$ being parallel to $\mathcal{P}^S$ and corresponding to the $[111]_{pc}$ pseudocubic direction] [13,15], and the corresponding magnetic space group allows for a linear ME response [16]. Indeed, there is experimental evidence of such a linear ME effect [17,18], but we still lack a detailed and well-established characterization.

We also studied situations in which, maintaining the 10-atom cell and basic structure of BFO, Fe is substituted by other magnetic species. In particular, we considered Fe → Cr, Fe → Mn, and Fe → Co substitutions, as well as Fe → (Fe, Cr) and Fe → (Mn, Ni) double perovskites [19]. Note that, except for $Bi_2FeCrO_6$, none of the studied substitutions corresponds to thermodynamically stable phases. The purpose of considering such fictitious compounds was to identify chemical trends in the magnitude of the ME effects.

For the calculations we used the projector augmented wave approach to density functional theory, within the so-called "LDA + $U$" approximation, as implemented in the VIENNA *ab initio* simulation package [20]. For all of the compositions studied, we proceeded as follows: taking the usual atomic and magnetic structure of rhombohedral BFO as a starting point, we relaxed the system to find a well-defined energy minimum. This energy minimization included a careful search for the magnetic easy axis. Having identified the equilibrium state, we computed the coefficients in Eq. (1) by finite differences. All of the calculations were fully self-consistent, allowed for noncollinear magnetism, and included spin-orbit couplings. We neglected orbital magnetization as well as the purely electronic ME response $\hat{\hat\alpha}$, which is likely to be relatively small [21], especially for materials with a significant structural response to electric fields.

Table I summarizes our results and Fig. 1(a) sketches the $\mathcal{E}$-induced spin canting that underlies the computed effects. The obtained ME tensors satisfy symmetry relationships

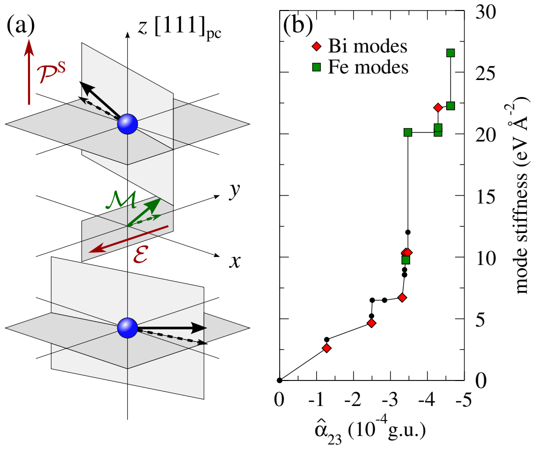

FIG. 1 (color online). Panel (a): sketch of the response associated to $\alpha_{23}$ of BFO. Only the two Fe atoms in the usual (rhombohedral) cell of BFO are shown. In equilibrium (dashed arrows), the spin of the Fe ions lies on the $xy$ plane; the easy axis is $x$ and a small canting results in a net $\mathcal{M}^S_y$. When $\mathcal{E}_y$ is applied we obtain an additional canting and a nonzero $\mathcal{M}_z$ (solid arrows). Panel (b): cumulative plot for the $\hat\alpha_{23}$ coefficient of BFO (see text). Modes dominated by Bi (◆) and Fe (■) displacements are highlighted.

within the calculation accuracy; e.g., for $BiCrO_3$ we got $\alpha_{12} = -\alpha_{21}$, as expected for the $3m$ magnetic point group [7]. Interestingly, the largest ME coefficients obtained share the following two features: (i) the applied $\mathcal{E}$ is perpendicular to $\mathcal{P}^S$, which reflects the *easy-polarization-rotation* mechanism that determines the largest electromechanical responses in ferroelectrics [22]; (ii) the change in $\mathcal{M}$ is perpendicular to the direction of the easy axis, which is a signature of spin canting and an underlying spin-orbit mechanism. In contrast, many symmetry-allowed coefficients were computed to be essentially null, which reflects (i) the structural hardness of specific directions and (ii) the energy cost of changing the magnetic moment along the direction of the easy axis (which would typically require charge transfer between magnetic ions [5]).

