Ferroelectricity due to Orbital Ordering in E-Type Undoped Rare-Earth Manganites

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Aiming at understanding the origin of the electronic contribution to ferroelectric polarization in undoped manganites, we evaluate the Berry phase of orbital-polarizable Bloch electrons as an orbital ordering (OO) establishes in the background of an antiferromagnetic *E*-type configuration. The onset of OO is tuned by the Jahn-Teller (JT) interaction in a tight-binding model for interacting electrons moving along zigzag chains. A finite polarization is found as soon as the JT coupling is strong enough to induce OO, supporting the large electronic contribution predicted from first principles.

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The coexistence of ferroelectrically polarized state with long-range magnetic order is usually referred to as multiferroic behavior [1]. Among other multiferroic materials, orthorhombic rare-earth manganites RMnO₃ (R belonging to lanthanum series) represent an important class of "improper multiferroics" [2], where the ferroelectric polarized state is not only coexisting with, but also intrinsically related to some kind of magnetic order. Several degrees of freedom (spin, charge, orbital, lattice) are active in these systems and are responsible for their very rich phenomenology. Starting from R = La and moving along the series to smaller ionic radius r_R , the ground state changes from antiferromagnetic A-type (AFM-A) to E-type (AFM-E), through an incommensurate spiral structure for R = Tb, Dy [3]. The incommensurate magnetic phase of $TbMnO_3$ and DyMnO₃ is responsible for the observed weak ferroelectric polarization [4], which is ultimately driven by spin-orbit coupling via the Dzyaloshinskii-Moriya interaction [5,6]. The relativistic origin of ferroelectricity in these compounds is reflected in the weak P (smaller than 0.1 μ C/cm² [4]). On the other hand, also collinear AFM-*E* magnetic order has been predicted to induce a ferroelectric polarization via an exchange-striction mechanism [7], where the double-exchange interaction between Mn e_{g}^{1} electrons in the symmetry-broken 111 spin configuration is responsible for polar atomic displacements of oxygens bridging Mn ions. In a later paper [8], this picture has been partially confirmed by means of density-functional theory (DFT) calculations, reporting $P \sim 6 \ \mu C/cm^2$ for o-HoMnO₃. The DFT analysis also pointed out that a comparable contribution to the total polarization has a purely quantum mechanical origin, possibly related to the AFM-E-induced asymmetric electron hopping of orbitally polarized e_{e}^{1} states. The microscopic origin of such electronic contribution to P has been provided in terms of maximally localized Wannier functions (WFs) [9]. The DFT study showed that WF centers in all AFM-E o-RMnO₃ (R = Ho, Er, Tm, Lu), are largely displaced with respect to corresponding ionic positions; thus, the total P arises from the sum of an ionic contribution (driven by the exchange-striction mechanism) and a purely electronic one [9].

From the experimental point of view, only a small polarization ($P \sim 0.01 \ \mu C/cm^2$) has been reported for *o*-HoMnO₃ [10], at odds with theoretical prediction. Only recently experimental results for AFM-*E o*-TmMnO₃ suggested that *P* could actually pass the 1 $\mu C/cm^2$ threshold [11]. By the way, we notice that the thermodynamically stable phase for *R*MnO₃ with r_R smaller than that of Dy is hexagonal rather than orthorhombic [12]: the desired perovskite structure can be obtained, e.g., by high-pressure synthesis, leading, however, to polycrystalline samples that can limit the accuracy in measuring the predicted properties.

The aim of this Letter is to set a clear correspondence between the electronic polarization and the onset of orbital ordering (OO) on the background of the magnetic AFM-Econfiguration. The proposed picture is completely new in the field of improper multiferroicity and relies on the orbital polarizability of electrons on a specific magnetic background. We will introduce a simple model which is expected to reproduce the general features of the ground state of AFM-E orbital-ordered RMnO₃. The AFM-E configuration of t_{2g} spins is treated as a constraint on the e_g electrons motion, a reasonable assumption in the limit of very large Hund coupling. Its stability has been already discussed, e.g., in Refs. [3,9], where the competition between kinetic energy (double exchange) and superexchange interactions between the Mn t_{2g} spins is discussed as a function of the ionic radius r_R (as pointed out recently, the Jahn-Teller (JT) interaction also may play a relevant role [13]). In the limit of infinite Hund coupling, e_g electrons can only hop between sites with ferromagnetically aligned core spins; this implies that hopping processes in the AFM-E phase are allowed only within one-dimensional zigzag chains of parallel core spins [Fig. 1(a)]. OO may be stabilized by an electron-lattice JT interaction, which causes also the Bloch electrons within the chains to acquire a geometric Berry phase arising from a conical intersection of the potential energy surfaces [14]; we stress the fact,



