Microscopic theory of temperature-dependent magnetoelectric effect in Cr$_2$O$_3$

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We calculate the temperature-dependent magnetoelectric response of Cr$_2$O$_3$ from first principles. The form of the dominant magnetoelectric coupling is determined using symmetry arguments, its strength is found using $ab$ initio methods, and the temperature dependence of the response is obtained from Monte Carlo simulations. The quantitative agreement of our results with experiment shows that the strong temperature dependence of the magnetoelectric effect in Cr$_2$O$_3$ results from non-relativistic exchange interactions and spin fluctuations.

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Introduction: Recent progress in understanding the subclass of multiferroics in which improper ferroelectric polarizations are induced by non-centrosymmetric magnetic orderings has led to a clarification of the microscopic origins for magnetoelectric coupling. In particular, two distinct coupling mechanisms have been identified. The first arises from relativistic effects linking electron spin and orbital momentum, resulting in the antisymmetric $\mathbf{S}_1 \times \mathbf{S}_2$ interaction between spins of magnetic ions. The dependence of the strength of this Dzyaloshinskii-Moriya interaction on polar displacements of ions makes magnets with non-collinear spiral orders ferroelectric.

In the second mechanism, polar deformations of the lattice are induced by Heisenberg spin exchange interactions $\mathbf{S}_1 \cdot \mathbf{S}_2$, originating from the Fermi statistics of electrons. This non-relativistic mechanism can give rise to stronger magnetoelectric couplings than those resulting from relativistic effects, which tend to be relatively weak in 3d transition metal compounds, and is not restricted to non-collinear spin arrangements. Indeed, the electric polarizations of the orthorhombic manganite $Y_{1-x}Lu_x$MnO$_2$ and orthoferrite GdFeO$_3$, which have collinear antiferromagnetic spin orderings and polarization arising from the Heisenberg mechanism, exceed the largest polarizations observed in spiral multiferroics by one order of magnitude.

In this work we show that, in addition to causing multiferroic behavior, the relativistic and Heisenberg exchange mechanisms can both give rise to the linear magnetoelectric effect, in which an applied magnetic field induces an electric polarization proportional to the field and, conversely, magnetization is induced by an applied electric field (for a review see Ref.[10]). Furthermore, the two mechanisms can co-exist in the same material and dominate in different temperature regimes. Using a combination of first-principles density functional theory and Monte Carlo methods we calculate the temperature-dependent magnetoelectric response of the prototype magnetoelectric material, chromium sesquioxide, Cr$_2$O$_3$. We show that the strong finite-temperature magnetoelectric response originates from the Heisenberg exchange mechanism combined with thermal spin fluctuations, whereas at zero temperature, where spin fluctuations vanish, the observed weak response arises from relativistic effects. Significantly, Cr$_2$O$_3$ is a collinear antiferromagnet, and so our work extends the recent suggestion that Heisenberg exchange interactions can give rise to a strong magnetoelectric effect in frustrated magnets in which spins are forced to form non-collinear orders with nonzero toroidal or monopole moments.

Magnetoelectric coupling: The magnetoelectric effect in Cr$_2$O$_3$ was predicted phenomenologically by Dzyaloshinskii and measured by Astrov shortly after the theoretical prediction. Cr$_2$O$_3$ has four Cr$^{3+}$ ions with spin $S = 3/2$ in the rhombohedral unit cell. Below $T_N = 307$K it shows collinear $\uparrow\uparrow\downarrow\downarrow$ spin ordering along the trigonal $z$ axis [see Fig. 1(a)]. This antiferromagnetic ordering preserves the three-fold and two-fold symmetry axes of the paramagnetic phase, but it breaks inversion symmetry $I$, reducing it to $I'$ (inversion combined with...
time reversal), which allows for two independent magnetoelectric coupling terms in the free energy:

\[ F_{\text{me}} = -g_{\parallel} G \cdot E + H - g_{\perp} G \cdot (E \cdot H + E \cdot H) \], \hspace{1cm} (1)

where \( G = \langle S_1^z - S_2^z + S_3^z - S_4^z \rangle \) is the antiferromagnetic order parameter. The two magnetoelectric coefficients, \( \alpha_{\parallel} = g_{\parallel} G \) and \( \alpha_{\perp} = g_{\perp} G \), show very different temperature dependences. While \( \alpha_{\perp} \) varies only in the immediate vicinity of the transition temperature, \( T_N \), the coefficient \( \alpha_{\parallel} \) is very strongly temperature dependent. \( \alpha_{\parallel} \) reaches its maximum at \( T_{\text{max}} \approx 260 \text{K} \), below which it steeply decreases and changes sign at \( \sim 100 \text{K} \). While at \( T_{\text{max}} \) the magnitude of \( \alpha_{\parallel} \) is one order of magnitude larger than \( |\alpha_{\perp}| \), at low temperatures \( |\alpha_{\parallel}| < |\alpha_{\perp}| \).