For all compounds, the full ME response is bigger than the frozen-cell effect, the increase being significant in $BiCrO_3$, $BiMnO_3$, and $BiCoO_3$. To illustrate how the strain-mediated response operates, we consider the representative case of the $\alpha_{12}$ coefficient of $BiCrO_3$. There, the largest strain response to $\mathcal{E}_1$ is associated with the shear $\eta_5$, as quantified by the *piezoelectric strain* coefficient $d_{15} = e_{1j}(C^{-1})_{j5} = 15$ pC/N. The resulting change in $\mathcal{M}_2$ is quantified by the piezomagnetic stress coefficient $h_{25} = -5 \times 10^4$ A/m. This leads to a strain-mediated contribution to the ME response of about $-3 \times 10^{-4}$ g.u.

Our calculations allow us to identify the atomic relaxation mechanisms that mediate the ME response. Let us consider first the frozen-cell ME tensor [Eq. (7)], whose lattice part can be expressed in terms of the eigenmodes of $K$ as $\Omega_0^{-1} p^d_{s\alpha} \kappa_s^{-1} p^m_{s\mu}$. Here, $\kappa_s$ is the mode eigenvalue or *stiffness*, and $p^d_{s\alpha}$ and $p^m_{s\mu}$ are, respectively, the dielectric and magnetic polarities introduced in Ref. [5]. This expression allows us to make a cumulative plot as the one shown in Fig. 1(b) for $\hat{\alpha}_{23}$ of BFO. Clearly, only two sets of modes contribute significantly: (i) low-lying Bi-dominated modes with a relatively small magnetic polarity (~78% of the response) and (ii) high-energy Fe-dominated modes that involve a relatively large change in $\mathcal{M}$. We can thus conclude that the ME response is largely driven by Bi modes that do not involve the magnetic species significantly, a result that applies to all of the studied compounds. The role of Bi is also preeminent in the strain-mediated part of the response, the largest $B_{mj}$ couplings being unequivocally associated with Bi.

The work of Ref. [23] allows us to compare theory and experiment for BFO. The authors studied the bulk material under magnetic fields up to 25 T, which allowed them to eliminate the spin cycloid and reach a phase that resembles the one we have simulated. One can thus extrapolate the $\mathcal{M}(\mathcal{H})$ curve measured within the high-field phase back to $\mathcal{H} = 0$ and estimate the magnetization at zero field. The result is 0.028 $\mu_B$/cell, in remarkable agreement with our computed 0.036 $\mu_B$/cell. Further, the magnitude of the ME response in the high-field phase is about $4 \times 10^{-4}$ g.u. at 10 K, again in excellent agreement with our computed $5 \times 10^{-4}$ g.u. While this comparison is not fully justified, it certainly supports the physical soundness of our results. Comparing our theory with measurements of BFO thin films [17] is unfortunately not possible, as the studied systems display effects (e.g., very large net magnetic moments and possible presence of $Fe^{2+}$) that clearly do not correspond to our simulations.

To put our results in perspective, note that the largest ME responses measured for transition-metal compounds correspond to boracites, with $\alpha_{\max} = 20 \times 10^{-4}$ g.u. for $Co_3B_7O_{13}Br$ (see Table 1.5.8.2 of Ref. [7]). Larger responses are observed in rare earth compounds, the greatest one being $\alpha_{\max} = 100 \times 10^{-4}$ g.u. for $TbPO_4$. It is important to realize, though, that these maximum $\alpha$s correspond to (very low) temperatures slightly below the magnetic ordering transition (17 K for $Co_3B_7O_{13}Br$ and 2.2 K for $TbPO_4$ [7]), where the ME effect is strongly enhanced. In contrast, the response of BFO computed at 0 K is of the same order of magnitude as the $\alpha_{\max}$s of boracites, is expected to grow with $T$ [24], and should occur at $T_{\text{room}}$ and above. Hence, BFO is clearly a unique, very promising material.

