Ab initio study of proper topological ferroelectricity in layered perovskite La$_2$Ti$_2$O$_7$

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We present a first-principles investigation of ferroelectricity in layered perovskite oxide La$_2$Ti$_2$O$_7$ (LTO), one of the compounds with highest Curie temperature known (1770 K). Our calculations reveal that LTO’s ferroelectric transition results from the condensation of two soft modes that have the same symmetry and are strongly coupled anharmonically. Further, the leading instability mode essentially consists of rotations of the oxygen octahedra that are the basic building block of the perovskite structure; remarkably, because of the particular topology of the lattice, such $O_6$ rotations give raise to a spontaneous polarization in LTO. The effects discussed thus constitute an example of how nano-structuring – provided here by the natural layering of LTO – makes it possible to obtain a significant polar character in structural distortions that are typically non-polar. We discuss the implications of our findings as regards the design of novel multifunctional materials. Indeed, the observed proper ferroelectricity driven by $O_6$ rotations provides the ideal conditions to obtain strong magnetoelectric effects.

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I. INTRODUCTION

Because of their physical appeal and technological importance, ferroelectrics and related materials have been the object of continued attention for decades. Bulk oxides with the ideal perovskite structure – ranging from classic ferroelectric BaTiO$_3$ to strong dielectric Ba$_{1-x}$Sr$_x$TiO$_3$, or from piezoelectric PbZr$_{1-x}$Ti$_x$O$_3$ to relaxor (PbMg$_{1/3}$Nb$_{2/3}$O$_3$)$_{1-x}$(PbTiO$_3$)$_x$ – have been especially well studied. Indeed, partly thanks to a number of key contributions from first-principles theory we now understand the fundamental atomic origin of the ferroelectric (FE) and response properties of the most important members of this family. During the past decade, the focus has increasingly shifted towards nanostructured materials, especially in the form of thin films. Work on films has led to a better understanding of how elastic (i.e., the epitaxial strain exerted by a substrate) and electric (e.g., the imperfect screening of the depolarizing field associated to particular metallic electrodes) boundary conditions affect the FE state. Further, it has been shown that exotic FE properties can be obtained in artificially created super-lattices, as e.g., in the recently discussed PbTiO$_3$/SrTiO$_3$ heterostructures.

The emergence of magnetoelectric multiferroics (i.e., materials with coupled magnetic and FE orders) has contributed to refuel interest in ferroelectrics, especially in what regards unconventional mechanisms for ferroelectricity. If we restrict ourselves to oxides with the ideal $ABO_3$ perovskite structure, ferroelectricity (usually driven by a $B$-site transition metal with an $nd^0$ electronic configuration) and magnetism (which requires localized $d$ or $f$ electrons) seem to be mutually exclusive, the known exceptions being very scarce. So far, the most notable ways around this problem consist in (i) having ferroelectricity driven by the $A$-site cation, as in room temperature multiferroic BiFeO$_3$ and (ii) moving away from the ideal perovskite structure and resorting to other mechanisms for ferroelectricity, as e.g. in the improper ferroelectrics YMnO$_3$ and Ca$_3$Mn$_2$O$_7$.

This is the context of our work on the layered perovskite oxide La$_2$Ti$_2$O$_7$ (LTO), whose structure is sketched in Fig. 1. LTO is one of the highest-temperature ferroelectrics known, with a Curie point ($T_C$) of approximately 1770 K and is lately being considered for applications as a high-$T$ piezoelectric. The FE transition temperature of LTO is enormous, especially when compared with the $T_{C}$’s of cubic perovskite titanates one might have expected to be similar to LTO: most significantly, BaTiO$_3$ (BTO) becomes ferroelectric at about 400 K, and the related compound SrTiO$_3$ remains (a quantum) paraelectric down to 0 K. In order to explain...
the surprising behavior of LTO, we need to identify the atomistic origin of its FE instability. LTO might owe its very high $T_C$ to the kind of mechanisms known to operate in the cubic titanates (in essence, long-range dipole-dipole interactions that destabilize the non-polar phase), which might somehow be enhanced by the peculiar topology of the LTO lattice. Alternatively, LTO might present some new form of very strong FE instability. Either way, the study of LTO will provide us with information that might be useful for the design of new ferroelectrics.

Let us also note that LTO is a member of the family of oxides with general formula $\text{La}_n\text{Ti}_n\text{O}_{3n+2}$ whose structure can be seen as the ideal cubic perovskite periodically truncated along the [011]$_c$ direction of the cubic lattice, $n$ being the number of perovskite-like planes within one layer (see Fig. 1). These structures are thus related to the well-known Ruddlesden-Popper, Aurivillius, and Dion-Jacobson families of layered perovskites for which the truncation direction is [001]$_c$ and which include very famous members such as $(\text{La},\text{Ba})_2\text{CuO}_4$, the parent compound of high-$T_C$ superconductors. The basic features of the electronic structure of the $\text{La}_n\text{Ti}_n\text{O}_{3n+2}$ compounds are controlled by $n$: The La and O atoms can be assumed to be in their most common ionization states – i.e., $\text{La}^{3+}$ and $\text{O}^{2-}$, which implies that the Ti cations will present a positive charge of $3 + 4/n$. Accordingly, the number of $3d$ electrons in the Ti atoms will be $1 - 4/n$, which allows us to move quasi-continuously from the Ti-$3d^0$ configuration of the $n=4$ compound (that is our $\text{La}_2\text{Ti}_2\text{O}_7$, the family member with smallest $n$ reported in the literature) to the Ti-$3d^1$ configuration of the $n=\infty$ compound (which has the prototype perovskite structure). The variety of electronic phenomena observed for intermediate values of $n$ – including phases of semi-conducting, normal metallic, and low-dimensional metallic character – constitutes an additional motivation to study in detail the structural behavior of the relatively simple end member $\text{La}_2\text{Ti}_2\text{O}_7$.

