Dynamical magnetic charges and linear magnetoelectricity

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(Dated: January 7, 2014)

Magnetoelectric (ME) materials are of fundamental interest and have been investigated for their broad potential for technological applications. The search for, and eventually the theoretical design of, materials with large ME couplings present challenging issues. First-principles methods have only recently been developed to calculate the full ME response tensor \( \alpha \) including both electronic and ionic (i.e., lattice-mediated) contributions. The latter is proportional to both the Born dynamical electric charge \( Z^e \) and its analogue, the dynamical magnetic charge \( Z^m \). Here we present a theoretical study of the magnetic charge \( Z^m \) and the mechanisms that could enhance it. Using first-principles density-functional methods, we calculate the atomic \( Z^m \) tensors in \( \text{Cr}_2\text{O}_3 \), a prototypical magnetoelectric, and in KITPite, a fictitious material that has previously been reported to show a strong ME response arising from exchange striction effects. Our results confirm that in \( \text{Cr}_2\text{O}_3 \), the \( Z^m \) values and resulting ME responses arise only from spin-orbit coupling (SOC) and are therefore rather weak. In KITPite, by contrast, the exchange striction acting on the non-collinear spin structure induces much \( Z^m \) values that persist even when SOC is completely absent.

PACS numbers: 75.85.+t, 75.30.Et, 71.15.Rf, 71.15.Mb

I. INTRODUCTION

There has been a recent resurgence of research on the magnetoelectric (ME) effect, which describes the coupling between electricity and magnetism. The linear ME effect is defined as

\[
\alpha_{\beta\nu} = \frac{\partial P_\beta}{\partial H_\nu} \epsilon = \mu_0 \frac{\partial M_\nu}{\partial E_\beta} H, \tag{1}
\]

where the polarization \( P \) is linearly induced by an external magnetic field \( H \), or the magnetization is linearly generated by an applied electric field \( E \). Here indices \( \beta \) and \( \nu \) denote the Cartesian directions and \( \mu_0 \) is the vacuum permeability. This coupling between electricity and magnetism is of fundamental interest and shows broad potential for technological applications.

The history of research on the ME effect dates back to the 1960s when the magnetic symmetry started to be emphasized. It was first realized by Landau and Lifshitz that the ME response is only allowed in media without time-reversal symmetry or inversion symmetry. In 1959, Dzyaloshinskii predicted that \( \text{Cr}_2\text{O}_3 \) should be a ME crystal based on its magnetic point group, and experiments successfully measured the linear induced magnetization by an external electric field and the inverse effect. The early theoretical studies and explanations for the ME effect were based on phenomenological models that typically do not distinguish carefully between microscopic mechanisms. The recent rapid development of first-principles methods has now allowed the underlying mechanisms in different materials to be classified and investigated.

The linear ME effect can be decoupled into three contributions, namely electronic (frozen-ion), ionic (lattice-mediated), and strain-mediated responses. Each term can be further subdivided into spin and orbital contributions. The early \textit{ab-initio} studies were focused on the spin-lattice and spin-electronic terms. First-principles methods have only recently been developed to calculate the full ME response tensor \( \alpha \) including both spin and orbital contributions. As the symmetry condition for the strain-mediated term is more restrictive, this term is absent in most bulk materials.

Previous studies have shown that the spin-lattice term is dominant in many materials, as for example in \( \text{Cr}_2\text{O}_3 \). Iñiguez has shown that the lattice contribution can be written as a product of the Born charge, the force-constant inverse, and the dynamical magnetic charge, which is the magnetic analogue of the dynamical Born charge. This dynamical magnetic charge is defined as

\[
Z^m_{\nu\rho} = \Omega_0 \frac{\partial M_\nu}{\partial u_m} \bigg|_{E,H,n}. \tag{2}
\]

Here \( \Omega_0 \) is the volume of the unit cell containing \( N \) atoms and \( u_m \) denotes a periodicity-preserving sublattice displacement, where \( m \) is a composite label running from 1 to \( 3N \) to represent the atom and its displacement direction. The magnetic charge tensor \( Z^m \) plays an important role in various lattice-mediated magnetic responses and contributes to the Lyddane-Sachs-Teller relationship in magnetoelectric materials, but the mechanisms that give rise to it are not yet well understood. In particular, one route to optimizing the magnetoelectric coupling is clearly to enhance \( Z^m \), but it is not obvious how to do so.

