Electric Field Control of Jahn-Teller Distortions in Bulk Perovskites

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The Jahn-Teller distortion, by its very nature, is often at the heart of the various electronic properties displayed by perovskites and related materials. Despite the Jahn-Teller mode being nonpolar, we devise and demonstrate, in the present Letter, an electric field control of Jahn-Teller distortions in bulk perovskites. The electric field control is enabled through an anharmonic lattice mode coupling between the Jahn-Teller distortion and a polar mode. We confirm this coupling and quantify it through first-principles calculations. The coupling will always exist within the Pb21m space group, which is found to be the favored ground state for various perovskites under sufficient tensile epitaxial strain. Intriguingly, the calculations reveal that this mechanism is not only restricted to Jahn-Teller active systems, promising a general route to tune or induce novel electronic functionality in perovskites as a whole.

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Perovskite ABO3 compounds, and related materials, are fascinating systems exhibiting a diverse collection of properties, including ferroelectricity, magnetism, orbital-ordering, metal-insulator phase transitions, superconductivity, and thermoelectricity [1]. Despite the wide range of physical behavior, a common point at the origin of many of them can be identified as being the Jahn-Teller (JT) distortion [2,3]. The Jahn-Teller distortion is, itself, intimately linked to electronic degrees of freedom, since, traditionally, it manifests to remove an electronic degeneracy, opening a band gap and favoring a particular orbital ordering which, in turn, can affect magnetic ordering. Furthermore, it plays an important role, for example, in colossal magnetoresistance phenomena in doped manganites [4], superconductivity [5,6], or the strong electronic correlation observed in the thermoelectric NaCoO2 family [7].

It would be highly desirable, for device functionality, for example, to be able to tune the Jahn-Teller distortion and, hence, its corresponding electronic properties, with the application of an external electric field. However, Jahn-Teller distortions are nonpolar and, hence, not directly tunable with an electric field.

Recently, the concept of “hybrid improper ferroelectricity” has emerged within the community of oxide perovskites [8–11]. This concept is related to an unusual coupling of lattice modes, giving rise to splitting in the free energy expansion to a trilinear term \( -\lambda P R_1 R_2 \) linking the polar motion \( P \) to two independent nonpolar distortions \( R_1 \) and \( R_2 \). Such a coupling was identified in various layered perovskites [8,9,12–15], metal-organic framework [16,17], and can even appear in bulk ABO3 perovskites [18,19]. Interestingly, in Ruddlesden-Popper compounds [9,20] and ABO3/A′BO3 superlattices [21], this trilinear coupling appeared as a practical way to achieve electric control of nonpolar antiferrodistortive (AFD) motions associated with the rotation of the oxygen octahedra (i.e., monitoring \( P \) with an electric field will directly and sizeably tune the nonpolar modes \( R_1 \) and/or \( R_2 \)).

Following this spirit, achieving an electric field control of Jahn-Teller distortions can be realized through the identification of a material exhibiting, by symmetry, a similar “trilinear” term involving both the polarization and the Jahn-Teller distortion which, to the best of our knowledge, has not yet been discovered in bulk ABO3 perovskites [11]. In the present Letter, we identify such conditions and demonstrate, explicitly, an electric field control in bulk perovskites using a combination of symmetry analysis and first-principles calculations.

The two required lattice distortions are pictured in Figs. 1(a) and 1(b). ABO3 perovskites often exhibit a nonpolar Pb21m ground state, resulting in a combination of three AFD motions (\( a^-a^-c^+ \) pattern of rotations of the oxygen octahedra in Glazer’s notation [22]). In this symmetry, Howard and Carpenter [23] pointed out that a Jahn-Teller distortion pattern automatically appears, which was later explained in terms of a trilinear coupling with AFD motions [14,24]. As a consequence, a Jahn-Teller distortion is not necessarily electronically driven but can, instead, arise from lattice mode couplings in which case a splitting of the electronic states may develop even in the absence of an electronic instability. The present Jahn-Teller lattice motion corresponds to a \( Q_2 \) mode as defined by Goodenough [3], corresponding to two B-O bond length contractions and two B-O elongations. This motion orders at the \( M \) point of the Brillouin zone, and hence, consecutive layers along the \( c \) axis of the \( Pb21m \) phase present in-plane distortions. This motion is labelled \( Q_2^+ \) throughout the whole Letter.
FIG. 1. Schematic view of the main four lattice distortions involved in the $Pb_2$m phase of perovskites under tensile epitaxial strain. (a) Polar distortion (irreps $\Gamma_7^-$), (b) $Q_2^+$ Jahn-Teller distortion (irreps $M_2^+$), (c) antipolar $A$ distortion (irreps $M_1^+$), (d) $a^0d^0c^+\phi_3^+$ antiferrodistortive motion (irreps $M_2^+$).