The paper is organized as follows. In Section II we describe the theoretical approach and first-principles methods used in this work. We present and discuss our results in Section III, which is split in the following way. In Section III.A we describe our results for the structure of the high-temperature paraelectric (PE) and FE phases of LTO. In Section III.B we show that the PE phase presents a strong FE instability whose topological nature is discussed in detail. In Section III.C we describe the phase transition between the PE and FE phases, and discuss the energetics of the transformation. In Section III.D we present our results for the spontaneous polarization, dielectric, and piezoelectric properties. Having established LTO’s peculiarity, which is made manifest by means of a detailed comparison with prototype compound BTO, in Section III.E we show that LTO also presents some features that are clearly reminiscent of the usual FE oxides with the ideal perovskite structure. In Section III.F we outline the exciting implications that our results have for the design of novel magneto-electric materials. Finally, in Section IV we summarize and present our conclusions. Whenever it is possible, we compare our first-principles results with the (scarce) experimental information available for LTO.

II. METHODOLOGY

A. Theoretical approach to $\text{La}_2\text{Ti}_2\text{O}_7$

We adopted the usual first-principles approach to the investigation of structural phase transitions of the displacive type, which is routinely applied with great success to FE perovskite oxides. Here we describe a simplified version of such an approach that is sufficient for our study of LTO (i.e., we will assume one-dimensional instability modes, will not discuss how to deal with cell strains, etc.). In essence, one needs to identify a reference equilibrium phase of high symmetry (HS) – which corresponds to the high-temperature PE phase of the compound – and study its stability against all possible structural distortions. More precisely, one writes the energy of the crystal as the following Taylor series:

$$E = E^0 + \frac{1}{2} \sum_{m,n} K_{mn} u_m u_n + \mathcal{O}(u^3),$$

where $E^0$ is the energy of the HS phase. The $u_m$ variables represent the structural distortions of the reference configuration; for the study of a FE transition, one can typically restrict oneself to the distortions compatible with the reference unit cell, i.e., those associated to the Γ-point of the Brillouin zone of the PE phase. The so-called force-constant matrix $K$ is the central quantity one needs to compute, as its negative eigenvalues (if any) correspond to unstable structural distortions – i.e., soft modes – that may result in a phase transition. Let us use the term mode stiffness to refer to the eigenvalues of $K$, which we denote by $\kappa_s$ with $s$ running from 1 to the dimension of the force-constant matrix. Note that the magnitude of a negative $\kappa_s$ determines the strength of the structural instability, and thus the likelihood of observing it experimentally. (In general, one may find several, possibly competing, instabilities of a HS phase: it is by no means guaranteed that all of them will lead to experimentally observable phase transitions.) Once a soft mode is identified, one can readily study the corresponding low-symmetry (LS) phase – by distorting the crystal according to the soft mode eigenvector and relaxing the resulting structure – and the energetics of the instability – by computing the usual double-well potential connecting the HS and LS phases.

In order to apply this program to LTO, we had to tackle one fundamental difficulty: We could not find any experimental information on the structure of the high-temperature PE phase of this compound. Note that this is never a problem when one works with the usual FE
perovskites, where the ideal cubic perovskite structure is the reference phase of choice. Such a choice is obviously correct in cases like those of BTO or PbTiO$_3$, where the cubic PE phase is experimentally accessible for $T > T_c$; more remarkably, this choice is also the most physically sound one for materials (e.g., BiFeO$_3$) whose cubic PE phase is not easy to access experimentally, as the samples tend to melt before reaching the corresponding transition temperature. In the general case, the problem of choosing an appropriate HS reference phase for the theoretical study of displacive phase transitions has long been solved. The basic idea is to look for pseudo-symmetries (i.e., slightly broken symmetries) of the known LS structure; we can thus identify possible HS phases that would transform into the known LS structure upon a relatively small distortion. This is a very powerful strategy that can lead to the discovery of complex phase transition sequences (e.g., when more than one possible HS phases are found) and, in particular, has been used to identify previously unnoticed FE transitions.$^{23,24}$

Using widely available crystallographic tools$^{25}$ we applied the pseudo-symmetry analysis to LTO and obtained a very clear prediction: We found that the FE phase of this compound, which presents space group $\text{Cmc2}_1$ and a 22-atom primitive unit cell, is most likely associated to a PE phase with the same primitive cell and space group $\text{Cmcm}$ (see sketch in Fig. 2). We thus performed our first-principles study using this $\text{Cmcm}$ phase as our HS reference structure.

A few additional points are in order: (1) The pseudo-symmetry analysis resulted in relatively large atomic distortions connecting the HS and LS phases, with maximum values of about 0.4 Å corresponding to the La atoms. Note that the magnitude of such distortions is expected to reflect the associated HS-LS transition temperature,$^{26}$ which is indeed very high in this case. (2) Experimental studies of the compounds Sr$_2$Nb$_2$O$_7$ and Ca$_2$Nb$_2$O$_7$$^{27,28}$ which share with LTO the same layered structure and a similar (udp) electronic configuration of the transition metal atoms, show that they present a high-temperature phase with $\text{Cmcm}$ space group. (3) The choice of $\text{Cmcm}$ as our PE space group results in specific predictions for the symmetry of the soft modes that would be associated with a FE transition to the $\text{Cmc2}_1$ phase. Indeed, the leading instability should transform with the $B_{1u}$ irreducible representation of $\text{mmm}$, the point group of the $\text{Cmcm}$ phase. As we will see, our first-principles results confirmed these expectations, thus supporting our choice of space group for the PE phase.

B. Details of the calculations

We used the local density approximation (LDA) to density functional theory (DFT) as implemented in the first-principles package VASP.$^{29}$ To represent the ionic cores we used the projector-augmented wave scheme$^{30}$ solving explicitly for the following electrons: La’s 5p, 5d, and 6s; Ti’s 3p, 3d, and 4s; and O’s 2s and 2p. The electronic wave functions were represented in a plane-wave basis truncated at 400 eV. We always worked with the 44-atom cell of LTO sketched in Fig. 2 (which is the conventional cell for both $\text{Cmcm}$ and $\text{Cmc2}_1$ phases), and used a $6 \times 1 \times 5$ $k$-point grid for Brillouin zone integrations. We checked these calculation conditions were well-converged by monitoring the computed equilibrium structure, bulk modulus, and phonon frequencies of the $\text{Cmcm}$ phase. For the calculation of the force-constant matrix $\mathbf{K}$ and the dielectric and piezoelectric responses, we employed a simple finite-displacement scheme and the corresponding linear-response tensor formulas, which can be found e.g. in Ref.$^{31}$ We only computed the lattice-mediated part of the static dielectric response, which has been repeatedly shown to dominate the effect in ferroelectric oxides.