In this work, we use first-principles density functional methods to study the dynamical magnetic charges in two materials and explore the different mechanisms responsible for them in these two cases. We first study the magnetic charges in \( \text{Cr}_2\text{O}_3 \), which are driven by the spin-orbital coupling (SOC) mechanism. Then we study a fictitious structure, “KITPite,” which was reported to have a large spin-lattice ME coupling according to a previous theory. The structure of KITPite is such that
the superexchange interactions between Mn moments are frustrated, leading to a 120° noncollinear spin structure. Our study shows that the $Z^m$ values, which are orders of magnitude stronger than in Cr$_2$O$_3$, are responsible for the strong ME coupling. We find that this enhancement is present even when SOC is completely absent, thus confirming that it arises from exchange striction acting on the non-collinear spins, in contrast to the case of Cr$_2$O$_3$ where $Z^m$ is driven only by SOC effects.

The paper is organized as follows. In Sec. II A we introduce the formalism that describes how the dynamical magnetic charge tensor enters into the lattice contributions to the magnetic, ME, and piezomagnetic responses. In Sec. II B we analyze the structure and the magnetic symmetry of Cr$_2$O$_3$ and KITPite. The computational details are described in Sec. II C. In Sec. II D we present and discuss the computed magnetic charge tensors for Cr$_2$O$_3$ and KITPite. Finally, Sec. IV provides a summary.

II. PRELIMINARIES

A. Formalism

Here, following Íñiguez [13] we generalize the formalism of Wu, Vanderbilt and Hamann [15] (WVH) to include the magnetic field, and use this systematic treatment to derive the ionic contribution of the ME coupling and other magnetic properties.

For an insulating system with $N$ atoms in a unit cell, we consider four kinds of perturbation: (i) a homogeneous electric field $\mathbf{E}$, whose indices $\beta, \gamma$ run over $\{x,y,z\}$; (ii) a homogeneous magnetic field $\mathbf{H}$, whose indices $\nu, \omega$ also run over $\{x,y,z\}$; (iii) a homogeneous strain $\eta$, with Voigt indices $i,j = \{1\ldots6\}$; and (iv) internal displacements $\mathbf{u}$, indexed by composite labels $m,n$ (atom and displacement direction) running over $1,\ldots,3N$. In this work we only consider internal displacements that preserve the bulk periodicity, corresponding to zone-center phonon modes.

The magnetoelectric enthalpy density is defined as

$$E(\mathbf{u}, \eta, \mathbf{E}, \mathbf{H}) = \frac{1}{\Omega_0} \left[ E^{(0)}_{\text{cell}} - \Omega_0 (\mathbf{E} \cdot \mathbf{P} + \mu_0 \mathbf{H} \cdot \mathbf{M}) \right], \quad (3)$$

where $E^{(0)}_{\text{cell}}$ is the the zero-field energy per cell and $\Omega_0$ and $\Omega$ are the undeformed and deformed cell volumes respectively. $E(\mathbf{u}, \eta, \mathbf{E}, \mathbf{H})$ can be expanded around the zero-field equilibrium structure as

$$E = E_0 + A_m u_m + A_{ij} \eta_{ij} + A_{\beta\gamma} \mathbf{E}_\beta \cdot \mathbf{E}_\gamma + A_{\nu\omega} \mathbf{H}_\nu \cdot \mathbf{H}_\omega + \frac{1}{2} B_{mn} u_m u_n + \frac{1}{2} B_{\beta\gamma} \eta_{\beta\gamma} + \frac{1}{2} B_{\nu\omega} \mathbf{E}_\nu \cdot \mathbf{E}_\omega + \frac{1}{2} B_{\omega\nu} \mathbf{H}_\nu \cdot \mathbf{H}_\omega + B_{mn} u_m H_\nu + B_{\beta\gamma} \mathbf{E}_\beta \cdot \mathbf{E}_\gamma + B_{\nu\omega} \mathbf{H}_\nu \cdot \mathbf{H}_\omega + B_{\nu\omega} \mathbf{H}_\nu \cdot \mathbf{H}_\omega (4)$$