Interestingly, from a materials-design perspective one could say that BFO is rather unsatisfactory for several reasons. (1) The distortions mediating the ME effect are dominated by nonmagnetic ions. (2) These materials are

TABLE I. Top: frozen-cell and full ME tensors for three representative cases. Results given in $10^{-4}$ Gaussian units (g.u.). $Bi_2FeCrO_6$ has nearly $R3$ symmetry, except for a tiny spin canting. Dots indicate coefficients that are zero by symmetry. Bottom: maximum ME response, as quantified by square root of largest eigenvalue of $\alpha^t \alpha$, for all considered substitutions.

| | $BiFeO_3$ | $Bi_2FeCrO_6$ | $BiCrO_3$ |
|---|---|---|---|
| Group/Easy axis/$\mathcal{M}(\mu_B/\text{cell})$ | $Bb'/x/0.036 \parallel y$ | $\sim R3/z/0.002 \parallel y, -2 \parallel z$ | $R3c/z/0$ |
| $\hat{\alpha}$, $\alpha$ | $\begin{bmatrix} 0 & . & . \\ . & 0 & -5 \\ . & 0 & 0 \end{bmatrix}\begin{bmatrix} 0 & . & . \\ . & 1 & -5 \\ . & 0 & 0 \end{bmatrix}$ | $\begin{bmatrix} -4 & -12 & . \\ 9 & -4 & . \\ . & . & 0 \end{bmatrix}\begin{bmatrix} -5 & -13 & . \\ 9 & -6 & . \\ . & . & 0 \end{bmatrix}$ | $\begin{bmatrix} . & -4 & . \\ 4 & . & . \\ . & . & . \end{bmatrix}\begin{bmatrix} . & -8 & . \\ 8 & . & . \\ . & . & . \end{bmatrix}$ |
| | (unique axis $x$) | (standard setting) | (standard setting) |

| Fe → | Fe | (Fe, Cr) | Cr | Mn | Co | (Mn, Ni) |
|---|---|---|---|---|---|---|
| $\alpha_{\max}(\hat{\alpha}_{\max})$ | 5(5) | 14(13) | 8(4) | 15(11) | 6(2) | 3(3) |

quite stiff, as reflected by the relatively small piezoelectric and lattice-mediated dielectric responses: the largest ones obtained were, respectively, $d_{\mathrm{max}} \approx 60$ pC/N for $\mathrm{BiMnO_3}$ and $\epsilon^{\mathrm{latt}}_{\mathrm{max}} \approx 45$ for $\mathrm{BiCoO_3}$, while for prototype ferroelectric $\mathrm{BaTiO_3}$ one gets $d_{\mathrm{max}} \approx 250$ pC/N and $\epsilon^{\mathrm{latt}}_{\mathrm{max}} \approx 60$ [8]. (3) These materials are poor piezomagnets: for the so-called *piezomagnetic strain tensor* $g_{\mu j} = h_{\mu k}(C^{-1})_{jk}$ we obtained a maximum value of $0.4 \times 10^{-10}$ $\mathrm{Oe}^{-1}$ for $\mathrm{BiCrO_3}$, which is about 1 order of magnitude smaller than what is typical in transition-metal compounds (see Table 1.5.7.2 of Ref. [7]).

If we were able to improve on some of these aspects, BFO might become an excellent magnetoelectric. Our results indicate that the ME response of the studied compounds owes its relatively large value to the structural response to electric fields. The secondary role of the magnetic effects is clearly reflected in the fact that the magnitude of $\alpha_{\mathrm{max}}$s (Table I) does not correlate with the magnitude of the spin-orbit coupling of the considered magnetic species, which rules out chemical substitution of iron as a direct way to enhance the ME response. It seems more promising to try to increase BFO's electromechanical responses, which might be achieved, for example, in (i) BFO thin films strain engineered to be monoclinic (as opposed to rhombohedral), since monoclinicity is usually accompanied by structural softness [22], or (ii) $\mathrm{Bi_{1-x}La_xFeO_3}$ solid solutions where structural transitions occur for small La concentrations [14]. We hope our work will stimulate detailed experimental studies of these and similar systems.

This is work funded by MaCoMuFi (Grant No. STREP_FP6-03321). It also received support from the Spanish Government (Grants No. FIS2006-12117-C04-01 and No. CSD2007-00041). Use was made of the Barcelona (BSC-CNS) and Galicia (CESGA) Supercomputing Centers. We thank D. Vanderbilt for insightful comments.

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