Our BTO simulations were analogous to the above described ones. We solved explicitly for Ba’s 5s, 5p, and 6s electrons (treating Ti and O as above), and used a 400 eV cut-off for the plane-wave basis. We worked with the 5-atom unit cell of BTO, and used a $6 \times 6 \times 6$ $k$-point grid for Brillouin zone integrations.

![FIG. 2: (Color on-line.) Structures of the $\text{Cmc2}_1$ (FE) and $\text{Cmcm}$ (PE) phases of La$_2$Ti$_2$O$_7$ studied in this work. The small (red), medium (blue), and big (violet) balls represent O, Ti, and La atoms, respectively. The shaded polyhedra are top-viewed O$_6$ groups. The two phases have the same 44-atom conventional cell depicted in the figure; the 22-atom unit cell, which is also common to both, is indicted with dashed lines in the $\text{Cmcm}$ case. The defined Cartesian axes $x$, $y$, and $z$ (which follow the convention adopted in Ref.$^{32}$) are used throughout the paper. The symmetry-independent atoms are labeled as in Table I; note that oxygens O(1) and O(3) of the $\text{Cmcm}$ structure split, respectively, into O(1)/O(2) and O(3)/O(4) in the $\text{Cmc2}_1$ structure.](image)
III. RESULTS AND DISCUSSION

A. Structure of the $Cmcm$ and $Cmce_2$ phases

Table I shows our results for the equilibrium structure of the $Cmcm$ (PE) and $Cmce_2$ (FE) phases of LTO considered in this study. For $Cmce_2$ we also report the experimental structure measured at 1173 K by Ishizawa et al. using X-ray diffraction.

While the overall agreement between the experimental and theoretical FE structures is acceptable, the deviations affecting some atomic positions and lattice constants are larger than what is usual for this type of calculations. For example, the predicted position of the La(1) atom differs notably from the experimentally determined one; more significantly, the computed $a$ and $c$ lattice constants deviate from the experimental values by almost a 3%. We attribute these discrepancies to the fact that we are comparing our first-principles results, which correspond to the limit of 0 K, with structural data taken at very high temperatures. Given that thermal expansion and other temperature-driven effects are not included in our simulations, our results seem compatible with the experimental information.

B. Ferroelectric instabilities of the $Cmcm$ phase

As described in Section II.A, we studied the structural stability of the $Cmcm$ phase against $Gamma$-point distortions (compatible with the PE unit cell) by computing the corresponding force-constant matrix $K$. From the diagonalization of $K$ we obtained two negative eigenvalues that correspond to two structural instabilities. The computed mode stiffnesses are $-0.81$ eV/Å$^2$ and $-0.01$ eV/Å$^2$, respectively. Hence, according to our calculations, LTO’s $Cmcm$ phase presents a structural instability comparable in strength with the PE soft mode of BTO’s PE phase (for which we obtained $-2.74$ eV/Å$^2$), as well as a marginally unstable mode with nearly zero stiffness.

Both instabilities transform with the $B_{1u}$ irreducible representation of the $mnm$ point group of the PE phase; more precisely, they are infra-red active (polar) modes that involve the development of a polarization along the $z$ direction defined in Fig. 2. Such $B_{1u}$ modes break the $C_{2y}$, $C_{2x}$, $I$, and $sigma_x$ point symmetries of the PE phase (where $I$ is the spatial inversion, $C_{2a}$ stands for a two-fold rotation around axis $alpha$, and $sigma_a$ is a mirror plane perpendicular to direction $alpha$), leading to the $Cmce_2$ space group. Hence, the obtained $B_{1u}$ soft modes are exactly the kind of instabilities that can drive a ferroelectric phase transition between the $Cmcm$ and $Cmce_2$ phases. Our first-principles results thus support the correctness of our working hypothesis, i.e., that the studied $Cmcm$ structure is indeed the high-symmetry PE phase of LTO.

We can gain insight into the origin of ferroelectricity in LTO by inspecting the eigenvector of the strongest instability mode, denoted by $xi_1$ in the following. In essence, $xi_1$ involves a rotation of the $O_6$ oxygen octahedra around the $x$ axis, as sketched in Fig. 3(a). Hence, the displacements of the equatorial oxygens amount to most of the eigenvector (11% of the norm of $xi_1$) is associated to O(1) displacements, 51% to O(3), and 28% to O(5), using the

| Atom | Wyc. | $x$ | $y$ | $z$ |
|------|------|-----|-----|-----|
| La(1) | 4c | 0 | 0.2924 | 1/4 |
| La(2) | 4c | 0 | 0.4453 | 3/4 |
| Ti(1) | 4c | 1/2 | 0.3389 | 3/4 |
| Ti(2) | 4c | 1/2 | 0.4437 | 1/4 |
| O(1) | 8f | 1/2 | 0.2881 | 0.9931 |
| O(3) | 8f | 1/2 | 0.3982 | 0.9869 |
| O(5) | 4a | 1/2 | 1/2 | 1/2 |
| O(6) | 4c | 0 | 0.3458 | 3/4 |
| O(7) | 4c | 0 | 0.4525 | 1/4 |

TABLE I: Computed equilibrium structures of the $Cmcm$ and $Cmce_2$ phases of La$_2$Ti$_2$O$_7$ discussed in the text. We show in parenthesis the experimental values reported in Ref. 32 for the $Cmce_2$ phase.

| $Cmcm$ | $a = 3.891$ Å | $b = 25.720$ Å | $c = 5.465$ Å |
|--------|--------------|--------------|--------------|
| $Cmce_2$ | $a = 3.845$ Å | $b = 25.626$ Å | $c = 5.464$ Å |

$alpha = beta = gamma = 90^circ$
FIG. 3: (Color on-line.) Panel (a): sketch of the largest atomic displacements associated to the strongest instability mode (ξ1) obtained for the Cmcm phase of La2Ti2O7. We show the displacements corresponding to one layer composed of n = 4 perovskite-like planes. The arrows on the side represent the electric dipoles associated to the displacement of oxygens in different y-planes (see text). The dipoles are labeled as the oxygen atoms in Fig. 2. Panel (b): sketch of a typical anti-ferrodistortive mode occurring in an ideal (non-layered) perovskite structure.

labels defined in Fig. 2 for the oxygen atoms); there are also significant La displacements (9% of the norm), while the Ti atoms and apical oxygens O(6) and O(7) have a negligible participation in ξ1. The character of the second soft mode (ξ2) is more complex: It is dominated by the displacements of oxygens O(1) and O(5) (with 21% and 35% of the norm, respectively) and involves a significant deformation of the O6 octahedra; it also presents a large participation of the La atoms (about 24% of the norm).

