First-Principles Approach to Lattice-Mediated Magnetoelectric Effects

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We present a first-principles scheme for the computation of the linear magnetoelectric response of magnetic insulators. We focus on the lattice-mediated part of the response, which we argue can be expected to be dominant in materials displaying strong magnetoelectric couplings. We apply our method to Cr_2O_3 and show that its low-temperature response has a significant lattice character.

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Magnetoelectric (ME) materials are insulators that allow control of their magnetic properties by means of external electric fields [1,2], thus attracting great technological interest. Current research focuses on obtaining compounds with a robust ME behavior at ambient conditions. This is proving to be a major challenge, as progress is hampered by one fundamental difficulty: the scarcity of ferromagnetic insulators (not to mention ferromagnetic *and* ferroelectric multiferroics [3]) with a high Curie temperature. An additional problem pertains to the magnitude of the effect: the ME response is usually very small, reflecting the weakness of the spin-orbit interactions that are typically responsible for the coupling.

Quantum calculations based on efficient schemes like density functional theory (DFT) have proved very useful in studies of magnetic and ferroelectric materials, and are expected to facilitate progress on magnetoelectrics. Indeed, there is a growing number of DFT works tackling the search for new compounds [4] and even proposing new coupling mechanisms [5,6]. However, we still lack a first-principles scheme to compute the ME coupling coefficients, something that is critical to aid the experimental work. In this Letter we introduce one such *ab initio* methodology and demonstrate its utility with an application to Cr_2O_3.

Lattice-mediated ME response.—Computing the full ME response of a material is now possible, as efficient methods for simulating insulators under external (particularly, electric [7]) fields have recently been developed. Nevertheless, it seems convenient to look for simplifications that can both facilitate the calculations and provide physical insight into the nature of the response.

In a linear magnetoelectric, the magnetization induced by the application of an electric field $\boldsymbol{\mathcal{E}}$ is given by

$$\mathcal{M}_j(\boldsymbol{\mathcal{E}}) = \sum_i \alpha_{ij}\mathcal{E}_i, \tag{1}$$

where $\boldsymbol{\alpha}$ is the linear ME tensor, i and j label spatial directions. The magnitude of the ME response is limited by the magnetic ($\boldsymbol{\chi}^{\mathrm{m}}$) and dielectric ($\boldsymbol{\chi}^{\mathrm{d}}$) susceptibilities as $\alpha_{ij}^2 < \chi_{ii}^{\mathrm{d}}\chi_{jj}^{\mathrm{m}}$ [8], which suggests that strong ME couplings will occur in materials displaying large dielectric and magnetic responses. On more physical grounds, one can argue that large ME effects will be associated to significant electronic hybridizations or orbital rearrangements induced by applied electric fields, as it is processes of that nature that may lead to a magnetic response via spin-orbit or exchangestrictive effects. It is then worth noting that (1) such a response to an electric field is typical of essentially all highly polarizable compounds used in applications and, most importantly, (2) such strong dielectric responses are never a purely electronic effect; rather, they are driven by the *structural* changes induced by the applied field. One can thus conclude that large ME effects will most likely be based on *lattice-mediated* mechanisms [9].

Formally, the lattice-mediated contribution to the dielectric susceptibility is defined as $\boldsymbol{\chi}_{\mathrm{latt}}^{\mathrm{d}} = \boldsymbol{\chi}^{\mathrm{d}} - \boldsymbol{\chi}_{\mathrm{elec}}^{\mathrm{d}}$, where $\boldsymbol{\chi}_{\mathrm{elec}}^{\mathrm{d}}$ accounts for the purely electronic effect corresponding to clamped atomic positions and lattice parameters. The ME tensor $\boldsymbol{\alpha}$ can also be decomposed in this way, and the discussion above suggests that $\boldsymbol{\alpha}_{\mathrm{latt}}$ will be the leading contribution in materials displaying strong ME effects. We shall thus focus on its computation.