Early measurements of the temperature dependence of the magnetoelectric coefficients\textsuperscript{16-18} as well as recent first-principles calculations\textsuperscript{19} show that the relatively weak magnetoelectric effects at low temperature result from relativistic interactions. In what follows, we demonstrate that the much stronger response at elevated temperatures originates from the Heisenberg exchange.

Phenomenologically, the coupling of the electric polarization \( P^z \) along the trigonal axis to spins, resulting from the dependence of spin-exchange constants on polar lattice distortions, is described by

\[ P^z = \lambda \langle S_1 \cdot S_2 - S_3 \cdot S_4 \rangle, \hspace{1cm} (2) \]

where \( S_\alpha \) with \( \alpha = 1, 2, 3, 4 \) denotes the sublattice magnetization and \( \lambda \) is the coupling strength that we will determine from \textit{ab initio} calculations. Here we take into account the fact that the exchange-driven polarization can only depend on scalar products of the magnetizations. The combination of scalar products in the right-hand side of Eq. (2) transforms as \( P^z \), which changes sign under \( C_2 \) and \( J \). The combination of scalar products that lead to this property can be seen by inspection of Table I which shows how the four inequivalent magnetic sites transform under the symmetry operations of \( \text{Cr}_2 \text{O}_3 \).

| \( C_3 \) | \( C_2 \) | \( I \) |
|-----|-----|-----|
| 1   | 2   | 4   |
| 2   | 1   | 3   |
| 3   | 4   | 2   |
| 4   | 3   | 1   |

TABLE I: Transformation of four independent Cr sites with the fractional coordinates \( r_1 = (u, u, u) \), \( r_2 = (1/2 - u, 1/2 - u, 1/2 + u) \), \( r_3 = (1/2 + u, 1/2 + u, 1/2 + u) \), and \( r_4 = (1 - u, 1 - u, 1 - u) \), where \( u \approx 0.153 \). Under the generators of space group \( R3c \): the 120°-rotation around the \( z \) axis, \( C_3 = (x_3, x_1, x_2) \), the 180°-rotation around the axis orthogonal to the \( z \)-direction, \( C_2 = (1/2 - x_2, 1/2 - x_1, 1/2 - x_3) \) and inversion \( I = (1 - x_1, 1 - x_2, 1 - x_3) \). Here, \( c = a_1 + a_2 + a_3 \), where \( a_i \) (\( i = 1, 2, 3 \)) are the rhombohedral unit vectors.

Equation (2) is clearly appropriate for describing electric polarization induced by spin ordering in a multiferroic material. In addition, it applies to the linear magnetoelectric effect, as can be seen from the following heuristic argument: In an applied magnetic field \( H_z \) the average value of spin on the sublattice \( \alpha \) changes by \( \langle S_\alpha \rangle \propto \chi_{\parallel} H_z \), where \( \chi_{\parallel} \) is the longitudinal magnetic susceptibility. Equation (2) then gives \( P^z = -\frac{\partial F_{\text{me}}}{\partial H_{\parallel}} = g_{\parallel} G^2 H_z \) obtained from Eq. (1).

Equation (2) is only meaningful within the mean field approach. To account for effects of spin fluctuations on the magnetoelectric response of \( \text{Cr}_2 \text{O}_3 \) we will use the microscopic expression for the exchange-driven polarization in terms of scalar products of Cr spins (rather than the sublattice magnetizations), which has the form

\[ P^z = \frac{\lambda}{6N} \sum_{j=1}^{6} \sum_{n=1}^{6} (S_{1,j} \cdot S_{3,j-b_n} - S_{2,j} \cdot S_{4,j-b_n}). \hspace{1cm} (3) \]