These FE instabilities are very different from the ones that are usual among ABO3 oxides with the ideal perovskite structure. The inset of Fig. 4(b) shows the representative case of BTO: the Ti cation moves away from the center of the O6 octahedron, which is only slightly distorted, giving raise to a large electric dipole. Further, the FE instability in BTO and related materials is known to originate from the strong interactions between such local dipoles. In contrast, the dominant FE instability found in LTO consists of O6 octahedra rotations, the off-centering of the Ti atoms being negligible. As quantified in Section III.D, such a pattern of atomic displacements does not lead to a large local dipole, which suggests that the mechanisms responsible for the ferroelectricity in LTO have to be of a different nature.

Interestingly, structural instabilities involving O6 octahedra rotations are very common among ABO3 perovskites, and are usually termed anti-ferrodistortive (AFD). Indeed, AFD modes as the one sketched in Fig. 3(b) are the driving force for most of the structural phase transitions occurring in these compounds, the examples including crystals as well-known as SrTiO3, LnMnO3 and LnNiO2 (where Ln is a lanthanide), multiferroics BiMnO3 (where M is a 3d transition metal), etc. Accordingly, there is extensive literature devoted to the study and classification AFD modes in ABO3 perovskites33,34 and it is known that size (e.g., the incompatibility of the ionic radii of the A and B cations to form a cubic perovskite lattice) and chemical (as in the Bi-based compounds that display the so-called stereochemical activity) effects are usually responsible for the occurrence of AFD distortions.35 Hence, it is not a surprise to find that layered perovskite structures may present AFD-like instabilities that allow for a better fulfillment of steric and/or chemical constraints at a local level. It is not our goal here to discuss the occurrence and origin of such soft modes in LTO-like layered perovskites; such a study should probably involve consideration of a number of representative crystals (e.g., a few members of the AnBnO3n+2 family) and falls beyond the scope of this work. Suffice it to say that the leading FE instability that we found in LTO is essentially analogous to the AFD distortions that are ubiquitous among perovskite oxides.

However, we must note a critical difference between LTO’s AFD-like mode depicted in Fig. 3(a) and the AFD modes occurring in ideal perovskite structures [Fig. 3(b)]: the former causes a spontaneous polarization, while the latter do not. To better explain this, in Fig. 3(a) we indicate with arrows the electric dipoles that appear as a consequence of the displacement of the oxygen atoms following the ξ1 eigenvector. The oxygens in each y-oriented plane give raise to a dipole along the z direction. Using the definitions in Fig. 3(a), the total dipole associated to one layer would be $\mathbf{p}_{\text{layer}} = p_x + 2p_y + 2p_z$. Since there is no symmetry relationship between the displacements of the O(1), O(3), and O(5) oxygens in the ξ1 eigenvector, it follows immediately that $\mathbf{p}_{\text{layer}}$ will be different from zero. Moreover, even if oxygens of different types were to displace by the same amount, so that $p_x = -p_3 = p_1 = p$, we would still have $\mathbf{p}_{\text{layer}} = \mathbf{p} \neq 0$, as the number of oxygen planes in each layer is odd. Finally, note that LTO’s unstable mode ξ1 involves an identical distortion of all layers in the structure, and thus gives raise to a net macroscopic polarization.

On the other hand, AFD distortions of the ideal (non-layered) perovskite structure do not result in a macroscopic polarization. In Fig. 3(b) we show a pattern of O6 rotations around the indicated xz axis; the situation is very similar to the one depicted in Fig. 3(a), except that in this case the network of O6 octahedra is not truncated. Again, we indicate with arrows the electric dipoles that appear as a consequence of the oxygen displacements: oxygens within a [011]c-oriented plane give raise to a dipole $\mathbf{p}$ along [011]c. It is apparent that the addition of all such dipoles gives no net polarization in this case, a result that can be viewed as a consequence of the three-dimensional nature of the O6 network.

In conclusion, we have found that the strongest structural instability in LTO’s high-symmetry phase is a very common and simple one: it involves concerted rotations of the O6 octahedra, much alike the AFD modes responsible for the structural phase transitions in most ABO3 crystals with the ideal perovskite structure. AFD distortions in the usual perovskites are well-known to be non-polar, a feature that can be viewed as a consequence
of the symmetry and three-dimensional character of the lattice. In contrast, because the structure of LTO is split in layers comprising an even number of perovskite planes, the O$_6$-rotation mode gives rise to a net polarization in this case. Hence, since the occurrence of a spontaneous polarization in LTO relies on the layered topology of the lattice, it seems appropriate to describe this compound as a topological ferroelectric. Let us stress that LTO’s peculiar lattice topology does not seem essential for the structural instability to exist, but it is critical for it to have a polar character.

C. Nature of the Cmcm-to-Cmce2$_1$ transition

In addition to the already discussed topological nature of the leading FE instability, the transformation between LTO’s Cmcm and Cmce2$_1$ phases presents a number of interesting aspects that we discuss in the following. Most importantly, our results show that the transition is driven by the combined action of the two soft modes discussed in the previous Section, and suggest that such a cooperation is critical for it to occur at a very high temperature.

To study a structural phase transition quantitatively, one can start by comparing the energies of the phases involved. Table II shows our results for LTO, along with the analogous data for the $Pm3m$ (PE) and $P4mm$ (FE) phases of BTO. Note that the energy change per unit volume involved in LTO’s transition is about one order of magnitude greater than the corresponding one for BTO. Such an enormous difference is compatible with the experimentally measured Curie temperatures, which are 1770 K and 400 K for LTO and BTO, respectively. Hence, our first-principles results for the energetics of LTO’s FE transition seem consistent with experiments.