Methodology.—The structural response of an insulator to a small electric field can be modeled in terms of the infrared (IR) modes of the material, which are obtained from the diagonalization of the force-constant matrix at the Γ point of the Brillouin zone (BZ). Let us denote by u_n the amplitude of the nth IR mode, with n running from 1 to N_{IR}, and by C_n the corresponding eigenvalue. Taking the u_n's and the applied electric ($\boldsymbol{\mathcal{E}}$) and magnetic ($\boldsymbol{H}$) fields as independent variables, we write the energy of a linear ME crystal around its equilibrium state as

$$\begin{aligned} E(\{u_n\},\boldsymbol{\mathcal{E}},\boldsymbol{H}) = E_0 &+ \frac{1}{2}\sum_{n=1}^{N_{\mathrm{IR}}} C_n u_n^2 - \Omega_0 \sum_i \mathcal{E}_i\Big[\mathcal{P}_{\mathrm{latt},i}(\{u_n\}) \\ &+ \frac{1}{2}\sum_{i'} \chi_{\mathrm{elec},ii'}^{\mathrm{d}}\mathcal{E}_{i'}\Big] - \Omega_0 \sum_j H_j\Big[\mathcal{M}_{\mathrm{latt},j}(\{u_n\}) \\ &+ \frac{1}{2}\sum_{j'} \chi_{\mathrm{elec},jj'}^{\mathrm{m}} H_{j'}\Big] - \Omega_0 \sum_{ij} \alpha_{\mathrm{elec},ij}\mathcal{E}_i H_j, \end{aligned} \tag{2}$$

where Ω_0 is the unit cell volume and we have assumed the crystal has no spontaneous magnetization or polarization (see the comment on the strain-mediated response below).

The lattice contributions to the polarization and magnetization are

$$\mathcal{P}_{\mathrm{latt},i} = \frac{1}{\Omega_0}\sum_{n=1}^{N_{\mathrm{IR}}} p^{\mathrm{d}}_{ni} u_n \quad (3)$$

and

$$\mathcal{M}_{\mathrm{latt},j} = \frac{1}{\Omega_0}\sum_{n=1}^{N_{\mathrm{IR}}} p^{\mathrm{m}}_{nj} u_n, \quad (4)$$

respectively. $\boldsymbol{p}^{\mathrm{d}}_n$ is the dielectric polarity of the nth IR mode, which can be obtained from the atomic Born effective charges and the mode eigenvector [10]. The $\boldsymbol{p}^{\mathrm{m}}_n$ coefficients are the magnetic analogue of the dielectric polarities and, similarly, can be computed from the mode eigenvector and the knowledge of the magnetizations induced by displacing individual atoms.

The magnetic response to an electric field is readily obtained from these expressions. Indeed, the equilibrium value of u_n for applied $\boldsymbol{\mathcal{E}}$ and zero magnetic field is

$$u_n = \frac{1}{C_n}\sum_i p^{\mathrm{d}}_{ni}\mathcal{E}_i, \quad (5)$$

from which the induced magnetization is obtained as

$$\mathcal{M}_j = -\frac{1}{\Omega_0}\frac{\partial E}{\partial H_j} = \sum_i \alpha_{\mathrm{elec},ij}\mathcal{E}_i + \frac{1}{\Omega_0}\sum_{n=1}^{N_{\mathrm{IR}}} p^{\mathrm{m}}_{nj} u_n$$
$$= \sum_i \alpha_{\mathrm{elec},ij}\mathcal{E}_i + \frac{1}{\Omega_0}\sum_{n=1}^{N_{\mathrm{IR}}} p^{\mathrm{m}}_{nj}\frac{1}{C_n}\sum_i p^{\mathrm{d}}_{ni}\mathcal{E}_i. \quad (6)$$

Then, the mode-decomposed lattice-mediated part of the linear ME response is given by

$$\alpha_{\mathrm{latt},ij} = \sum_{n=1}^{N_{\mathrm{IR}}}\alpha_{\mathrm{latt},nij} = \frac{1}{\Omega_0}\sum_{n=1}^{N_{\mathrm{IR}}}\frac{p^{\mathrm{d}}_{ni}p^{\mathrm{m}}_{nj}}{C_n}. \quad (7)$$

This equation encapsulates our method for an *ab initio* computation of the ME response. Its most remarkable feature is that all the parameters that appear in it can be computed without the need of simulating the material under applied electric or magnetic fields, which brings the calculation of ME effects within the scope of the most widely used DFT codes.