where summation over repeated indices is implied. The coefficients of the first-order terms correspond to the atomic forces $F_m = -\Omega_0 A_m$, the stress tensor $\sigma_{ij} = A_{ij}$, the spontaneous polarization $P^S_\beta = -A_{\beta\gamma}$, and the spontaneous magnetization $M^S_\nu = -\mu_0^{-1} A_{\nu\omega}$. For the equilibrium structure, the atomic forces and the stress tensor vanish. The diagonal second-order coefficients provide the force-constant matrix $K_{mn} = \Omega_0 B_{mn}$, the frozen-iron elastic tensor $C_{jk} = B_{jk}$, the frozen-iron susceptibility $\chi_{\beta\gamma}^0 = -e_0^{-1} B_{\beta\gamma}$, and the frozen-iron magnetoelectric susceptibility $\chi_{\nu\omega}^0 = -\mu_0^{-1} B_{\nu\omega}$, where the bar on a quantity indicates a purely electronic response computed at fixed internal coordinates of the atoms. The remaining terms correspond to off-diagonal responses, namely the force-response internal-strain tensor $\Lambda_{mj} = -\Omega_0 B_{mj}$, the frozen-iron piezoelectric tensor $e_{\nu\omega} = B_{\nu\omega}$, the frozen-iron magnetoelectric tensor $\alpha_{\beta\nu} = -B_{\beta\omega}$, the atomic Born charges

$$Z_{m\beta}^e = \Omega_0 \frac{\partial P_\beta}{\partial u_m} \bigg|_{\mathbf{E}, \eta} = \mu_0^{-1} \frac{\partial F_m}{\partial E_\beta} \bigg|_{\mathbf{H}, \eta} = -\Omega_0 B_{m\beta}, \quad (5)$$

and the atomic magnetic charges

$$Z_{m\nu}^m = \Omega_0 \frac{\partial M_\nu}{\partial u_m} \bigg|_{\mathbf{E}, \eta} = \mu_0^{-1} \frac{\partial F_m}{\partial H_\nu} \bigg|_{\mathbf{E}, \eta} = -\Omega_0 \mu_0^{-1} B_{m\nu}. \quad (6)$$

Static physical responses arise not only from the electronic part (barred quantities), but also from the ionic contribution associated with the change of the equilibrium internal displacements $u_m$ with fields or strain. The relaxed-ion magnetoelectric enthalpy is

$$\tilde{E}(\eta, \mathbf{E}, \mathbf{H}) = \min_{\mathbf{u}} E(\mathbf{u}, \eta, \mathbf{E}, \mathbf{H}), \quad (7)$$

and the minimization is accomplished by substituting

$$u_m = -(B^{-1})_{mn}(B_{nj} \eta_j + B_{n\beta} \mathbf{E}_\beta + B_{n\nu} H_\nu) \quad (8)$$

into Eq. (4) to obtain the total relaxed-ion response (including both electronic and ionic parts). The total relaxed-ion electric susceptibility, magnetic susceptibility, elastic, piezoelectric, piezomagnetic, and magnetoelectric tensors are then

$$\chi_{\beta\gamma}^e = -e_0^{-1} \frac{\partial^2 \tilde{E}}{\partial \mathbf{E}_\beta \partial \mathbf{E}_\gamma} \bigg|_{\mathbf{E}, \eta} = \chi_{\beta\gamma}^0 + \Omega_0^{-1} e_0^{-1} Z_{m\beta}^e (K^{-1})_{mn} Z_{n\gamma}^e, \quad (9)$$

$$\chi_{\nu\omega}^m = -\mu_0^{-1} \frac{\partial^2 \tilde{E}}{\partial H_\nu \partial H_\omega} \bigg|_{\mathbf{E}, \eta} = \chi_{\nu\omega}^0 + \Omega_0^{-1} \mu_0 Z_{m\nu}^m (K^{-1})_{mn} Z_{n\omega}^m, \quad (10)$$