Table II also contains information about the elastic deformation that accompanies the FE transitions. The properties of FE oxides with the ideal perovskite structure are known to be strongly sensitive to cell strains. This is clearly reflected in the results for BTO: If the compound is forced to keep the cubic cell of the PE structure, the energy gain involved in the FE transition is reduced by half (i.e., it drops from $-0.110 \text{ meV/Å}^3$ to $-0.051 \text{ meV/Å}^3$). On the other hand, if we only impose the PE volume (so that the FE cell is allowed to deform and acquire a $c/a \neq 1$ ratio), the energetics of the transformation is not strongly affected. In contrast, the analogous elastic constraints have a relatively small effect in the case of LTO (i.e., the energy gain drops from $-1.097 \text{ meV/Å}^3$ to $-0.938 \text{ meV/Å}^3$ when we impose the PE cell). Such a weak coupling between strain and the FE distortion is probably reflecting the AFD-like character of the instability. This result also suggests that LTO will display relatively small piezoelectric effects as compared with regular FE perovskites.

Let us now consider the atomic displacements that characterize the Cmcm-to-Cmce2$_1$ transformation. In most materials undergoing displacive transitions, the atomic distortion connecting the HS and LS phases is essentially captured by the eigenvector of the instability mode that triggers the transformation. One can easily quantify this by constructing a distortion vector $\Delta \mathbf{X}$ comprising all the atomic displacements associated to the HS-to-LS transition, and expressing it in the basis formed by the eigenvectors $\xi_i$ of the force-constant matrix of the HS phase. (For simplicity, we constructed our distortion vectors $\Delta \mathbf{X}$ using the atomic positions of a LS phase that is forced to have the same unit cell as the HS phase.) For BTO, this analysis led us to the expected result: the soft mode of the PE phase captures 98% of the atomic distortion involved in the $Pm3m$-to-$P4mm$ transition. However, the result for LTO was qualitatively different: the strongest instability mode ($\xi_1$, with $\kappa_1 = -0.81 \text{ eV/Å}^2$) captures 81% of the total distortion, and the second instability mode ($\xi_2$, with $\kappa_2 = -0.01 \text{ eV/Å}^2$) contributes with a 15%. (For both compounds, no other mode contributes more than a 1%.) Hence, our results suggest that the two soft modes $\xi_1$ and $\xi_2$ play an important role in LTO’s FE phase transition.

Such a large contribution of $\xi_2$ to the structural transformation seems incompatible with the computed mode stiffnesses; indeed, the values of $\kappa_1$ and $\kappa_2$ would suggest that $\xi_2$ is about 80 times weaker than $\xi_1$ as an instability. To resolve this apparent contradiction, we computed how LTO’s energy changes when the Cmcm phase is distorted according to the individual $\xi_1$ and $\xi_2$ modes. As shown in Fig. 4(a), we found a large energy reduction associated with the $\xi_1$ distortion, while the $\xi_2$ instability is almost negligible. We also computed the energy variation as the total distortion $\Delta \mathbf{X}$ is frozen in. Remarkably, as compared with the results for $\xi_1$, the $\Delta \mathbf{X}$ curve in Fig. 4(a) presents a much deeper minimum corresponding to a much larger distortion amplitude. This is a new indication that the $\xi_1$ soft mode cannot explain LTO’s FE transition by itself. This result contrasts with the situation for BTO [Fig. 4(b)], where the FE soft mode captures the energetics of the structural transformation almost exactly.

The results of Fig. 4(a) suggest that there is a strong and cooperative coupling between the two instability modes of LTO. To better describe this effect, let us write...
and $\xi$ the order couplings between soft modes. We have included in Eq. (2) only the lowest quadratic parameters coincide with the mode stiffness. Note that, in this case, the fitted quartic coefficient is a combination of the phase. A similar approach is taken in 

\begin{equation}
E = E^{Cmcn} + \frac{1}{2} \kappa_1 u_1^2 + \frac{1}{2} \kappa_2 u_2^2 + \frac{1}{4} \alpha_1 u_1^4 + \frac{1}{4} \alpha_2 u_2^4 + \gamma' u_3^2 u_2 + \gamma'' u_1^2 u_2^2 + \gamma''' u_1 u_3^3 + \mathcal{O}(u^6),
\end{equation}

where $E^{Cmcn}$ is the energy of the $Cmcn$ phase, and $u_1$ and $u_2$ are, respectively, the amplitudes (in Angstrom) of the $\xi_1$ and $\xi_2$ distortions. Note that this expression for the energy is greatly simplified by symmetry, and that the quadratic parameters coincide with the mode stiffnesses. We have included in Eq. (2) only the lowest-order couplings between $u_1$ and $u_2$, which are quantified by the primed $\gamma$ parameters. By fitting to the $\xi_1$ and $\xi_2$ energy curves of Fig. 4(a), we got $\kappa_1 = -0.79$ eV/Å$^2$ and $\kappa_2 = 0.00$ eV/Å$^2$, in fair agreement with the values obtained from the diagonalization of $K$; we also got $\alpha_1 = 0.65$ eV/Å$^2$ and $\alpha_2 = 0.66$ eV/Å$^2$. Then, to fit the $\Delta X$ curve we considered distortions characterized by $u_1/u_2 = 0.81/0.15$, as it corresponds to the $Cmc2_1$ phase. Note that, in this case, the fitted quartic coefficient is a combination of the $\alpha$ and $\gamma$ parameters of Eq. (2). Given the large $u_1/u_2$ ratio associated with the $\Delta X$ distortion, and in view of further tests discussed in Section III.D, it seems reasonable to assume that $\gamma'$ dominates over $\gamma''$ and $\gamma'''$; we thus got $\gamma' = -0.35$ eV/Å$^4$. As compared with the computed $\alpha'$, this clearly is a very strong anharmonic coupling that favors the combined $\xi_1 + \xi_2$ distortion.

To the best of our knowledge, such a cooperation between soft modes is rare among perovskite oxides. There are many examples of materials in which several strong instabilities exist; in most cases, the strongest one leads to a phase transition that tends to suppress, partially or totally, the other instabilities. The competition between the FE and AFD soft modes in compounds like SrTiO$_3$ is a representative and well studied case. In contrast, we find that the reciprocal enhancement of the two soft FE modes is critical to explain the structural transformation in LTO. The $\xi_1$ mode is clearly the leading instability, and it would occur even in absence of $\xi_2$. Yet, as the results in Fig. 4(a) show, the magnitude and strength of the transformation are boosted by the interaction between $\xi_1$ and $\xi_2$. Thus, our results seem to suggest that LTO owes its very high $T_C$ to such an interaction; indeed, in view of Fig. 4(a), it is hard to imagine LTO’s $T_C$ would remain essentially the same if the coupling between $\xi_1$ and $\xi_2$ was suppressed.

