Ferroelectricity in the Magnetic E-Phase of Orthorhombic Perovskites

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We show that the symmetry of the spin zigzag chain E phase of the orthorhombic perovskite manganites and nickelates allows for the existence of a finite ferroelectric polarization. The proposed microscopic mechanism is independent of spin-orbit coupling. We predict that the polarization induced by the E-type magnetic order can potentially be enhanced by up to two orders of magnitude with respect to that in the spiral magnetic phases of TbMnO3 and similar multiferroic compounds.

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Introduction. The switching of the electric polarization $\mathbf{P}$ by a magnetic field of a few Tesla discovered in TbMnO3 $\mathbf{1}$ and TbMn2O5 $\mathbf{2}$ has ignited enormous interest in a class of materials that can be termed improper magnetic ferroelectrics (IMF’s). While there is no intrinsic ferroelectric (FE) instability in the IMF’s, $\mathbf{P}$ emerges due to its coupling to the primary magnetic order parameter. Hence, the FE phase transition coincides with the corresponding magnetic transition, and $\mathbf{P}$ is very sensitive to magnetic field induced changes of the magnetic state $\mathbf{1}$, $\mathbf{2}$, $\mathbf{3}$, $\mathbf{4}$, $\mathbf{5}$, $\mathbf{6}$, $\mathbf{7}$, $\mathbf{8}$. Symmetry imposes rather strict conditions on the possible magnetic order parameters—the magnetic structure must have low enough symmetry in order for the system to form a polar axis. As a consequence, the IMF’s often have complicated non-collinear structures, including spiral and incommensurate $\mathbf{6}$, $\mathbf{7}$, $\mathbf{8}$, $\mathbf{9}$, $\mathbf{10}$, $\mathbf{11}$, $\mathbf{12}$, $\mathbf{13}$, while the IMF phases with collinear magnetism are rare $\mathbf{14}$, $\mathbf{15}$. Non-collinear magnetic structures are stabilized due to either competing interactions (frustration) or anisotropies generated by spin-orbit coupling, which leads to reduced transition temperatures and weaker order parameters. The magnitude of $\mathbf{P}$ ($\approx 0.1 \mu \text{C/cm}^2$) is also affected by its weak coupling to magnetism. In turn, collinear IMF’s may prove more promising for future applications as they are less prone to the obstacles mentioned above.

In our present study we turn our attention to the collinear E-type magnetic phase that has been observed in perovskite manganites $\mathbf{14}$, $\mathbf{16}$ and nickelates $\mathbf{18}$, $\mathbf{19}$, $\mathbf{20}$, $\mathbf{21}$. First, we show that this is a previously overlooked example of an IMF. Second, in contrast to the most extensively theoretically studied case of spiral magnetism $\mathbf{22}$, $\mathbf{23}$, $\mathbf{24}$, the mechanism responsible for ferroelectricity in the magnetically ordered phase does not rely on the presence of anisotropic Dzyaloshinskii-Moriya interaction. In our case, $\mathbf{P}$ appears due to a gain in the band energy of the $e_g$ electrons in the double-exchange model. We estimate that $\mathbf{P}$ can be potentially larger than that in the spiral magnets by up to two orders of magnitude, thus paving a way for IMF’s to reach the values of $\mathbf{P}$ common for other multiferroic systems with better ferroelectric properties $\mathbf{25}$, $\mathbf{26}$.

In the perovskite manganite family $\text{RMnO}_3$ (space group $\text{Pbnm}$), the E-phase was first reported for $\text{R}=$Ho as a result of magnetic structure refinement by neutron diffraction $\mathbf{17}$. The magnetic unit cell of the E-phase, forming at low temperature below $T_L = 26 - 29.6 \text{ K}$ $\mathbf{17}$, is shown in Fig $\mathbf{1}$a. The Mn atoms with parallel spins form zigzag chains in the $ab$-plane, with the chain link equal to the nearest-neighbor Mn-Mn distance. The neighboring zigzag chains in the $b$-direction have antiparallel spins. Figures $\mathbf{1}$b and (c) show that the equal-spin E-phase structure can be obtained from the simple sine-wave structure by locking-in its modulation vector $k_b = \frac{1}{3}$ and fine-tuning its phase. The $ab$-planes are stacked antiferromagnetically $(+ - + -)$ along the $c$-direction. Interestingly, Lorenz $\text{et al.}$ $\mathbf{27}$ reported on a
large magnetic field dependence of the dielectric constant below $T_L$, which may be an indication of the multiferroic state.