$$C_{jk} = \frac{\partial^2 \tilde{E}}{\partial \eta_j \partial \eta_k} \bigg|_{\mathbf{E}, \mathbf{H}} = \tilde{C}_{jk} - \Omega_0^{-1} \Lambda_{mj} (K^{-1})_{mn} \Lambda_{nj}, \quad (11)$$

$$e_{\beta\nu} = -\frac{\partial^2 \tilde{E}}{\partial \mathbf{E}_\beta \partial \eta_j} \bigg|_{\mathbf{E}, \mathbf{H}} = \tilde{e}_{\beta\nu} + \Omega_0^{-1} Z_{m\beta}^e (K^{-1})_{mn} \Lambda_{nj}, \quad (12)$$
FIG. 1. (Color online) Sketch showing how the six lattice-mediated responses indicated by solid circles (orange) are each built up from the four elementary tensors indicated by open circles: the Born charge $Z^e$ (yellow), magnetic charge $Z^m$ (blue), internal strain $\Lambda$ (green), and force-constant inverse $K^{-1}$ (magenta). Each lattice-mediated response is given by the product of the three elementary tensors connected to it, as indicated explicitly in Eqs. (13-14).

$$h_{\nu j} = -\frac{\partial^2 \hat{E}}{\partial H_{\nu} \partial n_j} |_{\mathcal{E}} = \tilde{h}_{\nu j} + \Omega_0^{-1} Z^m_{\nu \mu} (K^{-1})_{\mu \nu} \Lambda_{n j}, \tag{13}$$

$$\alpha_{\beta \nu} = -\frac{\partial^2 \hat{E}}{\partial \mathcal{E}_\beta \partial H_{\nu}} |_{\mathcal{B}} = \tilde{\alpha}_{\beta \nu} + \Omega_0^{-1} \mu_0 Z^{e \gamma}_{\beta \nu}(K^{-1})_{\gamma \mu} Z^m_{\mu \nu}. \tag{14}$$

The six lattice-mediated responses in Eqs. (13-14) are all made up of four fundamental tensors: the Born charge tensor $Z^e$, the magnetic charge tensor $Z^m$, the internal strain tensor $\Lambda$, and the inverse force-constant matrix $K^{-1}$. The manner in which these six lattice responses are computed from the four fundamental tensors is illustrated in Fig. 1, which depicts the linear-response connections between elastic, electric and magnetic degrees of freedom.

If the crystal symmetry is low enough that piezoelectric or piezomagnetic effects are present, then the strain degrees of freedom can similarly be eliminated by minimizing the magnetoelectric enthalpy with respect to them, leading to additional strain-relaxation contributions to $\chi^e, \chi^m$, and/or $\alpha$. We do not consider these contributions in the present work because such terms are absent by symmetry in the materials under consideration here.

The above derivations are carried out in the $(\mathcal{E}, \mathcal{B})$ frame, which is consistent with the usual experimental conventions. In the context of first-principles calculations, however, it is more natural to work in the $(\mathcal{E}, \mathcal{H})$ frame, as $\mathcal{E}$ and $\mathcal{B}$ are directly related to the scalar and vector potentials $\phi$ and $A$. The magnetoelectric tensor $\alpha$ has different units in these two frames. In the $(\mathcal{E}, \mathcal{H})$ frame, $\alpha$ is defined through Eq. (14) so that the units are s/m. In the $(\mathcal{E}, \mathcal{B})$ frame, $\alpha$ is instead defined as

$$\alpha^B_{\beta \nu} = \frac{\partial M_{\nu}}{\partial \mathcal{E}_\beta} |_{\mathcal{B}} = \frac{\partial P_{\nu}}{\partial B_{\beta}} |_{\mathcal{E}} \tag{15}$$

and carries units of inverse Ohm, the same as for $\sqrt{\mu_0/\mu}$, the inverse of the impedance of free space. The ME tensors in these two frames are related by $\alpha^B_{\beta \nu} = (\mu \alpha)^B_{\beta \nu}$, where $\mu$ is the magnetic permeability. The electric and magnetic dynamical charges in the two frames are related by $(Z^e)^B_{\mu \nu} = (Z^e + \alpha \mu Z^m)^B_{\mu \nu}$ and $(Z^m)^B_{\mu \nu} = (\mu Z^m/\mu_0)^B_{\mu \nu}$.