Studying from first-principles the temperature dependence of the $\xi_1$ and $\xi_2$ distortions, and the details of how these two soft modes freeze in at LTO’s FE transition, is a challenging endeavor that remains for future work. Nevertheless, a few observations can be made based on the present results. In principle, one could try to approach the problem by introducing a Landau potential of the form:

\begin{equation}
F - F_0 = \frac{1}{2} A_1 (T - T_C) Q_1^2 + \frac{1}{4} B_1 Q_1^4 + \frac{1}{2} A_2 Q_2^2 + \frac{1}{4} B_2 Q_2^4 + C' Q_1^4 Q_2 + C'' Q_1^2 Q_2^2 + C''' Q_1 Q_2^3,
\end{equation}

which is written in terms of two one-dimensional order parameters, $Q_1$ and $Q_2$, that have the same symmetry. In the following heuristic argument we will consider only the $Q_1^2 Q_2$ crossed term — in accordance with our above conjecture regarding the couplings in Eq. (3), and because this is the most relevant crossed term in vicinity of the phase transition — thus assuming that $C'' = C''' = 0$.

If we were dealing with a simple transition, we would have a primary order parameter $Q_1$ corresponding to the unstable eigenmode of the $K$ matrix of the high-symmetry phase; the temperature dependence of the Landau potential would be restricted to the $Q_1^2$ term, as indicated in Eq. (3), and we would have positive $A_1$ and $B_1$ coefficients. Further, a secondary order parameter $Q_2$ would be stable by itself, with positive $A_2$ and $B_2$ coefficients. Hence, the corresponding Landau theory would predict a phase transition at $T = T_C$, with

\begin{equation}
Q_1 = \left[ \frac{A_1}{B_1} (T_C - T) \right]^{1/2}
\end{equation}
below the transition temperature. (The indicated formulas were derived assuming that we remain close to the transition temperature.) Then, $Q_2$ would present the following temperature dependence below $T_C$:

$$ Q_2 = -\frac{C''}{A_2}Q_1^3 = -\frac{C''}{A_2} \left[ \frac{A_1}{B_1}(T_C - T) \right]^{3/2}. $$

In a simple case, the coefficients in Eq. (2) may be a good approximation to the coefficients in Eq. (3) in the limit of low temperatures. Thus, by supplementing the Eq. (2) deduced from first-principles with a piece experimental information – i.e., the value of the transition temperature $T_C$ –, we could construct the corresponding Landau potential and obtain a quantitative description of the temperature dependence of $Q_1$ and $Q_2$.

The doubts quickly appear when one tries to apply this model to LTO. It seems natural to associate this model to LTO. It seems natural to associate $Q_1$ and $Q_2$ with our computed FE soft modes $\xi_1$ and $\xi_2$, respectively. However, that identification implies that the transition temperature for $Q_1$ is independent of $Q_2$: such an approximation would be an awkward one, given the large influence that $\xi_2$ has in the energetics of the $Cmcm$-to-$Cmc2_1$ transformation. Additionally, we would be forced to speculate regarding the $T$-dependence of the $A_2$ coefficient, as our guess for this parameter – i.e., the $\kappa_2$ of Eq. (2) which was found to be essentially zero – does not comply with the usual requirements for the quadratic coefficient of a secondary mode. Note that, for example, if we had a small value of $A_2$ and thus a dominant $B_2$ term, the behavior with temperature of both $Q_1$ and $Q_2$ would vary: $Q_1$ would have the same functional $T$-dependence but with a different prefactor, and $Q_2$ would go as $(T_C - T)^{1/2}$ instead of $(T_C - T)^{3/2}$. The results of this study do not allow us to resolve such details of LTO’s transition.

D. Polarization and response properties

Table III shows the computed spontaneous polarization, lattice-mediated dielectric tensor, and piezoelectric tensor for the $Cmc2_1$ phase of LTO. For comparison, we also show results from the literature corresponding to the $P_2$ phase that is stable at room temperature.

We obtained a value of 0.29 C/m$^2$ for the spontaneous polarization, which is compatible with the result of 0.38 C/m$^2$ that we obtained for the tetragonal phase of BTO. The dielectric response is also very significant, as the obtained values are comparable with those typical of FE perovskites (e.g., we got $\epsilon_{zz} = 23$ for the $z$-polarized tetragonal phase of BTO). As regards piezoelectricity, the computed responses are considerable but not particularly large: for example, for the low-temperature rhombohedral phase of BTO, the piezoelectric coefficients reach values of 200 pC/N.31 while for LTO we got maximum values of about 20 pC/N. LTO’s relatively small piezoelectric response seems compatible with the minor role that the cell strains play in determining the energetics of the $Cmcm$-to-$Cmc2_1$ phase transition, as mentioned in the discussion of Table II.

The large spontaneous polarization obtained may seem incompatible with the AFD-like character of the structural instability ($\xi_1$) that dominates the $Cmcm$-to-$Cmc2_1$ transition. To clarify this point, we performed alternative calculations using linear-response expressions,31 based on the Born effective-charge tensors $Z_{ij}^*$ that quantify the polarization change associated to the displacement of an individual atom $i$.

The polarization reported in Table III was obtained in the standard way: We used the Berry-phase theory of King-Smith and Vanderbilt40 to compute the variation of $P$ as the $Cmc2_1$ structure is deformed into a symmetry-equivalent one with opposite polar distortion; then, $P^S$ is half of the computed polarization change. $P^S$ can also be estimated using the approximate formula

$$ P^S_\alpha \approx \sum_{i\beta} Z_{i,\alpha\beta}^* \Delta X_{i\beta}, $$

where $\Delta X$ is the vector capturing the distortion that connects the $Cmcm$ and $Cmc2_1$ phases, $\alpha$ labels the atoms in the unit cell, and $\alpha$ and $\beta$ label spatial directions. Using different choices for the effective-charge tensors (i.e., those computed for the $Cmcm$ phase, as well as the corresponding results for the $Cmc2_1$ phase subject to different cell constraints) we obtained values of $P^S$ in the 0.25-0.32 C/m$^2$ range, which are perfectly compatible with the result in Table III.