**Landau theory.** Independently of the microscopic mechanism, the possibility of a FE state in magnets can be examined by considering the symmetry allowed terms in the Landau potential \([17, 23, 24, 28]\). We define the symmetric coordinates corresponding to the E-phase as

\[
\begin{align*}
E_1 &= S_1 + S_2 - S_3 - S_4 - S_5 + S_6 + S_7 - S_8, \\
E_2 &= S_1 - S_2 - S_3 + S_4 - S_5 + S_6 - S_7 + S_8,
\end{align*}
\]

where $S_i$ is the spin of the $i$th Mn atom in the magnetic unit cell, as shown in Fig. 1(a). Since the Mn spins in HoMnO$_3$ point along the $a$-axis, below we consider only the $b$-components of $E_{1,2}$ denoted by $E_{1,2}$. However, the expression for the Landau potential derived below is valid for any component of $E_{1,2}$. $E_1$ and $E_2$ span an irreducible representation of the space group $Pbmm$ corresponding to $k = (0,0,0)$. The properties of this representation are summarized in Table I. Taking into account that $\mathbf{P}$ transforms as a polar vector, we obtain the following form of the Landau potential corresponding to the E-phase,

\[
F = a(E_1^2 + E_2^2) + b_1(E_1^2 + E_2^2) + b_2E_1E_2 + \frac{1}{2\chi}\mathbf{P}^2,
\]

where $\chi$ is the dielectric susceptibility of the paraelectric phase, and the other coefficients are phenomenological parameters. Minimizing $F$ with respect to $\mathbf{P}$, we obtain $P_a = -\chi(E_1^2 - E_2^2)$, $P_b = -\chi(E_1^2 - E_2^2)E_1E_2$, and $P_c = 0$. Therefore, each of the four domains of the E-phase $[\pm E_1,0]$ and $(0, \pm E_2)$ is IMF with the polarization along the $a$-axis and different signs of $P_a$ for $E_1$ and $E_2$. We also notice that the $b$-axis component of $\mathbf{P}$ can be locally present within the domain walls where $E_1$ and $E_2$ coexist [31].

The E-type phase in the nickelates also consists of spin zigzag chains that have a different direction in the $ab$-plane and a different stacking along the $c$-axis (+ + − −) [13, 14, 20, 21]. The corresponding modulation vector is $\mathbf{k} = (\frac{1}{4}00)$. The Landau theory analysis leads to results similar to the manganite case. For nickelates, the symmetric coordinates $E_1$ and $E_2$ (not given here) are written in terms of 16 Ni spins of the magnetic unit cell which is 4 times the crystallographic unit cell. It leads to a Landau potential similar to (2) with $P_a$ replaced by $P_b$ in the fourth term and $d = 0$. Thus, $\mathbf{P}$ in the E-phase of nickelates is parallel to the $b$-axis.

**Microscopic model.** To understand microscopically the possible mechanism of ferroelectricity in the E-phase we use Monte Carlo (MC) simulations to study the ground state properties of the following Hamiltonian for manganites based on the orbitally degenerate double-exchange model [31, 32, 33] with one $e_g$-electron per Mn$^{3+}$ ion,

\[
H = -\sum_{i\alpha\beta} C_{i\alpha\beta} d_{i\alpha}^\dagger d_{i\beta} + J_{\text{AF}} \sum_{i\alpha} S_i \cdot S_{i+1} + \frac{1}{2} \sum_{i,m} \kappa_m Q_{mi}^2,
\]