Starting from the reference $Pm\bar{3}m$ cubic perovskite phase, the condensation of the polar mode $P$ (irreps $\Gamma_7^-$) and the JT mode $Q_2^+$ (irreps $M_2^+$) lowers the symmetry to a $Pb_2$m phase, a polar subgroup of $Pbnm$. We, then, perform a free energy expansion [25] (around the reference structure) in terms of the lattice distortions allowed by symmetry in this new phase, and we identify, among all the possible terms, some intriguing couplings

$$\mathcal{F} \propto \mathcal{P}Q_2^+A + \mathcal{P}^2Q_2^+\phi_3^+ + P\phi_3^+A + Q_2^+\phi_3^+A^2.$$  \hspace{1cm} (1)

In this phase, the first two terms of Eq. (1) provide a link between the polarization and the Jahn-Teller distortion. These terms also involve two additional distortions: one antipolar $A$ motion pictured in Fig. 1(c) and one $a^0d^0c^+$ AFD motion (labelled $\phi_3^+$) pictured in Fig. 1(d). Among all the terms, the lowest order trilinear term of the form $PQ_2^+A$ provides the desired direct coupling between the polarization and the JT distortion. Thus, acting on the polarization with an external electric field may modify the amplitude of the JT motion and, therefore, all related electronic properties.

However, the $Pb_2$m symmetry is not the common ground state in bulk perovskites [26]. Strain engineering, through thin film epitaxy, for example, can provide a powerful tool to unlock a polar mode in perovskites [10,27–32]. This is the case for BiFeO$_3$ which was recently proposed to adopt an unusual $Pb_2$m symmetry under large epitaxial tensile strain [27,33–35]. This particular phase was shown to develop polar, antipolar, and $a^0d^0c^+$ AFD motions [33], which were later demonstrated to be coupled together through the third term of Eq. (1) [18]. Amazingly, the authors reported the existence of an orbital ordering of the Fe$^{3+}$ 3$d$ orbitals, explained from the coexistence of the polar and the antipolar mode yielding a particular lattice distortion pattern [33]. This orbital ordering is unusual since, in this system, no Jahn-Teller effect is required to form a Mott insulating state (Fe$^{3+}$ are in a half filled high spin $t^3_2e^2_0$ configuration). A Jahn-Teller effect or distortion is yet to be reported in the $Pb_2$m phase of BiFeO$_3$ to the best of our knowledge. From our symmetry analysis, we clearly demonstrate that, as this $Pb_2$m develops the three aforementioned distortions ($P$, $A$, and $\phi_3^+$), the free energy of Eq. (1) is automatically lowered through the appearance of a fourth lattice distortion: a Jahn-Teller $Q_2^+$ motion. Therefore, while it may not be unstable itself, the Jahn-Teller motion is forced into the system via this “improper” mechanism arising from the trilinear coupling [8]. This result clarifies the origin of the unusual orbital ordering displayed by BiFeO$_3$; moreover, it provides a pathway to achieve an electric field control of the orbital ordering in bulk perovskites.

The predicted highly strained $Pb_2$m phase in bulk perovskites is not restricted to BiFeO$_3$, and it was predicted to occur also in some titanates (CaTiO$_3$ and EuTiO$_3$) [33], in BaMnO$_3$ [33], and even in a Jahn-Teller active compound TbMnO$_3$ [36]. The highly strained bulk perovskites are then an ideal playground to demonstrate our coupling between the polarization and the Jahn-Teller distortion. In order to check the generality of our concept, we propose, in this Letter, to investigate several types of highly strained perovskites on the basis of first principles calculations: (i) nonmagnetic (NM) SrTiO$_3$ ($t^0_2e^0_0$); (ii) magnetic BaMnO$_3$ ($t^1_2ge_0$) [37], and BiFeO$_3$ ($t^1_2e^2_0$); (iii) Jahn-Teller active YMnO$_3$ ($t^3_2p^1_0$).