For non-ferromagnetic materials we have $\mu \approx \mu_0$, so that the $Z^m$ values are essentially the same in the two frames. The same is also true for $Z^e$, since the product $(\alpha \mu Z^m)^B_{\mu \nu}$ is at least five orders of magnitude smaller than $Z^e$ in most magnetoelectric materials. In this work we report our results in the more conventional $(\mathcal{E}, \mathcal{H})$ frame, even though the computations are carried out in the $(\mathcal{E}, \mathcal{B})$ frame.

### B. Structure and symmetry

#### 1. Cr$_2$O$_3$

Cr$_2$O$_3$ adopts the corundum structure with two formula units per rhombohedral primitive cell as shown in Fig. 2(a). Each Cr atom is at the center of a distorted oxygen octahedron.

FIG. 2. (Color online) Structure of Cr$_2$O$_3$. (a) In the rhombohedral primitive cell, four Cr atoms align along the rhombohedral axis with AFM magnetic moments shown by (blue) arrows. (b) Each Cr atom is at the center of a distorted oxygen octahedron.

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FIG. 3. Symmetry pattern of the Born and magnetic charge tensors for (a) the Cr atom in Cr$_2$O$_3$, (b) the O atom in Cr$_2$O$_3$ and the O$^2$ atom in CaAlMn$_2$O$_7$, (c) the Ca, Al and O$^3$ atoms in CaAlMn$_2$O$_7$, and (d) the Mn and O$^3$ atoms in CaAlMn$_2$O$_7$. The elements indicated by an asterisk vanish in the absence of SOC for Z$^m$ in CaAlMn$_2$O$_7$.

vice versa, so that pseudovectors and ordinary vectors transform in the same way, implying that the magnetic charge Z$^m$ and the Born charge Z$^b$ have the same tensor forms. The three-fold symmetry on each Cr atom restricts its tensor to have the form shown in Fig. 3(a). The symmetry is lower on the O atoms; for the one lying on the two-fold rotation axis along $\hat{x}$, for example, the charge tensor take the form shown in Fig. 3(b).

2. KITPite

The fictitious “KITPite” structure with chemical formula CaAlMn$_3$O$_7$ is Kagome-like with 120° in-plane AFM spin ordering as showed in Fig. 4. The unit cell includes two formula units made by stacking two MnO layers with 180° rotations between layers. Each Mn atom is surrounded by an oxygen bipyramid and the O atoms are in three nonequivalent Wyckoff positions: O$^1$ are in the voids of the Mn triangles; O$^2$ are the apical ions located between the two MnO layers (not shown in the planar view); and O$^3$ form the MnO hexagons. The magnetic space group is 6$_3$/m$m'$/m$'c'$; this has the same symmetry feature as Cr$_2$O$_3$, namely that all the improper rotations and time-reversal symmetries are coupled together, so that the Born charges and the magnetic charges follow the same symmetry restrictions. The charge tensors for Ca, Al and O$^1$ atoms have the symmetry pattern shown in Fig. 3(c), and the Mn and O$^3$ atoms have the charge tensor form of Fig. 3(d). For the apical O$^2$ atoms, the five independent components in the charge tensor can be written in the form of Fig. 3(b) when the on-site two-fold axis is along the $\hat{z}$ direction.

The elements marked by asterisks in Fig. 3 are those that vanish for Z$^m$ in CaAlMn$_3$O$_7$ when SOC is neglected. The system of magnetic moments is exactly coplanar in the absence of SOC, and will remain so even after the application of any first-order nonmagnetic perturbation. Thus, spin components along $\hat{z}$ cannot be induced, and it follows that the elements in the third col-

FIG. 4. (Color online) Planar view of the CaAlMn$_3$O$_7$ (KITPite) structure. The broad arrows (blue) on the Mn atoms represent the magnetic moment directions in the absence of electric or magnetic fields. Small (black) arrows indicate the atomic forces induced by an external magnetic field applied in the $\hat{y}$ direction.