FIG. 1. (a) Unit cell for the zigzag ferromagnetic chain in the AFM-E phase: the hopping direction changes periodically within the chain as {...x, y, x, y...}. (b) Orbital densities $\rho_{3x^2-r^2}$, $\rho_{3y^2-r^2}$ as a function of position within a chain at $E_{\rm JT} = 1$, when OO is almost fully developed. (c) Average orbital density for the $d_{3x^2-r^2}$ state at site 1 as a function of JT interaction (inset: total energy smooth evolution). Dotted line is the same quantity evaluated in a linear chain, when $\varphi_{|i-j|} = \text{const.}$ (d) Same as (c), but for different values of interorbital Coulomb interaction.

however, that also a correlation-mediated mechanism may stabilize OO [15]. In the framework of the modern theory of polarization, the appearance of this Berry phase can give rise to a polarization whose origin is purely quantum mechanical, being intimately connected to a current flow inside the bulk [16]. We will show that this is indeed the case, but that the geometric phase of the OO state is actually not enough, being the interplay with the specific topology induced by the underlying magnetic background the boost for ferroelectric polarization.

Let us introduce the Hamiltonian which describes the motion of interacting e_g electrons within zigzag chains:

$$H = -\sum_{\langle jl \rangle \gamma \gamma'} t_{\gamma \gamma'} a_{\gamma j}^{\dagger} a_{\gamma' l} + U \sum_{j} n_{\alpha j} n_{\beta j} + E_{\rm JT} \sum_{j} [2(q_{2j} \tau_{xj} + q_{3j} \tau_{zj}) + q_{2j}^{2} + q_{3j}^{2}].$$
(1)

The first term describes the electron transfer between nearest-neighbor Mn sites, where $a_{\gamma j}^{\dagger}$ creates a particle at site *j* in electronic states stemming from Mn⁺³ orbitals $d_{x^2-y^2}(\alpha)$ and $d_{3z^2-r^2}(\beta)$. The hopping amplitudes are $t_{\alpha\alpha} = 3t_0/4$, $t_{\beta\beta} = t_0/4$, and $t_{\alpha\beta} = \pm \sqrt{3}t_0/4$ [17], where $t_0 = (pd\sigma)^2$ is the energy unit and the sign appearing in $t_{\alpha\beta}$ depends on the hopping direction along the zigzag chain (i.e., $t_{\alpha\beta}^x = -t_{\alpha\beta}^y$). As we will see, this implies that at each site electrons gain a phase that depends on the orbital through which they pass. The second term describes the interorbital interaction, the only Coulomb interaction that is left between e_g electrons in the infinite Hund coupling limit, while the last term accounts for the JT interaction with dimensionless $q_{\nu j} = (k/g)Q_{\nu j}$, where $Q_{\nu j}$ are the Jahn-Teller-active modes [18], k, g are, respectively, the elastic JT stiffness and the bare JT coupling, and $E_{\rm JT} = g^2/(2k)$ is the static JT energy. $\tau_{\mu j} = \sum_{\gamma \gamma'} a_{\gamma j}^{\dagger} \sigma_{\gamma \gamma'}^{\mu} a_{\gamma' j}$ is the orbital pseudospin, being $\sigma_{\gamma \gamma'}^{\mu}$ the Pauli matrices, while $n_{\gamma j} = a_{\gamma j}^{\dagger} a_{\gamma j}$ are orbital density operators. We treat the on-site correlation in a mean-field framework, by linearizing it in the optimum local basis in order to keep track of the orbital degrees of freedom [19], finding $n_{\alpha j} n_{\beta j} \approx (2n_j \langle n_j \rangle - 2\tau_{zj} \langle \tau_{zj} \rangle - 2\tau_{xj} \langle \tau_{xj} \rangle - \langle n_j \rangle^2 + \langle \tau_{zj} \rangle^2 + \langle \tau_{zj} \rangle^2 / 4$.