First-principles calculations were performed with the VASP package [40,41]. We used the PBEsol [42]+U framework as implemented by Lichtenstein et al. [43] (see the Supplemental Material [44] for a discussion on the choice of the U and J parameters). The plane wave cutoff was set to 500 eV, and we used a $6 \times 6 \times 4k$-point mesh for the 20 atom $Pb_2$m phase. Projector Augmented Wave pseudopotentials [55] were used in the calculations with the following valence electron configuration: $3s^23p^64s^2$ (Sr), $4s^24p^65s^2$ (Ba), $4s^24p^65s^24d^1$ (Y), $6s^26p^3$ (Bi), $3p^64s^23d^2$ (Ti), $3p^64s^23d^5$ (Mn), $3p^64s^23d^6$ (Fe), and $2s^22p^4$ (O). Spontaneous polarizations were computed using the Berry-phase approach and Phonons, and Born effective charges were computed using the density functional perturbation theory [56]. The electric field effect was modeled using a linear response approach by freezing in some lattice distortion into the system [57,58]. Symmetry mode analyses were performed using the AMPLIMODES software from the Bilbao Crystallographic server [45,46].

We begin by investigating the possibility of a $Pb_2$m ground state under large epitaxial tensile strain (the growth

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direction is along the [001] axis of the Pb2m structure. Beyond around 5% tensile strain, the four compounds, indeed, develop the desired Pb2m ground state. Strained BaMnO3 [ferromagnetic (FM)] and YMnO3 [G-type antiferromagnetic (AFMG)] exhibit a different magnetic ground state compared to the bulk (AFMG and E-type antiferromagnetic, $\uparrow\downarrow\uparrow\downarrow$ zigzag chains coupled antiferromagnetically along the $c$ axis, respectively) while BiFeO3 (AFMG) remains in its bulk magnetic ground state. We, then, perform a symmetry mode analysis with respect to a hypothetical $P4/mmm$ phase (corresponding to $Pm\bar{3}m$ for unstrained bulk compounds) in order to extract the amplitude of the relevant lattice distortions [59] (see Table I). As expected, the four materials develop the required distortions, and amazingly, the magnitude of the $Q_{z}^{+}$ Jahn-Teller distortion is relatively large, being, for instance, of the same order of magnitude as the one developed in the prototypical Jahn-Teller system LaMnO3 (around 0.265 Å [60]). Additionally, the values of the spontaneous polarization are rather large, reaching 76 $\mu$C cm$^{-2}$ for SrTiO3, for instance. Despite being highly strained, all materials remain insulating, adopting reasonable electronic band gap values (see Table I).

To shed more light on the origin of this unusual Pb2m phase, we compute the energy potentials with respect to the four distortions by individually condensing each mode in a hypothetical $P4/mmm$ phase (see Fig. 2). Surprisingly, the appearance of the Pb2m phase is rather different for the four materials. SrTiO3 and BaMnO3 only exhibit a polar instability, producing an $Amm2$ symmetry, consistent with previous reports of a polar phase for these two materials under tensile strain [27,39]. Computing the phonons in this particular $Amm2$ symmetry, only one hybrid unstable phonon mode is identified for these two materials, having a mixed character between the $A$, $\phi Z^+$, and $Q_{z}^{+}$ distortions. For BiFeO3 and YMnO3, the $a^0d^0c^{+}$ AFD motion is already unstable, which is expected since the Pb2m symmetry for these two systems is derived from their bulk $R3c/Pbnm$ phases [59]. Additionally, the JT lattice distortion is also unstable in the $P4/mmm$ phase of YMnO3 and appears as an electronic instability [63], which is expected since YMnO3 is known to be Jahn-Teller active in the bulk. We emphasize, at this stage, that the polar mode in BiFeO3 (and YMnO3) is not unstable, and therefore, highly strained BiFeO3 appears as an improper ferroelectric in contradiction to Ref. [18] (see note [64]). Computing the phonons in the intermediate strained $Pbnm$ phase of both BiFeO3 and YMnO3 compounds reveals only one hybrid unstable mode, having a mixed character between $P$ and $A$ distortions. Despite the apparent universal stability of this highly strained polar phase, the mechanism yielding it is surprisingly different between the compounds and seems linked to the tolerance factor.