Then, we used the effective-charge tensors of the $Cmcm$ phase (given in Table IV) to compute the polar-

| $Cmcm_2$ phase | $P_2$ phase |
|----------------|-------------|
| **this work**  | **exp. ($T_{room}$)** | **theory** |
| $P^S_\alpha$   | $0.29$      | $0.05$    |
| $\epsilon_{xx}$ | 62 (61)    | 52        |
| $\epsilon_{yy}$ | 44 (44)    | 42        |
| $\epsilon_{zz}$ | 65 (54)    | 62        |
| $d_{11}$       | 12 (0)     | 3         |
| $d_{12}$       | 4 (1)      | 6         |
| $d_{13}$       | -22 (0)    | 16        |
| $d_{23}$       | -2 (0)     | -         |
| $d_{33}$       | 1 (0)      | -         |
TABLE IV: Computed effective-charge tensors (given in units of elementary charge) for the \( \text{Cmcm} \) (PE) and \( \text{Cmc21} \) (FE) phases of \( \text{La}_2\text{Ti}_2\text{O}_7 \). To facilitate the comparison between phases, we list the tensors corresponding to all the symmetry-invariant atoms of the FE phase. Atoms are labeled as in Table I.

|          | \( \text{Cmcm} \) (PE) | \( \text{Cmc21} \) (FE) |
|----------|--------------------------|--------------------------|
| \( \text{La}(1) \) | \( \begin{pmatrix} 4.63 & 0 & 0 \\ 0 & 4.17 & 0 \\ 0 & 4.72 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 4.64 & 0 & 0 \\ 0 & 4.09 & -0.21 \\ 0 & -0.69 & 4.71 \end{pmatrix} \) |
| \( \text{La}(2) \) | \( \begin{pmatrix} 4.37 & 0 & 0 \\ 0 & 3.76 & 0 \\ 0 & 4.28 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 4.63 & 0 & 0 \\ 0 & 4.13 & 0.41 \\ 0 & 0.24 & 4.24 \end{pmatrix} \) |
| \( \text{Ti}(1) \) | \( \begin{pmatrix} 6.91 & 0 & 0 \\ 0 & 6.70 & 0 \\ 0 & 5.72 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 6.16 & 0 & 0 \\ 0 & 5.60 & -0.36 \\ 0 & 0.24 & 5.31 \end{pmatrix} \) |
| \( \text{Ti}(2) \) | \( \begin{pmatrix} 6.33 & 0 & 0 \\ 0 & 5.32 & 0 \\ 0 & 7.45 & 0 \end{pmatrix} \) | \( \begin{pmatrix} 6.11 & 0 & 0 \\ 0 & 5.29 & 0.09 \\ 0 & -0.15 & 6.32 \end{pmatrix} \) |
| \( \text{O}(1) \) | \( \begin{pmatrix} -2.52 & 0 & 0 \\ 0 & -3.20 & 0.73 \\ 0 & 0.86 & -3.26 \end{pmatrix} \) | \( \begin{pmatrix} -2.52 & 0 & 0 \\ 0 & -3.14 & 0.53 \\ 0 & 0.38 & -2.92 \end{pmatrix} \) |
| \( \text{O}(2) \) | \( \begin{pmatrix} -2.52 & 0 & 0 \\ 0 & -3.20 & -0.73 \\ 0 & -0.86 & -3.26 \end{pmatrix} \) | \( \begin{pmatrix} -2.15 & 0 & 0 \\ 0 & -2.35 & -0.89 \\ 0 & -0.90 & -3.44 \end{pmatrix} \) |
| \( \text{O}(3) \) | \( \begin{pmatrix} -2.08 & 0 & 0 \\ 0 & -3.27 & -1.72 \\ 0 & -1.56 & -3.98 \end{pmatrix} \) | \( \begin{pmatrix} -1.76 & 0 & 0 \\ 0 & -3.33 & -1.36 \\ 0 & -1.38 & -2.95 \end{pmatrix} \) |
| \( \text{O}(4) \) | \( \begin{pmatrix} -2.08 & 0 & 0 \\ 0 & -3.27 & 1.72 \\ 0 & 1.56 & -3.98 \end{pmatrix} \) | \( \begin{pmatrix} -2.49 & 0 & 0 \\ 0 & -3.19 & 1.28 \\ 0 & 1.19 & -3.64 \end{pmatrix} \) |
| \( \text{O}(5) \) | \( \begin{pmatrix} -2.49 & 0 & 0 \\ 0 & -3.15 & 1.19 \\ 0 & 0.98 & -3.64 \end{pmatrix} \) | \( \begin{pmatrix} -2.63 & 0 & 0 \\ 0 & -3.11 & 1.04 \\ 0 & 1.00 & -3.36 \end{pmatrix} \) |
| \( \text{O}(6) \) | \( \begin{pmatrix} -5.50 & 0 & 0 \\ 0 & -2.15 & 0 \\ 0 & 0 & -1.66 \end{pmatrix} \) | \( \begin{pmatrix} -5.04 & 0 & 0 \\ 0 & -2.08 & 0.24 \\ 0 & 0.14 & -1.75 \end{pmatrix} \) |
| \( \text{O}(7) \) | \( \begin{pmatrix} -5.10 & 0 & 0 \\ 0 & -1.73 & 0 \\ 0 & 0 & -2.41 \end{pmatrix} \) | \( \begin{pmatrix} -4.99 & 0 & 0 \\ 0 & -1.91 & -0.03 \\ 0 & -0.02 & -2.20 \end{pmatrix} \) |

TABLE V: Computed effective-charge tensors (given in units of elementary charge) for the \( \text{Pnm3m} \) (PE) and \( \text{P4mm} \) (FE) phases of \( \text{BaTiO}_3 \). The tensors are given in the conventional Cartesian axes for a rectangular lattice. They correspond to the following atoms (PE phase positions given in relative units): Ba located at \((0,0,0)\), Ti at \((1/2,1/2,1/2)\), O(1) at \((1/2,1/2,0)\), and O(2) at \((1/2,1/2,1/2)\).