where $d_{i\alpha}^\dagger$ is the creation operator for the $e_g$ electron on orbital $\alpha = x^2 - y^2(a_1), 3z^2 - r^2(b)$; $\mathbf{a} = x, y$ is the direction of the link connecting the two nearest neighbor Mn sites; and $S_i$ is the classical unit spin, given by the polar angle $\theta_i$ and azimuthal angle $\phi_i$, representing the electrons occupying the $t_{2g}$ orbitals on the $i$-th Mn site. The $t_{2g}$ spins interact directly through the antiferromagnetic superexchange $J_{\text{AF}} > 0$. $C_{ij} = \cos \theta_i \cos \frac{\theta_j}{2} + \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} e^{-i(\phi_i - \phi_j)}$ is the double-exchange factor arising due to the large Hund’s coupling that projects out the $e_g$ electrons with spin antiparallel to $S_i$. $Q_{mi}$ represent the classical adiabatic phonon modes, with stiffnesses $\kappa_m$, due to the displacements of the ligand oxygen ions surrounding the $i$-th Mn site. The phonon stiffnesses were chosen as follows – for the Jahn-Teller modes: $\kappa_1 = 2.0$, $\kappa_2 = \kappa_3 = 1.0$; for the FE mode $\kappa_{\text{FE}} = 8.0$ and for the rest of the modes, $\kappa = 10.0$. Except for the Jahn-Teller modes [31, 32], this choice is driven only by the efficiency of the MC simulations, and it does not reflect the actual frequencies of the phonon modes, which are presently unknown. We illustrate below how $P$ can be obtained in physical units. The third term in Eq. (4) is the Jahn-Teller coupling with constant $\lambda$ and the $e_g$-orbital operators $p_i = d_{i\alpha}^\dagger d_{i\alpha} + d_{i\beta}^\dagger d_{i\beta}$, $\tau_{x,i} = d_{i\alpha}^\dagger d_{i\beta} + d_{i\beta}^\dagger d_{i\alpha}$ and $\tau_{z,i} = d_{i\alpha}^\dagger d_{i\alpha} - d_{i\beta}^\dagger d_{i\beta}$.

Our improvements over previous approaches to this model are the following. First, we explicitly consider the dependence of the hoping parameters $t_{\alpha\beta}^{\text{in}}$ on the angle of the Mn-O-Mn bond $\varphi_{\text{in}}$. Taking into account only the largest Mn-O $\sigma$-bond contribution, we find [34] $t_{\alpha\beta}^x = t_{\alpha\beta}^y = -t \cos^2 \varphi_{\text{in}}, t_{\alpha\beta}^z = -t \cos \varphi_{\text{in}}/\sqrt{3}$, $t_{\alpha\beta}^x = t_{\alpha\beta}^y = -t \cos \varphi_{\text{in}}/\sqrt{3}$, where $t = \frac{1}{3} (pd\sigma)^2$ is taken as the energy unit hereafter. We neglect the $\varphi_{\text{in}}$ dependence of $J_{\text{AF}}$ since it has a smaller energy scale than $t$. Second, $Q_{mi}$’s are defined such that the elastic energy term in (4) is minimal for $\varphi_{\text{in}} = \varphi_{\text{in}} < 180^\circ$. This allows us to model the initial structural buckling (GdFeO$_3$-type)
to the spontaneous symmetry breaking caused by the E-phase. However, the ferromagnetic zigzag chains are clearly essential in generating ferroelectricity in the E-phase. The local arrangement of the Mn-O bonds with disordered Mn spins (full circles). Right. Oxygen displacements (arrows) within the chains of opposite Mn spins (open and crossed circles) in the E-phase (see also Refs. 8, 12). (d) MC results for the polarization at T=0.01 for different values of $J_{AF}$. Figure 2(d) shows the calculated absolute value of the polarization $P_{calc}$, defined as the oxygen displacement per one “unit cell” containing one Mn and two O atoms averaged over MC steps, plotted versus $\varphi_0$ for different values of $J_{AF}$. $P$ vanishes for $\varphi_0 = 180^\circ$ for all values of $J_{AF}$. In this case both the hopping and elastic energies are optimal when $\varphi = \varphi_0 = 180^\circ$, the same for ferromagnetic and antiferromagnetic bonds. To demonstrate this it is also consistent with the symmetry arguments of Landau theory, we note that the symmetry of the lattice with $180^\circ$ bonds is higher than that with $\varphi_0 < 180^\circ$. Particularly, additional inversion centers are located at the O sites if $\varphi_0 = 180^\circ$. While the E-type magnetic structure breaks inversion symmetry for centers located at the Mn sites, it is invariant with respect to the O-site centers, and thus the magnetic phase transition cannot induce FE order. In terms of the Landau potential, the coefficients $c$ and $d$ must be zero in this case.