Regarding the electronic structure, we checked for the appearance of an orbital ordering as observed in BiFeO3 [33]. For the four compounds, we report the projected density of states on the $d$ levels of two neighboring $B$ sites in the $(ab)$ plane (see Fig. 3). For SrTiO3, a splitting of the $t_{2g}$ states, and especially between the $d_{xz}$ and $d_{yz}$ orbitals,

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**Table I.** Epitaxial strain (%), magnetic ground state, amplitudes of distortions (Å), and electronic band gap value (eV) for each material. The spontaneous polarization is also reported in $\mu$C cm$^{-2}$. Only the relevant distortions are summarized in the present table [59].

<table>
<thead>
<tr>
<th></th>
<th>SrTiO3</th>
<th>BaMnO3</th>
<th>BiFeO3</th>
<th>YMnO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain (%)</td>
<td>+7.35</td>
<td>+6.1</td>
<td>+5.8</td>
<td>+4.0</td>
</tr>
<tr>
<td>Magnetism</td>
<td>NM</td>
<td>FM</td>
<td>AFMG</td>
<td>AFMG</td>
</tr>
<tr>
<td>$P$ ($I_{z}$) (Å)</td>
<td>0.615</td>
<td>0.421</td>
<td>0.346</td>
<td>0.753</td>
</tr>
<tr>
<td>$Q_{z}^{+}$ ($M_{z}^{+}$) (Å)</td>
<td>76</td>
<td>45</td>
<td>29</td>
<td>7 [62]</td>
</tr>
<tr>
<td>$A$ ($M_{z}^{+}$) (Å)</td>
<td>0.558</td>
<td>0.217</td>
<td>1.072</td>
<td>0.940</td>
</tr>
<tr>
<td>$\phi Z^{+}$ ($M_{z}^{+}$) (Å)</td>
<td>0.640</td>
<td>0.059</td>
<td>1.668</td>
<td>1.733</td>
</tr>
<tr>
<td>Gap (eV)</td>
<td>3.02</td>
<td>0.28</td>
<td>1.88</td>
<td>1.88</td>
</tr>
</tbody>
</table>

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**FIG. 2.** Potentials with respect to the amplitude of distortions of the four lattice motions producing the required Pb2m for SrTiO3 (black filled circles), BaMnO3 (red filled squares), YMnO3 (blue filled diamonds), and BiFeO3 (green filled triangles) starting from the ideal $P4/mmm$ phase.
located at the bottom of the conduction band arises. For BaMnO$_3$ and BiFeO$_3$, a similar splitting between the $t_{2g}$ levels is observed near the Fermi level, even if it is less pronounced for BaMnO$_3$ since it has the smallest $Q^2_2$ distortion. Finally, YMnO$_3$ displays an orbital ordering of the $e_g$ levels with predominantly $d_{x^2-y^2}$ occupation. This splitting is known to result from the Jahn-Teller distortion in this A$^{3+}$Mn$^{3+}$O$_3$ class of material [65]. Additionally, an orbital ordering of the $t_{2g}$ levels is occurring both in the conduction and the valence bands. To prove that the Jahn-Teller distortion, and not another motion, is solely responsible for the orbital ordering, we have condensed all the modes individually and studied the density of states (see Supplemental Material [44], Fig. 1).

