Magnetoelectric Response of Multiferroic BiFeO$_3$ and Related Materials

Jacek C. Wojdel and Jorge Íñiguez

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

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 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.

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Magnetoelectric (ME) multiferroics present coupled electric and magnetic orders, which may allow the development of a variety of magnetic devices, from memories to spin filters, whose behavior would be switchable by application of a voltage. The experimental search for robust room-temperature ($T_{\text{room}}$) multiferroics is proving a major challenge. The first-principles contribution to this effort is quickly increasing, as shown by recent predictions of new materials and novel ME coupling mechanisms. Yet, many key issues remain to be addressed theoretically, as even the ME response of the most promising systems (e.g., thin films of BiFeO$_3$) 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: 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 linear magnetoelectric is multiferroic – and thus ferroelectric – there is a third contribution associated to the piezoelectric response to the electric field. Indeed, it can be shown that all commensurate multiferroics must be piezomagnetic, as the symmetries that preclude piezomagnetism are broken in such systems. Hence, the combination of piezelectricity and piezomagnetism in multiferroics results in a strain-mediated contribution to the linear ME response.

In order to model such effects, we have generalized to the magnetoelectric case the formalism that Wu, Vanderbilt, and Hamann (WVH in the following) introduced for a systematic ab initio treatment of dielectric and piezoelectric responses. Let us consider how the energy of a multiferroic crystal varies as a function of the following perturbations: displacements $u_m$ of atoms away from their equilibrium positions, homogeneous strains $\eta_j$, and applied electric ($E$) and magnetic ($H$) fields. Here, $m$ is a composite label that runs over the atoms in the unit cell and displacement directions, $j$ runs from 1 to 6 in Voigt notation, and $\alpha$ and $\mu$ are Cartesian directions.

We write the energy per undeformed unit cell volume of the multiferroic crystal, expanded to second order around its zero-field equilibrium structure, as

$$E = E_0 + A_\alpha E_\alpha + A_{\mu H_\mu} + \frac{1}{2} B_{\alpha m n \mu} u_m u_n + \frac{1}{2} B_{\alpha \beta} E_\alpha E_\beta$$

$$+ \frac{1}{2} B_{\alpha \mu} H_\alpha H_\mu + \frac{1}{2} B_{\mu j \eta k} \eta_j \eta_k + B_{\alpha m u} E_\alpha + B_{\mu m \mu} H_\mu$$

$$+ B_{\alpha j m} \eta_j + B_{\alpha \mu} E_\alpha H_\mu + B_{\mu j} E_\mu \eta_j + B_{\mu j} H_\mu \eta_j,$$

assuming summation over repeated indexes. The equilibrium condition implies the terms linear in $u_m$ and $\eta_j$ are zero; the term $A_\alpha = -P_{\alpha 0} S$ is the spontaneous polarization (magnetization). The second derivatives of Eq. (1) correspond to well-known physical quantities, such as the force constant matrix $K_{mn} = \Omega_0 B_{mn}$, the frozen-ion elastic tensor $C_{jk} = B_{jk}$, the Born dynamical effective charges $Z_{m\alpha} = -\Omega_0 B_{m\alpha}$, the force-response internal strain tensor $A_{\alpha j m} = -\Omega_0 B_{\alpha j m}$, or the frozen-ion piezoelectric stress tensor $\tilde{\varepsilon}_{\alpha j} = -B_{\alpha j}$, where $\Omega_0$ is the unit cell volume and the bar stands for frozen-ion. Additionally, the purely electronic ME response is

$$\partial \alpha_{\alpha \mu} = -\frac{\partial^2 E}{\partial E_\alpha \partial H_\mu} \bigg|_{u, \eta} \quad \partial \alpha_{\mu j} = -\frac{\partial^2 E}{\partial H_\mu \partial \eta_j} \bigg|_{u, \varepsilon} \quad -B_{\alpha \mu} \quad .$$

where the hat stands for frozen-cell. The frozen-ion piezomagnetic stress tensor is

$$\tilde{\eta}_{\mu j} = -\frac{\partial^2 E}{\partial H_\mu \partial \eta_j} \bigg|_{u, \varepsilon} \quad \partial \mu_{\mu j} = -B_{\mu j} \quad .$$

Lastly, the magnetization change driven by an atomic displacement is

$$\zeta_{\alpha \mu} = -\Omega_0 \frac{\partial^2 E}{\partial u_m \partial H_\mu} \bigg|_{\eta, \varepsilon} = -\Omega_0 B_{\alpha \mu} .$$