The above expression offers some insight into the microscopic ingredients needed to have a strong lattice-mediated ME response. In essence, one would like to find materials in which the response is dominated by a *soft mode*; ideally, such a mode should also be highly polarizable and cause a large magnetic response. It is clear that, in order to have IR modes with simultaneously large $\boldsymbol{p}^{\mathrm{d}}_n$ and $\boldsymbol{p}^{\mathrm{m}}_n$, we need materials in which the magnetic atoms present large Born effective charges. While rare, this is the case of compounds like $CaMnO_3$ [3] (although this particular crystal is not a linear magnetoelectric).

A few additional comments are in order. (1) The proposed method constitutes a linear-response theory. Note that Eq. (2) can be extended to include higher-order terms, thus gaining access to higher-order responses. However, the computation of such additional terms would typically require simulations under applied fields. (2) We have not considered strain ($\boldsymbol{\eta}$) contributions to the linear ME response, which may be allowed by symmetry in some cases. Indeed, such contributions always exist in materials displaying a spontaneous polarization or magnetization: In polar crystals the strain-mediated response arises from coupling terms of the form $\boldsymbol{\eta}u_n$ and $\boldsymbol{\eta}\boldsymbol{\mathcal{E}}$, which must be included in Eq. (2); in crystals with a net magnetization, there will be terms of the form $\boldsymbol{\eta}\boldsymbol{H}$. (3) While the above derivation is made in terms of the eigenvectors of the force-constant matrix, one could imagine an analogous scheme using the IR eigenmodes of the dynamical matrix as structural variables. It would then be possible to model the dynamical ME response.

Results for Cr_2O_3.—One would like to demonstrate the proposed method by studying a material whose response is dominated by the type of soft-mode mechanism suggested above. However, partly because of the scarcity of detailed experimental studies, we were not able to identify any such model crystal, and decided to work on the linear magnetoelectric compound that is probably best characterized experimentally: Cr_2O_3.

The work on magnetoelectrics starts with the prediction [11] and experimental confirmation [12,13] that linear ME effects occur in Cr_2O_3 (chromia). Cr_2O_3 is an antiferromagnetic (AFM) insulator with a 10-atom unit cell and the magnetic structure sketched in Fig. 1. The magnetic easy axis lies along the rhombohedral direction c. This crystal has the magnetic space group $R\bar{3}'c'$, and is thus paraelectric. Cr_2O_3 presents six IR modes: two polarized along the rhombohedral c axis, corresponding to the A_{2u} irreducible representation of $\bar{3}m$, and four double-degenerate modes with E_u symmetry and polarization within the ab plane. The linear ME tensor is diagonal with two independent terms: $\alpha_{aa} = \alpha_{bb} = \alpha_\perp$ and $\alpha_{cc} = \alpha_\parallel$. Naturally, the lattice-mediated part of $\alpha_\perp$ ($\alpha_\parallel$) can be decomposed into contributions from the E_u (A_{2u}) modes, which we can compute with our method. (In the following we drop the "latt" subscript from the α's to alleviate the notation.)