Up to this point, we have demonstrated the existence of a JT distortion and a related orbital ordering in the desired $Pb_2/m$ polar phase. Now, we quantify how the trilinear couplings allow us to achieve practical electric field control of the JT distortion. To that end, we compute the magnitude of the JT distortion as a function of the electric field $E$, and exemplify its consequences on the electronic band gap. Results are displayed in Fig. 4. The Jahn-Teller distortion is effectively tuned by the application of an electric field along the polar axis through the first and second terms of Eq. (1). As the electric field increases, the amplitude of the JT distortion is either amplified or decreased, being renormalized to around 175% for SrTiO$_3$ for an electric field around 20 MV cm$^{-1}$. The largest effect is, however, reached for YMnO$_3$ which displays a renormalization of 130% under moderate electric field (around 5 MV cm$^{-1}$). Therefore, this renormalization of the JT distortion has consequences, for instance, on the electronic band gap value, with an opening or closure around 0.6 eV for YMnO$_3$ or 0.25 eV for SrTiO$_3$. It is then possible, through the coupling between the polarization and the Jahn-Teller distortion, to act on the electronic properties.

Here, we have exemplified a sizeable electric control of the band gap of direct interest for electrochromic and photovoltaic applications. Acting directly on the amplitude of the JT distortion might, alternatively, allow one to control the magnetic state with an electric field, as recently proposed independently in superlattices [14] and metal organic frameworks [16], or to control metal-insulator phase transitions.

In conclusion, we have demonstrated, in the highly strained $Pb_2/m$ phase of bulk $ABO_3$ perovskites, the existence of a trilinear coupling involving a polar mode and the Jahn-Teller distortion. This improper anharmonic coupling, established on universal symmetry arguments, enables an electric field control of the Jahn-Teller distortion, even in the case of traditionally non Jahn-Teller active systems. The generic mechanism may open novel functionalities in perovskites as it will have consequences on related electronic properties as proposed in the present Letter.

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[26] Being in the Pb2m phase is a priori not mandatory to achieve electric field control of the Jahn-Teller distortions. In a metastable phase, only developing the antipolar A distortion, applying an electric field would activate the polar mode and, through the first term of Eq. (1), the Jahn-Teller distortion may automatically appear. In practice, however, this metastable phase does not seem to be favored, and being in the ground state ferroelectric phase may bring added functionality such as switchable behavior.
[35] In Ref. [33], the space group reported for BiFeO3 under large tensile strain is Pmc21, which is just an alternative setting of Pb2m.
[37] While BaMnO3 adopts a hexagonal polar P63cm ground state [38], it can also be stabilized with a perovskite form under tensile strain [39].
[59] In Table I, we only report the distortions relevant to the proposed mechanism. Notice that, due to a small tolerance factor, BiFeO$_3$ and YMnO$_3$ still develop large $a^-a^-c^0$ rotations in their ground state, in addition to other antipolar modes. Their $Pb_21m$ phase may appear to be derived from a $R3c$ or $Pbnm$ structure, respectively.
[61] The strain amplitude is defined with respect to the average in-plane pseudocubic lattice parameters of the fully relaxed ground state structure of each compound as given in the Supplemental Material [44].
[62] Despite a polar mode amplitude in strained YMnO$_3$ larger than in the other compounds, the polarization is much smaller. This is due to the specific atomic pattern of the polar mode in YMnO$_3$: the $A$ and $B$ cations move in opposite directions with similar magnitudes while O motions nearly cancel each other, resulting in a weak polarization. For the three other compounds, both $A$ and $B$ cations move in opposite direction to O anions, maximizing the polarization.
[63] The JT distortion in YMnO$_3$ results from an electronic instability in the high symmetry phase. Indeed, only removing the symmetry on the electronic wave function while keeping the centrosymmetric positions for the cations already produces an energy gain and a lowering of symmetry that is then amplified by the resulting JT lattice distortions.
[64] In Ref. [18], the authors report a weak polar instability in the $P4/mmm$ phase that we do not observe. This may be related to technical details or the magnitude of the strain applied and does not affect the present discussion.
[65] The two average $ab$ plane Mn-O bond lengths are $\langle d_{MnO}\rangle_{ab,1} = 1.903$ Å and $\langle d_{MnO}\rangle_{ab,2} = 2.438$ Å, while the average Mn-O bond length along the $c$ axis is $\langle d_{MnO}\rangle_c = 1.900$ Å. Consequently, the $d_{z^2-r^2}$ orbital should be more stable than the $d_{x^2-y^2}$ orbital. Considering the sole $Q^2$ distortion, the two in-plane Mn-O bond lengths are 2.294 Å and 1.772 Å, while the out-of-plane bond length is 1.769 Å.