C. First-principles methods

The first-principles calculations for Cr$_2$O$_3$ are performed with the QUANTUM ESPRESSO package using the generalized-gradient approximation parametrized by the Perdew-Burke-Ernzerhof functional. We employ Troullier-Martins norm-conserving pseudopotentials with SOC included and Cr 3s and 3p states incorporated in the valence. The wavefunctions are expanded in a plane-wave basis with cutoff energy 150 Ry, and a 4 × 4 × 4 Monkhorst-Pack k-point mesh is used for the self-consistent-field loop. In the Berry-phase polarization calculation, a 4 × 4 × 5 k-point sampling is found to be sufficient. In order to calculate magnetic charges, Born effective charges and the Γ-point force-constant matrix, the finite-difference method is used by displacing each atomic sublattice in each Cartesian direction and computing the total magnetization, the Berry-phase polarization and the Hellmann-Feynman forces. The orbital magnetization is calculated using the modern theory of orbital magnetization.

The calculations for the fictitious KITPite material are carried out with plane-wave density-functional theory implemented in VASP with PAW pseudopotentials, with energy cutoff 400 eV are sufficient in the non-collinear magnetization computation without SOC. For the exchange-correlation functional we use the rotationally invariant LSDA+$U$ functional with Hubbard $U = 5.5$ eV and $J = 2.0$ eV on the $d$ orbitals of the Mn atoms. The Born effective charge tensor and the Γ-point force-constant matrix are obtained by linear-response methods. The dy-
namical magnetic charges are computed by applying an uniform Zeeman field in the crystal and computing the resulting forces. A $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh is used in the calculations.

III. RESULTS

A. Cr$_2$O$_3$

The Cr$_2$O$_3$ ground-state structural parameters predicted by our first-principles calculations are in good agreement with experiment, as shown in Table I. A group-theory analysis of the long-wavelength phonons shows that the infrared (IR) active phonon modes, which couple to the electromagnetic excitations, are the longitudinal $A_{2u}$ modes and the transverse doubly-degenerated $E_u$ modes,

$$\Gamma_{IR} = 2A_{2u} + 4E_u,$$

(16)

where the acoustic modes have been excluded. The IR-active mode frequencies shown in Table II are computed using linear-response methods, and the results are in good agreement with experiment.

The main results for the magnetic charge tensors of Cr$_2$O$_3$ are reported both in the atomic basis and in the IR-active mode basis in Tables III and IV. The spin contributions are dominant in the transverse direction, but much weaker in the longitudinal direction. This is to be expected from the nearly collinear spin order of Cr$_2$O$_3$, considering that the magnitudes of the magnetic moments are quite stiff while their orientations are relatively free to rotate. The main effect in the longitudinal direction is from the orbital-magnetization contribution.

TABLE II. Frequencies (cm$^{-1}$) of zone-center IR-active phonon modes of Cr$_2$O$_3$ from first-principles calculations and experiments. The two $A_{2u}$ modes are longitudinal; the four $E_u$ modes are transverse (doubly degenerate).

|        | $A_{2u}$ modes | $E_u$ modes |
|--------|----------------|-------------|
| This work | 388 522 297 427 510 610 | |
| Expt. (Ref. [31]) | 402 533 305 440 538 609 | |

Incidentally, we also find that the longitudinal components of the magnetic charge for Cr atoms are very sensitive to the lattice constant of Cr$_2$O$_3$, especially the Cr-O distance in the longitudinal direction. Thus, it is essential to choose a proper exchange-correlation functional to mimic the experimental ground state structure.