As the phase change in hopping amplitudes plays a relevant role in establishing a ferroelectric polarization, we transform the e_g electron basis through the unitary transformation $c_j = (a_{\alpha j} + ia_{\beta j})/\sqrt{2}$ and $d_j = (a_{\alpha j} - ia_{\beta j})/\sqrt{2}$ [14]. In the new basis the Hamiltonian (1) is rewritten as

$$H = -\sum_{\langle j,l \rangle} (tc_{j}^{\dagger}c_{l} + td_{j}^{\dagger}d_{l} + sc_{j}^{\dagger}d_{l} + s^{*}d_{j}^{\dagger}c_{l}) + \sum_{j} \left[V_{j}c_{j}^{\dagger}d_{j} + V_{j}^{*}d_{j}^{\dagger}c_{j} + \frac{U}{2} \langle n_{j} \rangle (c_{j}^{\dagger}c_{j} + d_{j}^{\dagger}d_{j}) + E_{\rm JT}(q_{2j}^{2} + q_{3j}^{2}) - \frac{U}{4} (\langle n_{j} \rangle^{2} - \langle \tau_{zj} \rangle^{2} - \langle \tau_{xj} \rangle^{2}) \right],$$
(2)

with $t = t_0/2$ and $s = e^{i\phi_{|i-j|}}t_0/2$, the phase $\phi_{|i-j|}$ depending on the hopping direction as $\phi_y = -\phi_x = \pi/3$. Therefore, the e_g electrons pick up a phase change as they move between different neighboring orbitals. The local interaction $V_j = |V_j|e^{i\xi_j}$ acquires a phase too [14], being

$$|V_{j}| = 2E_{\rm JT}[(q_{2j} - u\langle\tau_{xj}\rangle)^{2} + (q_{3j} - u\langle\tau_{zj}\rangle)^{2}]^{1/2},$$

$$\xi_{j} = \tan^{-1}\frac{q_{2j} - u\langle\tau_{xj}\rangle}{q_{3j} - u\langle\tau_{zj}\rangle},$$
(3)

where we set $u = U/2E_{\rm JT}$, while $\langle \tau_{\mu j} \rangle$ are the averaged pseudospin operators in the original basis to be selfconsistently determined. As in undoped manganites there is only one e_g electron per site, according to Ref. [14] we can take $q_{3j} = q_3$ and $q_{2j} = (-1)^j q_2$ [we numerically checked this assumption by minimization of Hamiltonian (2) with respect to $q_{\alpha i}$]. The absolute value of the interaction potential is then found to be constant, while its phase changes within the chain with a periodicity equal to π . The Hamiltonian in momentum space can be rewritten then in the electron basis $(c_k^{\dagger}, d_k^{\dagger}, c_{k+\pi}^{\dagger}, d_{k+\pi}^{\dagger})$, being k defined, with the unit cell chosen as shown in Fig. 1(a), in the reduced Brillouin zone $-\pi/2 < k < \pi/2$:

$$h_{k} = \begin{pmatrix} \mathcal{H}_{k,k} & \mathcal{H}_{k,k+\pi} \\ \mathcal{H}_{k,k+\pi} & \mathcal{H}_{k+\pi,k+\pi} \end{pmatrix},$$
(4)

where
$$\mathcal{H}_{k,k+\pi}^{11} = \mathcal{H}_{k,k+\pi}^{22} = 0$$
, and
 $\mathcal{H}_{k,k}^{11} = \mathcal{H}_{k,k}^{22} = -t_0 \cos k$,
 $\mathcal{H}_{k,k}^{12} = (\mathcal{H}_{k,k}^{21})^* = -\frac{t_0}{2}(\cos k_+ + \cos k_-) + V_0$,
 $\mathcal{H}_{k,k+\pi}^{12} = (\mathcal{H}_{k,k+\pi}^{21})^* = -\frac{t_0}{2}(\cos k_- - \cos k_+) + V_{\pi}$,
 $\mathcal{H}_{k+\pi,k+\pi}^{11} = \mathcal{H}_{k+\pi,k+\pi}^{22} = t_0 \cos k$,
 $\mathcal{H}_{k+\pi,k+\pi}^{12} = (\mathcal{H}_{k+\pi,k+\pi}^{21})^* = \frac{t_0}{2}(\cos k_+ + \cos k_-) + V_0$