For the calculations we used the LDA [14] approximation to DFT as implemented in the plane-wave code VASP [16]. We used the PAW scheme [17] to represent the atomic cores. Only the nominal valence electrons were explicitly solved, which we checked is sufficient. Let us just note that all the *trivial* calculations involved in this study (e.g., for the equilibrium atomic structure, force-constant matrix, or induced polarizations [18]) were performed accurately and following well-established procedures, and that all of them were done at the collinear level. To obtain the p^{m}_{nj} parameters in Eq. (4), we computed the magnetic response upon condensation of the IR modes by running fully self-consistent noncollinear simulations including spin-orbit couplings. Interestingly, we found that a non–self-consistent approach, as usually employed for the compu-

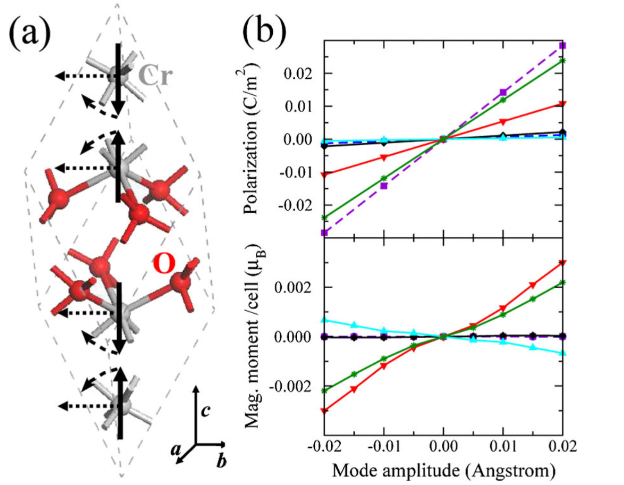

FIG. 1 (color online). Panel (a): Primitive cell of Cr_2O_3. Solid arrows represent the AFM ground state. Dashed arrows sketch the atomic displacements within the *ab* plane associated to a typical E_u IR mode, as well as the induced spin rotations that render a net magnetic moment. Panel (b): Computed polarization and magnetization induced by the condensation of the IR modes. Dashed and solid lines correspond to A_{2u} and E_u modes, respectively. Note that the polarizations and magnetizations associated to the E_u (A_{2u}) modes lie within the *ab* plane (along the *c* direction). Note also that the magnetization induced by the A_{2u} modes is essentially zero.

tation of magnetic anisotropy energies, renders qualitatively incorrect results in this case. Let us also stress that, given the small magnitude of the energy differences associated to the ME effects in Cr_2O_3, one has to be very careful with the choice of the parameters controlling the accuracy of the calculations. In particular, we found it necessary to use a very demanding stopping criterion for the self-consistent-field calculations (namely, energies converged down to 10^{-10} eV) to obtain, in a computationally robust way, reliable values of the magnetic moments induced by the condensation of the IR modes. We also determined that a *k*-point grid of at least $7 \times 7 \times 7$ is needed for accurate BZ integrations. (A magnetic easy axis in the *ab* plane is incorrectly predicted if grids that are not dense enough are used.) The plane-wave cutoff was found to be less critical; we used 400 eV. We employed the ''LDA + U'' scheme of Dudarev *et al.* [19] for a better treatment of the 3*d* electrons of Cr. We chose $U_{\rm eff} = 2$ eV, which renders results in acceptable agreement with experiment for the atomic structure, IR phonon frequencies, electronic band gap, and magnetic moments [20]. At any rate, we checked the choice of $U_{\rm eff}$ is not critical, even for the computation of ME coefficients. Finally, let us note the orbital degrees of freedom can be expected to be *quenched* in Cr_2O_3; thus, we neglected their contribution to the magnetization.