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 energy $\tilde{E}(E, H, \eta) = \min_u E(u, E, H, \eta)$, which is obtained from Eq. (1) by replacing

$$u_m = -(B)^{-1}_{mn} (B_{mn} E_\alpha + B_{n\mu} H_\mu + B_{nm} \eta_j) .$$

$\tilde{E}$ can be written in a form analogous to Eq. (1), with $\tilde{B}$ coefficients that are combinations of the original $B$'s. By
computing the second derivatives of $\tilde{E}$ we can obtain, for example, the piezomagnetic stress tensor
\[
h_{\mu j} = \frac{\partial^2 \tilde{E}}{\partial \delta \alpha_{\mu j}} = -B_{\mu j} + B_{m \mu} (B)_{m n} B_{n j} - \Omega_0^{-1} \zeta_{m j} (K^{-1})_{m n} \Lambda_{n j}
\]
(6)
or the frozen-cell ME tensor
\[
\hat{\alpha}_{\alpha \mu} = -\frac{\partial^2 \tilde{E}}{\partial \epsilon_{\alpha \mu}} = \hat{\alpha}_{\alpha \mu} + \Omega_0^{-1} Z_{m a} (K^{-1})_{m n} \zeta_{n a}.
\]
(7)

Finally, in order to compute the full ME response we go one step beyond WVH and introduce the energy $\epsilon(\mathcal{E}, \mathcal{H}) = \min_{\delta \epsilon} \tilde{E}(\mathcal{E}, \mathcal{H}, \eta)$, from which we derive
\[
\alpha_{\alpha \mu} = -\frac{\partial^2 \epsilon}{\partial \epsilon_{\alpha \mu}} = \hat{\alpha}_{\alpha \mu} + \Omega_0^{-1} Z_{m a} (K^{-1})_{m n} \zeta_{n a} + \epsilon_{\alpha j} (C^{-1})_{j k} h_{n k}.
\]
(8)

Note that, except for the purely electronic $\hat{\alpha}_{\alpha \mu}$, all the terms in Eq. (8) can be obtained from finite difference calculations that do not require the simulation of applied fields. Thus, the present formalism brings the study of ME effects in multiferroics within the scope of the most widely used Density Functional Theory (DFT) codes.

Finally, let us remark 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 [13]. Equivalently, the desired result is obtained if the $B_{\alpha j}$ coefficients of Eq. (1) are computed by finite differences as described in Ref. [14]. Interestingly, the proper vs improper distinction applies to the piezomagnetic case too, a fact that has seemingly remained unnoticed. Indeed, we want our proper $B_{\alpha j}$ 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 $B_{\alpha j}$ coefficients from strain-induced changes in the magnetic moment per cell, as opposed to changes in the magnetization [13].

Application to BiFeO₃ and related materials.– We applied our method to BiFeO₃ (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 looses the spin cycloid that occurs in bulk samples [16, 17, 18] 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. 1a), $z$ being parallel to $P^S$ and corresponding to the [111]$_{PC}$ pseudocubic direction [17, 19], and the corresponding magnetic space group allows for a linear ME response [20]. Indeed, there is experimental evidence of such a linear ME effect [21, 22], 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 have considered Fe$\rightarrow$Cr, Fe$\rightarrow$Mn, and Fe$\rightarrow$Co substitutions, as well as Fe$\rightarrow$(Fe,Cr) and Fe$\rightarrow$(Mn,Ni) double perovskites [24]. Note that, except for Bi₂FeCrO₆, none of the studied substitutions corresponds to thermodynamically stable phases. The purpose of considering such fictitious compounds (denoted with italics) was to identify chemical trends in the magnitude of the ME effects.

For the calculations we used the Projector Augmented Wave approach to DFT, within the so-called “LDA+U” approximation, as implemented in the Vienna Ab initio Simulation Package [25]. For all the compositions studied, we proceeded as follows: Taking the usual atomic and magnetic structure of rhombohedral BFO as 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 the calculations were fully self-consistent, allowed for non-collinear magnetism, and included spin-orbit couplings. We neglected orbital magnetization as well as the purely electronic ME response $\hat{\alpha}$, which is likely to be relatively small [20], 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 within the calculation accuracy; e.g., for BiCrO₃ we get $\alpha_{12} = -\alpha_{21}$, as expected for the 3m

| TABLE 1: Top: Frozen-cell and full ME tensors for three representative cases. Results given in 10⁻¹⁷ Gaussian units (g.u.). Magnetic space groups and easy axes are indicated. Bi₂FeCrO₆ 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 $\alpha_\alpha$, for all considered substitutions. |
|---|---|---|---|
| **space group** | **easy axis** | **α** | **α** |
| **BiFeO₃** | **Bb'** | ~ R3 | R3c |
| **space group** | **x** | **z** | **null** |
| **M(μB/cell)** | 0.036 | 0.002 | -y, -2z |
| **α** | 0.0 | 9.0 | -12.0 |
| **z** | 0.0 | 4.0 | -8.0 |
| **α** | 0.0 | 9.0 | -6.0 |
| **z** | 0.0 | 8.0 | -4.0 |
| **α** | 0.0 | 0.0 | 0.0 |
| **z** | 0.0 | 0.0 | 0.0 |

| **α_{max}(α_{max})** | **5(5)** | **14(13)** | **8(4)** | **15(11)** | **6(2)** | **3(3)** |
| **Fe** | **(Fe,Cr)** | **Cr** | **Mn** | **Co** | **(Mn,Ni)** |

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magnetic point group \[10\]. Interestingly, the largest ME coefficients obtained share the following two features: (i) The applied \(E\) is perpendicular to \(P^S\), which reflects the easy-polarization-rotation mechanism that determines the largest electromechanical responses in ferroelectrics \[27\]. (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 \[2\]).