The hopping phase change enters in $k_{\pm} = k \pm \pi/3$, whereas the Fourier components of the local potential are $V_0 = |V| \cos \xi_- e^{i\xi_+}$ and $V_{\pi} = |V| i \sin \xi_- e^{i\xi_+}$, being $\xi_{\pm} =$ $(\xi_1 \pm \xi_2)/2$. We note that the system is always in a bandinsulating state, even when the JT coupling and U are set to zero. The band insulator is stabilized by the phase difference between the interorbital hopping amplitudes, as it happens in the AFM-CE phase of half-doped manganites [19,20], and it is very robust due to its topological origin. However, the OO emerges only when the JT and Coulomb interactions are sufficiently strong to induce a nonzero |V|. In order to inspect the OO in real space, we can evaluate the local average orbital occupancy $\rho_{\gamma j} = \langle \phi_{\gamma j}^{\dagger} \phi_{\gamma j} \rangle$, where $\phi_{\gamma j} = -\sin(\theta_{\gamma j}/2)a_{\alpha j} + \cos(\theta_{\gamma j}/2)a_{\beta j}$ and $\theta_{\gamma i} = 2\pi/3(4\pi/3)$ for $\gamma = 3x^2 - r^2(3y^2 - r^2)$. In Fig. 1(c) we show the evolution of $\rho_{3x^2-r^2}$ on site 1 (equivalent to $\rho_{3y^2-r^2}$ on site 2) as a function of JT interaction at U = 0and the OO pattern of alternating $3x^2 - r^2/3y^2 - r^2$ within the chain. We note that a similar result is obtained for the linear chain, where the hopping direction and the related phase $\phi_{|i-j|}$ are unchanged, while the OOinduced phase change is retained [14]: in this case the band insulator has no topological origin and emerges in an orbitally ordered pattern because of the local interaction, being metallic for |V| = 0 [dotted line in Fig. 1(c)]. On the other hand, the inclusion of U, albeit at a mean-field level, makes the OO onset more robust [Fig. 1(d)].

We consider now the possible ferroelectricity. Following the prescription described in Ref. [21], we evaluate the polarization as

$$P = -\frac{e}{2\pi} \lim_{L \to \infty} \operatorname{Im} \operatorname{Indet} S, \tag{5}$$

where *L* is the chain length (periodic boundary conditions are assumed) and *S* is the overlap matrix, defined as $S_{m,m'}(k, k') = \langle \psi_{m,k} | e^{-i(2\pi/L)\hat{x}} | \psi_{m',k'} \rangle$. The eigenvectors $\psi_{m,k}$, where *m* is a band index, can be expressed as

$$|\psi_{k,m}\rangle = (U_k(m,1)c_k^{\dagger} + U_k(m,2)d_k^{\dagger} + U_k(m,3)c_{k+\pi}^{\dagger} + U_k(m,4)d_{k+\pi}^{\dagger})|0\rangle.$$
(6)

Here U_k is the unitary matrix which diagonalizes the Hamiltonian (4) at each k, and $|0\rangle$ is the vacuum state.

By defining the position operator as $\hat{x} = \sum_{j} j(c_{j}^{\dagger}c_{j} + d_{j}^{\dagger}d_{j})$, one sees that *S* elements vanish except when each pair of vectors *k*, *k'* differs by an amount $\varepsilon = 2\pi/L$; then the determinant can be factorized into *L* small determinants whose dimension is equal to the number of occupied bands [21], giving det*S* = $\Pi_{k} detS(k, k + \varepsilon)$, with the small overlap matrix being

$$S_{m,m'}(k,k+\varepsilon) = \sum_{\gamma=1,4} U_k^{\dagger}(\gamma,m) U_{k+\varepsilon}(m',\gamma).$$
(7)

In Fig. 2 we show the polarization evaluated through formula (5) for the ground state of our model: it remains equal to zero in the insulating phase as far as no OO is induced in the zigzag chain by the local interaction, then it rapidly increases, closely following the evolution of the occupied orbital density. The sign of P can be changed by rotating the OO pattern, in such a way that orbital state $3y^2 - r^2(3x^2 - r^2)$ is occupied at site 1(2) instead of $3x^2 - r^2(3x^2 - r^2)$ $r^2(3y^2 - r^2)$. It is worthwhile to notice that P is always zero in the orbital-ordered insulating phase found in the linear chain, even though the interaction phase ξ_i has been shown to induce a Berry phase in the electronic Bloch function for a given k [14]. Indeed, this geometric phase takes into account the difference in the electron motion, clockwise or counterclockwise, around each site displaying OO within the linear chain; however, this difference sums up to zero when evaluated along the whole linear chain. Similarly, when the local interaction is not strong enough to induce OO along the zigzag chains, the difference in the electron motion due to direction-dependent interorbital hopping amplitudes, which induces a phase change in the electronic Bloch functions, does not give rise alone to any nonvanishing P. On the other hand, our result suggests that the interplay between the phase changes induced by the OO and direction-dependent hopping amplitudes is responsible for the onset of a ferroelectric state, which has ultimately a topological origin. We stress that this polarization has a purely electronic origin,