The MC calculated value of the polarization $P_{calc}$ for $\varphi_0 \approx 145^\circ$ corresponding to HoMnO$_3$ reaches 0.08. It can be shown from the model that the FE displacements scale as $t/\kappa_{FE}V_0$. In the simulations we set $t = 1$ and $a_0 = 1$, and the polarization in the physical units, in the point charge approximation, is given by $P = \frac{2\pi e^2 c}{\kappa_{FE} \kappa_{FE} \kappa_{FE} V_0}P_{calc}$, where $e$ is the elementary charge, $\kappa_{FE}$ is the FE phonon stiffnesses in the physical units, and $V_0$ is the unit cell volume. Using $a_0 = 2.35$ Å, $V_0 = 226$ Å$^3$, $t = 0.1 - 0.5$ eV [31], $\kappa_{FE} = 1 - 5$ eV/Å$^2$ [22], we obtain a range of values for $P$ between 0.5 and 12
\( \mu C/cm^2 \), substantially larger than the \( P \) observed in helical IMF’s. We can also estimate \( P \) from the known experimental results for TbMnO\(_3\). Its crystal structure is modulated in the collinear sine-wave phase with wave vector \( k_L = 2k_M \) where \( k_M = 0.29 \) is the magnetic wave vector. The displacement of the O atom \( n \) in a Mn-O chain running along the \( x \)- or \( y \)-direction [see Fig. 2(b)] is given by \( \delta r_n = \delta r_0 (-1)^{n} \cos \pi k_M + \cos [(2n + 1)\pi k_M + 2n] \), for the magnetic structure defined by \( S_a = S_c = 0, S_b = S_0 \cos n k_M + \alpha \) \([24]\). If \( k_M \neq 1/2 \), then \( \sum_n \delta r_n = 0 \) and the state is paraelectric. The E-phase corresponds to \( k_M = 1/2, \alpha = 3\pi/4 \), and hence \( \delta r_n \equiv \delta r_0 \) represents a coherent displacement within one chain. While the \( b \) and \( c \) components of \( \delta r_0 \) have different signs in different chains, \( \delta r_n \)'s are the same. Considering the TbMnO\(_3\) value \( \delta r_0 = 10^{-2} \) Å \([27]\) as an estimate for \( \delta r_0 \) in HoMnO\(_3\), we obtain \( P \approx 2 \mu C/cm^2 \) consistent with the calculated values.

**Summary.** We argue that the symmetry of the spin zigzag chain magnetic E-phase in orthorhombic perovskites with buckling distortion of the oxygen octahedra allows the formation of a polar axis along the \( a \)-axis. The microscopic mechanism of ferroelectricity is independent of spin-orbit coupling, and \( P \) can potentially be up to two orders of magnitude higher than that in the helical IMF’s. Note that the ideas described here are general, and the E-phase provides just one example. In fact, the microscopic model considered here is not applied to them directly \([35]\). However, we expect that the same interplay between the optimization of the electron hopping and the elastic energy in the presence of the buckling distortion will lead to ferroelectricity.

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**Note added.** Following our prediction, B. Lorenz et al. \([39]\) reported on experimental evidence of ferroelectricity in perovskite HoMnO\(_3\) and YMnO\(_3\). For the latter, the E-phase was proposed in Ref. \([17]\).

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