For all compounds, the full ME response is bigger than the frozen-cell effect, the increase being significant in \(\text{BiCrO}_3\), \(\text{BiMnO}_3\), and \(\text{BiCoO}_3\). To illustrate how the strain-mediated response operates, we consider the representative case of the \(\alpha_{23}\) coefficient of \(\text{BiCrO}_3\). There, the largest strain response to \(E_1\) is associated with the shear \(\eta_{xy}\), as quantified by the piezoelectric strain coefficient \(d_{15} = e_{13}(C^{-1})_{15} = 15\) pC/N. The resulting change in \(\mathcal{M}_2\) is quantified by the piezomagnetic stress coefficient \(\kappa_{25} = -5 \times 10^4\) 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 \(\Omega_{\alpha}^{-1} P_{\alpha m} \kappa_s^{-1} P_{m j}^h\). Here, \(\kappa_s\) is the mode eigenvalue or stiffness, and \(P_{\alpha m}^h\) and \(P_{m j}^h\) are, respectively, the dielectric and magnetic polarizability introduced in Ref. \[3\]. This expression allows us to make a cumulative plot as the one shown in Fig. \[1\]b) for \(\alpha_{23}\) 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 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. \[28\] allows us to compare theory and experiment for BFO. These authors studied the bulk material under magnetic fields up to \(25\) T, which allowed them to eliminate the spin cycloid and reach a phase (G-type AFM) that resembles the one we have simulated. One can thus extrapolate the \(\mathcal{M}(H)\) curve measured within the high-field phase back to \(H=0\), and estimate the magnetization at zero field. The result is \(0.25\) emu/g = \(0.028\) \(\mu_B\)/cell, in remarkable agreement with our computed \(0.036\) \(\mu_B\)/cell. Further, the ME response of 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 \[21\] 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 \(\text{Co}_3\text{B}_2\text{O}_6\text{Br}\) (see Table Table 1.5.8.2 of Ref. \[10\]). Larger responses are observed in rare earth compounds, the greatest one being \(\alpha_{\max} = 100 \times 10^{-4}\) g.u. for \(\text{TbPO}_4\). 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 \(\text{Co}_3\text{B}_2\text{O}_6\text{Br}\) and \(2.2\) K for \(\text{TbPO}_4\) \[10\]), 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 \(T\) \[29\], and should occur at \(T_{\text{room}}\) and above. Hence, when compared with other magnetoelectrics, BFO is clearly an 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 non-magnetic ions, which is obviously not ideal. (2) These materials are quite stiff, as reflected by the relatively small piezoelectric and lattice-mediated dielectric responses: The largest ones obtained were, respectively, \(d_{\max} \approx 60\) pC/N for \(\text{BiMnO}_3\) and \(e_{\max} \approx 45\) for \(\text{BiCoO}_3\), while for prototype ferroelectric \(\text{BaTiO}_3\) one gets \(d_{\max} \approx 250\) pC/N and \(e_{\max} \approx 60\) \[13\]. (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

![FIG. 1](image-url) 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 \(\mathcal{M}_2\). When \(E_\parallel\) is applied we obtain an additional canting and a non-zero \(\mathcal{M}_2\) (solid arrows). Panel (b): Cumulative plot for the \(\hat{\alpha}_{23}\) coefficient of BFO (see text). Modes dominated by Bi (green diamonds) and Fe (red squares) displacements are highlighted.
maximum value of $0.4 \times 10^{-10} \text{ Oe}^{-1}$ for $\text{BiCrO}_3$, which is about one order of magnitude smaller than what is typical in transition-metal compounds (see Table 1.5.7.2 of Ref. 10). Yet, in spite of all these drawbacks, BFO is a competitive magnetoelectric.

If we were able to improve on some of these aspects, BFO might become an excellent magnetoelectric. Our results indicate 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 $\alpha_{\text{max}}$'s (Table 1) 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, or (ii) $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ solid solutions where structural transitions occur for small La concentrations. We hope our work will stimulate detailed experimental studies of these and similar systems, which our theory suggests constitute the best hope for obtaining very large linear ME effects in BFO.

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