FIG. 2. Polarization in the one-dimensional zigzag chain as a function of $E_{\rm JT}$; the electron charge *e* is taken equal to unity. Solid (dashed) line is evaluated for the $3x^2 - r^2/3y^2 - r^2$ ($3y^2 - r^2/3x^2 - r^2$) OO pattern; dot-dashed line is evaluated within the linear chain. Inset: polarization for different values of *U*.

since the position of the ions is fixed within the chains, supporting the DFT calculations which report a large electronic contribution to *P* in the whole class of AFM-*E o*-*R*MnO₃ [9]. We can estimate the magnitude of the calculated electronic *P* for a realistic three-dimensional system multiplying it by a scale factor a_0/V_0 , where a_0 is the Mn-Mn distance (corresponding to the lattice constant in our simplified model) and V_0 is the unit cell volume. We estimate $a_0 = 3.89-4$ Å and $V_0 = 244 - 220$ Å³ for *R*MnO₃ [22], implying *P*_{el} of the order of $\sim 10 \ \mu C/cm^2$. On the other hand, both E_{JT}/t_0 and U/t_0 are of the order of unity in manganites, being $t_0 = 0.1-0.5$ eV, $E_{JT} \simeq 0.25$ eV, and $U \ge 1$ eV [19], suggesting that the OO found in our simple model is easily realized in undoped manganites.

To get more physical insight, we evaluated the position of the WF centers in the chain. For this purpose, the construction of maximally localized WFs is not needed in one-dimensional systems. Indeed, they can be obtained as the eigenvalues of a matrix Λ , constructed as the product of the unitary parts of the S matrices along the k-point string (by "unitary part" we mean the matrix product VW^{\dagger} taken from the singular value decomposition $S = V \Sigma W^{\dagger}$, where V and W are unitary and Σ is a diagonal matrix with nonnegative diagonal elements) [23]. We find that (i) in the insulating phase with no OO, the WFs are bond centered. their centers located exactly in the middle of each bond connecting two neighboring sites along the zigzag chain, and (ii) when OO is established, WF centers move (in the same direction along the zigzag chain) toward lattice sites. This unveils the reduced symmetry of the system, that loses the center of symmetry in the middle of each bond, thus allowing for a finite P. The displacement direction is related to the character of the occupied orbitals, in the sense that each WF center moves from the middle of the bond toward the neighboring site where the occupied orbital is aligned parallel to the vector connecting each pair of sites. Since the OO pattern is $3x^2 - r^2/3y^2 - r^2$ (or $3y^2 - r^2$) $r^2/3x^2 - r^2$) and the direction along the chain changes as $\{\ldots x, y, x, y \ldots\}$, there is a net "leftward" (or "rightward") displacement of WF centers.

Because of the analogies shared with the AFM-CE phase relevant for half-doped manganites, showing double zigzag spin chains [19], let us briefly discuss the outcome of our analysis in that case. The Hamiltonian (2) is still suitable to describe the motion of e_g electrons within chains where the hopping direction changes as {...x, x, y, y...}, as expected on the background of the ferromagnetically aligned corespin chains characteristic of the AFM-CE configuration. We can then distinguish between corner Mn sites, where it does not [20]. As pointed out before, the system is a band insulator even in the absence of any interaction, due to the effective dimerization induced by the phase change in the hopping amplitudes at corner sites. However, an OO pattern of $3x^2 - r^2/3y^2 - r^2$ states already occurs on bridge sites [19,20], at odds with the AFM-E phase considered so far, where only corner sites appear. Turning on the local interaction gives rise to a charge transfer from corner to bridge sites, but leaves the OO pattern unchanged. We can evaluate *P* along the same lines described before. We notice, however, that electrons pick up a phase on corner sites, depending on the change of hopping direction, and a different one on bridge sites, related to the orbital-ordered state, which do not interfere with each other. As a result, we find that *P* is always zero with a CE-type constraint on the electron motion.

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