Table I and Fig. 1 summarize our results, which present the following features. (1) We obtain $\alpha_\parallel$ much smaller than $\alpha_\perp$. Indeed, our calculations indicate that the magnetic response associated to the A_{2u} modes is nearly zero, and provide an explanation for such an effect. We find that, for the E_u modes, the induced in-plane magnetization occurs via a canting of the Cr spins, as sketched in Fig. 1. In contrast, in the case of the A_{2u} modes, no symmetry-allowed spin canting can induce a magnetization along the *c* direction. Instead, the simulations show that the magnetization originates from a tiny charge transfer between the spin-up and spin-down Cr sublattices. Probably, the smallness of the corresponding $p_n^{\rm m}$ coefficients reflects the relatively large energy cost associated to such a mechanism. (2) The ME response $\alpha_\perp$ is dominated by the hardest E_u modes and, interestingly, such a result could have been anticipated from the mode eigenvectors. More precisely, the two hardest modes present a relatively large Cr contribution, which should lead to relatively large values of $p_n^{\rm m}$, as we indeed find. In addition, in the hardest eigenmode the Cr and O sublattices move rigidly and in opposite directions, which must result in a large $p_n^{\rm d}$, exactly as found. (3) We obtain both positive (from three modes) and negative (from one mode) contributions to $\alpha_\perp$. (Given the smallness of the magnetic effects computed, we have not tried to identify the electronic underpinnings of having positive or negative α_n's.) This result suggests that, in a general case, a small static ME effect may be the result of cancellations between contributions from different IR modes. Hence, large static ME effects will most likely be associated to compounds in which a single IR mode dominates the response.

To the best of our knowledge, the low-temperature ME response of Cr_2O_3 is not totally understood, which reflects both the difficulties involved in ME measurements and the rich nature of the problem. The experimental results at 4.2 K are quite scattered [24]: $|\alpha_\perp|$ ranges from 0.2×10^{-4} to 4.7×10^{-4} in Gaussian units (g.u.) and $|\alpha_\parallel|$ from 0.4×10^{-4} to 1.2×10^{-4} g.u. There are reasons to believe that the magnitude of the ME effects was underestimated in the early experiments [25], and that the largest coefficients measured [24,26] are the most reliable ones. In particular, $|\alpha_\perp|$ probably lies somewhere between 2×10^{-4} and 4×10^{-4} g.u., which is remarkably close to our result. Interestingly, it is not clear how to explain this

TABLE I. Parameters of Eq. (7) computed for the IR modes of Cr_2O_3. Modes are divided in two groups, A_{2u} and E_u, according to their symmetry. The last line shows the results for the two independent α coefficients, obtained from the addition of the corresponding mode contributions. The α's are given in Gaussian units (g.u.) [23].

	A_{2u} modes			E_u modes		
C_n (eV/Å^2)	10.8	25.7	10.4	16.9	21.6	32.5
$p_n^{\rm d}$ ($\lvert e \rvert$)	0.39	8.52	0.65	0.16	3.24	7.14
$p_n^{\rm m}$ ($10^{-2}\mu_B$/Å)	0.02	0.04	0.41	−2.70	11.32	8.51
α_n (10^{-4} g.u.)	0.00	0.00	0.01	−0.01	0.62	0.68
$\sum_n \alpha_n$ (10^{-4} g.u.)	$\alpha_\parallel = 0.00$			$\alpha_\perp = 1.30$		

relatively large value of $\alpha_\perp$ in terms of the purely electronic mechanisms typically considered [26–28]. It is thus worth noting our computed lattice-mediated ME response is of the same magnitude as the one measured. As for the parallel response, all the experiments render $|\alpha_\parallel| < |\alpha_\perp|$ at low temperatures, but none reports an essentially zero value as we obtain. Our results are thus compatible with the notion that either a purely electronic mechanism, as the electric-field-induced g shift proposed in Ref. [28], or a magnetic effect not related to the ME coupling [27] is responsible for the nonzero $\alpha_\parallel$ at low temperatures.

Our calculations of the low-temperature lattice-mediated ME response of Cr_2O_3 thus seem to account for the main part of the effect associated to $\alpha_\perp$ and render a nearly null $\alpha_\parallel$. Because of the experimental uncertainties and the approximations involved in our method, it is not possible to fully validate our results. Nevertheless, it seems remarkable that our calculations have captured such tiny ME effects, offering information that will be relevant to clarify the behavior of Cr_2O_3.

In summary, we have described an *ab initio* theory of the linear lattice-mediated magnetoelectric response. We hope our work will enable a more effective interaction between theory and experiment in the search for materials that can be used in applications.

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