Here \( j \) labels unit cells, \( N \) is the total number of unit cells, and \( b_3 = a_1, b_2 = a_2, b_3 = a_3, b_4 = a_1 + a_2, b_5 = a_2 + a_3, b_6 = a_3 + a_1 \) (\( a_i \) being the rhombohedral unit vectors). Remarkably, the interaction between the fourth nearest-neighbor Cr ions separated by the distance \( r_4 (3-\alpha_1) = r_6 (3-\alpha_1-\alpha_2) = 3.65 \text{\AA} \) turns out to give rise to the magnetoelectric effect in \( \text{Cr}_2 \text{O}_3 \). The short-range exchange interactions do not couple the sublattices 1 and 3 (or 2 and 4) and, therefore, do not contribute to \( P^z \), while other interactions between these sublattices correspond to much longer exchange paths and are negligibly small. This allows us to accurately pinpoint the microscopic origin of the strong magnetoelectric effect in \( \text{Cr}_2 \text{O}_3 \).

Importantly, Eqs. (2) and (3) apply to any four-sublattice spin ordering in \( \text{Cr}_2 \text{O}_3 \). The \( \uparrow \uparrow \downarrow \downarrow \) spin ordering realized in the low-temperature ground-state of \( \text{Cr}_2 \text{O}_3 \) induces no electric polarization, and so a straightforward density-functional study of \( \text{Cr}_2 \text{O}_3 \) does not give information about the strength of the finite-temperature perpendicular magnetoelectric coupling. However, the \( \uparrow \uparrow \downarrow \downarrow \) ordering shown in Fig. 1(b) renders \( \text{Cr}_2 \text{O}_3 \) multiferroic and induces the electric polarization

\[ \mathcal{P} = P^z (\uparrow \uparrow \downarrow \downarrow) = 2\lambda S^z . \hspace{1cm} (4) \]

We next extract \( \lambda \) using \textit{ab initio} methods by enforcing \( \uparrow \uparrow \downarrow \downarrow \) spin ordering and calculating the magnetoelectrically-induced polarization \( \mathcal{P} \).

First-principles calculations of the magnetoelectric coupling: We compute \( \lambda \) and the spin exchange parameters using plane-wave density-functional theory, as implemented in the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{22}. We use PAW potentials\textsuperscript{23} for core-valence partitioning, and the local-spin-density approximation (LSDA+) for the exchange-correlation potential\textsuperscript{24}. Our Hubbard \( U = 2.0 \text{eV} \) is the same value that was taken for computing the magnetoelectric response at zero temperature\textsuperscript{27}. We deliberately do not include spin-orbit coupling, and all calculations are for collinear spin densities, so that \( \lambda \)
corresponds only to polarizations induced by exchange striction.

We find that a plane-wave cutoff of 500 eV and Monkhorst-Pack $k$-point sampling of $4 \times 4 \times 4$ are sufficient for computing the properties of interest. Note that much finer $k$ meshes would be required for accurately resolving the magnetocrystalline easy axis but non-relativistic properties are well converged with our chosen parameters.

We work with space group R$ar{3}$c at the experimental volume of 96.0 Å$^3$ and rhombohedral angle of 55.13°. The internal coordinates are relaxed within our density functional calculations for the $\uparrow \uparrow \uparrow$ magnetic configuration, yielding coordinates $x = 0.1536$ for Cr, and $x = 0.9426$ for O in Wyckoff positions 4c and 6c respectively. Subsequently, the Heisenberg exchange couplings $J_{1}-J_{5}$ corresponding to Cr-Cr distances of 2.65 to 4.10 Å, are computed by fitting a Heisenberg Hamiltonian to DFT total energies of twelve different spin configurations with fixed ion coordinates in the hexagonal setting of R$ar{3}$c. This method is analogous to that employed by Shi et al.

Finally, we compute $\lambda$ by enforcing the spin configuration of $\uparrow \uparrow \downarrow \downarrow \downarrow$ and re-relaxing the ionic coordinates in the rhombohedral unit cell. The resulting ionic configuration has a polar lattice distortion. We compute the magnitude of $\mathcal{P} = 0.585 \, \mu C/cm^2$ using the Berry phase approach which allows us to extract $\lambda$. We note that $\mathcal{P}$ is of the same order of magnitude as the polarization induced by exchange interactions in multiferroics with collinear spins.

Monte Carlo simulations: Using Eq. (3) we can express the magnetoelastic coefficient $\alpha_{||}$ in terms of spin correlation functions:

$$\alpha_{||} = \frac{\partial \langle P^z \rangle}{\partial H^z} \bigg|_{H^z=0} = \frac{2\mu_B}{k_B T} \langle P^z \sum_{a,j} S_{a,j}^z \rangle,$$

where $\langle \ldots \rangle$ denotes the thermal average at temperature $T$, $k_B$ is the Boltzmann constant and $\mu_B$ is the Bohr magneton.