The Born charge tensors for Cr and O are computed to be

$$Z^e(Cr) = \begin{pmatrix} 3.02 & -0.30 & 0 \\ 0.30 & 3.02 & 0 \\ 0 & 0 & 3.18 \end{pmatrix} e,$$

$$Z^e(O) = \begin{pmatrix} -2.36 & 0 & 0 \\ 0 & -1.66 & -1.00 \\ 0 & -0.88 & 2.12 \end{pmatrix} e.$$

While the symmetry constraints on the non-zero elements are the same as for $Z^m$, the pattern is quite different. For example, the diagonal elements are of similar magnitude for $Z^e$ but not for $Z^m$.

The lattice-mediated magnetic and electric responses for Cr$_2$O$_3$ computed from Eqs. (9-14) are summarized in the bottom panel of Table IV. Our computational results are in reasonable agreement with the experimental room-temperature lattice-mediated $\chi^e$ = 4.96 and $\chi^m$ = 3.60 obtained from IR reflectance measurements.

TABLE III. Magnetic charges $Z^m$ (10$^{-2}\mu_B$/Å) for Cr$_2$O$_3$ in the atomic basis. The magnetic charge tensors for Cr and O atoms take the forms shown in Figs. 3(a-b).

|        | spin | orbital | orbital |
|--------|------|---------|---------|
| $Z^m_{Cr}$ | 5.88 | 0.25 | $Z^m_{O}$ | -1.95 | -0.38 |
| $Z^m_{Cr}$ | -5.69 | 0.02 | $Z^m_{O}$ | 0.00 | 1.12 |
| $Z^m_{Cr}$ | 0.02 | 0.23 | $Z^m_{O}$ | -1.10 | -0.72 |
| $Z^m_{Cr}$ | -5.92 | 0.06 | $Z^m_{O}$ | -0.02 | -0.15 |

TABLE IV. Top: Mode decomposition of the Born charges $Z^e$, and of the spin and orbital contributions to the magnetic charges $Z^m$, in Cr$_2$O$_3$. $C_n$ are the eigenvalues of the force-constant matrix. Bottom: Total $A_{2u}$-mode (longitudinal) and $E_u$-mode (transverse) elements of the lattice-mediated electric susceptibility $\chi^e$, magnetic susceptibility $\chi^m$, and the spin and orbital parts of the ME constant $\alpha$.

|        | $A_{2u}$ modes | $E_u$ modes |
|--------|----------------|-------------|
| $C_n$ (eV/Å$^2$) | 10.5 22.9 10.2 16.0 20.2 30.9 | |
| $Z^e$ (µe) | 1.15 8.50 0.55 0.39 3.71 7.07 | |
| $Z^m$ spin (10$^{-2}$µB/Å) | 0.02 0.05 -0.76 -3.97 16.14 10.55 | |
| $Z^m$ orb (10$^{-2}$µB/Å) | 2.74 -0.59 0.66 -0.80 -0.29 1.06 | |
| Latt. $\chi^e$ | 6.2 | 4.37 | |
| Latt. $\chi^m$ | 0.05 × 10$^{-8}$ | 1.28 × 10$^{-8}$ | |
| $\alpha$ spin (ps/m) | 0.0024 | 0.633 | |
| $\alpha$ orb (ps/m) | 0.0097 | 0.025 | |
TABLE V. Magnetic charges Zm (10⁻²μB/Å) for CaAlMn₃O₇ (KITPite) in the atomic basis (spin only). The magnetic charge tensors for Ca, Al and O¹ are of the form of Fig. 3 (c); those for Mn and O³ are of the form of Fig. 3 (d); and that for O² is of the form of Fig. 3 (b).

|       | Zm m (10⁻²μB/Å) |
|-------|-----------------|
| Zm⁺(Ca) | -43.46          |
| Zm⁺(Al) | -24.63          |
| Zm⁺(Mn) | 341.53          |
| Zm⁺(O²) | -75.23          |

B. KITPite

When we relax KITPite CaAlMn₃O₇ in the assumed 6₃/m/m'/c' structure, the unit cell has a volume of 311.05 Å³ with a c/a ratio of 0.998. The Wyckoff coordinates for the Mn atoms (6h) and O³ atoms (6g) are 0.5216 and 0.1871. Other atoms are in high-symmetry Wyckoff positions. The IR-active modes are

\[ \Gamma_{\text{IR}} = 6A_{2u} + 9E_{1u} \] (17)

excluding the acoustic modes. The longitudinal A₂u modes do not contribute to the magnetic response when spin-orbit interaction is absent in CaAlMn₃O₇, because the longitudinal components of the magnetic charges Zm are zero.