In the mean-field approximation, equivalent to replacing the scalar products of spins $S_{a,j} \cdot S_{\beta,k}$ by $(S_{a,j}) \cdot (S_{\beta,k})$ in the expression for $P^z$, one obtains:

$$\alpha_{||} = \frac{\lambda v_0 G^2 \chi_{||}}{8 \mu_B},$$

where $v_0$ is the unit cell volume, in agreement with the simple argument given above. The mean-field expression qualitatively explains the observed temperature dependence of $\alpha_{||}$: It first grows, together with the order parameter $G^2$, as the temperature drops below $T_N$, then subsequently decreases and vanishes at $T = 0$, together with the longitudinal magnetic susceptibility $\chi_{||}$.

In Ref.[18] an attempt was made to take into account the effects of spin fluctuations using a higher-order decoupling scheme. This approximation fails, however, close to the transition temperature where spin fluctuations are large. We include spin fluctuations by calculating $\alpha_{||}$ numerically using Monte Carlo simulations of a system of 864 classical spins with exchange constants and the magnetoelastic coupling $\lambda$ obtained from our first principles calculations, as described above.

Since the correlation function in the right-hand side of Eq. (5) is zero unless a single antiferromagnetic domain is selected, we apply to our finite spin system a weak staggered field along the $z$ axis, $h(-\alpha)$, where $\alpha = 1, 2, 3, 4$ labels magnetic sublattices. This mimics the easy magnetic anisotropy of Cr$_2$O$_3$ as well as the cooling in electric and magnetic fields, used in measurements of magnetoelastic coefficients to select the domain with a given sign of magnetic order parameter. The field strength, $h = 0.165$ meV, was chosen so that it is small compared to the scale of exchange interactions, but large enough to make the Monte Carlo results independent of $h$.

Figure 2 shows the temperature dependence of $\alpha_{||}$ obtained from Monte Carlo simulations (blue circles) and in the mean-field approximation described above (red solid line). The onset of the magnetoelastic response in our Monte Carlo simulations, as well as the sharp peak in the specific heat (inset), shows that the antiferromagnetic order sets in at $\sim 290$ K, close to the experimentally observed transition temperature $T_N = 307$ K. The maximal value of the magnetoelastic coefficient obtained from our simulations is $0.9 \times 10^{-4}$ (in CGS units), in excellent agreement with the experimental value of $1.0 \times 10^{-4}$ (see Ref[18]). The maximum value is reached at $\sim 240$ K that compares well to $T_{\text{max}} \sim 260$ K found in experiment. The mean field transition temperature (425 K) and maximal $\alpha_{||}$ are significantly higher than the Monte Carlo values, indicating the importance of spin fluctuations in this material.

Conclusions: We have presented the first ab initio calculations of temperature-dependent linear magnetoelastic responses. The quantitative agreement of our results with experimental data on Cr$_2$O$_3$ demonstrates that the dominant parallel magnetoelastic coupling in this material originates from non-relativistic exchange interactions between electrons. The strong temperature dependence of the magnetoelastic coefficient $\alpha_{||}$ underscores the general importance of spin fluctuations for magnetoelastic responses of materials with collinear spin orders. The magnetic-field-induced electric polarization of Cr$_2$O$_3$ is comparable to that predicted recently for an exchange-interaction-driven Kagome antiferromagnet with non-collinear spin ordering. However, the magnetoelastic response of non-collinear magnets does not vanish at zero temperature as it involves transverse rather than longitudinal magnetic susceptibility and originates from the dynamic ‘electromagnon’ modes, which can be excited by both electric and magnetic fields and which are absent in collinear magnets.

The approach used in this paper, specifically the combination of first principles calculations for artificially imposed magnetic states to extract parameters with Monte Carlo simulations of physically interesting quantities,
FIG. 2: (Color online) Temperature dependence of the magnetoelectric coupling $\alpha_\parallel$ obtained using ab initio values of the exchange constants and magnetoelectric coupling combined with Monte Carlo simulations (blue circles) and mean field calculations (solid red line). The inset shows the temperature dependence of magnetic specific heat.

opens a route to theoretical studies of a large variety of temperature-dependent static and dynamic magnetoelectric phenomena. Accurate predictions of the magnitude of magnetoelectric responses at finite temperature will greatly facilitate the search for and design of materials with the strongest responses.

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