The results for the magnetic charge tensors are reported in the atomic basis and the IR-active mode basis in Tables V and VI respectively. The calculated force-constant eigenvalues and Born charges Z⁺ are also listed in Table VI. The Born charges in KITPite and Cr₂O₃ are all close to the atomic valence charge values. As the KITPite structure is fictitious and two E₁u modes are unstable in the high-symmetry structure, we will focus on the results for the magnetic charges and omit any discussion of the electric and dielectric responses.

The magnetic charges in the KITPite structure are found to be much larger than for Cr₂O₃. For the transition-metal ion, the magnetic charge of Mn in KITPite is ~50 times larger than for Cr in Cr₂O₃. The magnetic charges in Cr₂O₃ are driven by SOC, which acts as an antisymmetric exchange field. Thus, the weakness of the SOC on the Cr atoms implies that the magnetic charges and magnetic responses are small in Cr₂O₃. In the KITPite structure, we deliberately exclude spin-orbit interaction, so the magnetic charges are purely induced by the spin frustration and the super-exchange between Mn-O-Mn atoms. This exchange striction mechanism causes the magnetic charges in CaAlMn₃O₇ to be dozens of times larger than the SOC-driven responses in Cr₂O₃.

Since the orbital magnetization is strongly quenched in most 3d transition metals, we expect the orbital contribution to the Zm tensors in CaAlMn₃O₇ to be comparable with those in Cr₂O₃, i.e., on the order of 10⁻²μB/Å. Since this is ~2 orders of magnitude smaller than the typical spin contribution in CaAlMn₃O₇, we have not included it in our calculation. The main point of our study of KITPite CaAlMn₃O₇ has been to demonstrate that exchange-striction effects can give rise to large Zm values based on a mechanism that does not involve SOC at all.

IV. SUMMARY

In summary, we have begun by presenting a systematic formulation of the role played by the dynamic magnetic charge tensor Zm in the lattice magnetic, magnetoelectric, and piezomagnetic responses of crystalline solids. We have then used first-principles density-functional methods to compute the atomic Zm tensors for two prototypical materials, namely Cr₂O₃, a well-studied magnetoelectric material, and fictitious KITPite, which displays a very large lattice ME effect. We find that the physics is quite different in the two cases, with mechanisms based on SOC giving only small Zm values in the collinear antiferromagnet Cr₂O₃, while exchange-striction effects induce large Zm's in noncollinear KITPite.

Our calculations are part of a broader effort to identify mechanisms that could induce large magnetic charge values. They help to reinforce a picture in which SOC effects give only weak contributions, at least in 3d transition-metal compounds, whereas exchange striction can induce much larger effects in materials in which spin frus-
tration gives rise to a noncollinear spin structure. In this respect, the conclusions parallel those that have emerged with respect to the polarization in multiferroics and magnetically-induced improper ferroelectrics, where exchange striction, when present, typically produce much larger effects than SOC.

Our work points to some possible future directions for exploration. One obvious direction is to identify experimentally known materials in which exchange striction gives rise to large $Z_m$ values. In such systems, lattice-mediated effects might even contribute significantly to the magnetic susceptibility; while such contributions are normally neglected for $\chi_m$, we note that $Z_m$ appears to the second power in Eq. (10), so this contribution might be significant, especially in soft-mode systems. It might also be interesting to explore the role of these magnetic charges in the phenomenology of electromagnons. Finally, we point out that, unlike $Z_e$, $Z_m$ remains well-defined even in metals; while magnetoelectric effects do not exist in this case, it would still be interesting to explore the consequences of large $Z_m$ values in such systems.

ACKNOWLEDGMENTS

This work was supported by ONR Grant N00014-12-1-1035.

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