|          | \( \text{Pnm3m} \) (PE) | \( \text{P4mm} \) (FE) |
|----------|--------------------------|--------------------------|
| \( \text{Ba} \) | \( \begin{pmatrix} 2.72 & 0 & 0 \\ 0 & 2.72 & 0 \\ 0 & 0 & 2.72 \end{pmatrix} \) | \( \begin{pmatrix} 2.71 & 0 & 0 \\ 0 & 2.71 & 0 \\ 0 & 0 & 2.81 \end{pmatrix} \) |
| \( \text{Ti} \) | \( \begin{pmatrix} 7.31 & 0 & 0 \\ 0 & 7.31 & 0 \\ 0 & 0 & 7.05 \end{pmatrix} \) | \( \begin{pmatrix} 7.05 & 0 & 0 \\ 0 & 7.05 & 0 \\ 0 & 0 & 5.83 \end{pmatrix} \) |
| \( \text{O}(1) \) | \( \begin{pmatrix} 0 & -2.13 & 0 \\ 0 & 0 & -5.77 \\ 0 & 0 & -1.98 \end{pmatrix} \) | \( \begin{pmatrix} 0 & -1.98 & 0 \\ 0 & 0 & -4.79 \\ 0 & 0 & -1.96 \end{pmatrix} \) |
| \( \text{O}(2) \) | \( \begin{pmatrix} 0 & -2.13 & 0 \\ 0 & 0 & -5.77 \\ 0 & 0 & -2.14 \end{pmatrix} \) | \( \begin{pmatrix} 0 & -2.14 & 0 \\ 0 & 0 & -4.79 \\ 0 & 0 & -1.96 \end{pmatrix} \) |

In contrast, the second soft mode \( \xi_2 \) is found to have a considerably polar character. It can then be trivially shown that the two soft modes have a very similar contribution to the total spontaneous polarization of the \( \text{Cmc21} \) phase of LTO, in spite of the fact that \( \xi_1 \) embodies 81% of the PE-to-FE distortion. Hence, the two-mode character of the transition is critical to explain the relatively large \( P_S \) of the \( \text{Cmc21} \) phase.

Unfortunately, we were unable to find experimental results for the ferroelectric and response properties of the \( \text{Cmc21} \) phase of LTO. Table III shows some results for the \( P2_1_1 \) phase of the compound that is stable at room temperature. Interestingly, the dielectric and piezoelectric responses measured for this phase seem compatible (at least in magnitude) with our values for \( \text{Cmc21} \). As regards the spontaneous polarization, the value for the \( P2_1_1 \) phase is smaller than ours by a factor of 6; this experimental result was essentially confirmed by the first-principles study of Ref. 16, which employed a DFT theory similar to ours.\textsuperscript{22} Hence, we can tentatively conclude that the \( \text{Cmc21} \)-to-\( P2_1_1 \) transformation, which is experimentally determined to occur at 1053 K,\textsuperscript{22} involves a reduction of LTO’s spontaneous polarization. While such a reduction in the magnitude of \( P_S \) as the temperature decreases is not typical in FE perovskites, in principle there is no reason to question this possibility.

Finally, let us discuss an intriguing possibility suggested by the very different magnitudes of the computed mode charges \( \bar{Z}_{i,z} \) and \( \bar{Z}_{2,z} \). Since \( Z_\ast \) quantifies the coupling between a polar mode and an applied electric field, we can expect \( \xi_2 \) to be much more reactive to an external...
bias than $\xi_1$. One can thus imagine the following possibility: to apply an electric field to LTO in its Cmce21 phase and switch only the part of the spontaneous polarization associated to $\xi_2$. More precisely, if $(u_1^1, u_2^1)$ represents the FE phase discussed so far, an electric field might allow us to take the material into a qualitatively different polarization state $(u_1^1, u_2^1) \approx (u_1^1, -u_2^1)$. LTO would thus be a four-state ferroelectric, as the $(u_1^1, u_2^1)$ and $(-u_1^1, -u_2^1)$ variants would be accessible as well. A necessary condition for such a partial switching to occur is that the $(u_1^1, u_2^1)$ state be a minimum of the energy. More precisely, we need the coupling between $\xi_1$ and $\xi_2$ to be dominated by the $\gamma''u_1^2u_2^2$ term of Eq. (2): Note that, for $|\gamma''|$ much greater than $|\gamma'|$ and $|\gamma'''|$, the four states $(\pm u_1^1, \pm u_2^1)$ would have essentially the same energy; in contrast, if $\gamma'$ or $\gamma'''$ dominate, the “$\xi_2$-switched” state would have a much higher energy and might not be a minimum of $E(u_1, u_2)$. In order to confirm or disprove such a partial switching, we considered the equilibrium structure of the Cmce21 phase (i.e., the one reported in Table I) and generated configurations in which the $\xi_2$ distortion was inverted and given various magnitudes; we relaxed such transformed structures and invariably obtained the original Cmce21 phase as final result. Hence, while we did not explore the $E(u_1, u_2)$ energy landscape in detail, our results clearly indicate there is no stable “$\xi_2$-switched” state. Equivalently, this implies that the $\gamma'$ and $\gamma'''$ terms of Eq. (2) dominate over $\gamma''$ (which supports the assumption made in Section III.C).

E. BaTiO$_3$-like ferroelectric modes in La$_2$Ti$_2$O$_7$

Thus far we have discussed the main features of LTO’s high-temperature FE transition, showing that this compound is very different from the FE oxides with the ideal perovskite structure. In particular, our results seem to suggest that LTO and BTO have little in common, in spite of the fact that they share the same building block: TiO$_6$ octahedra with Ti$^{4+}$ in the 3d$^0$ electronic configuration. In the following we show that such a conclusion would be a deceptive one.

Ferroelectricity in the usual FE perovskite oxides relies on strong dipole-dipole interactions whose fingerprint is the anomalously large magnitude of the Born effective charges of some atomic species.$^{22}$ A prototypical example of this behavior is BTO, for which we computed the effective-charge tensors shown in Table V. Most notably, in the PE phase the Ti$^{4+}$ cations display $Z^*$ values above 7e, almost doubling their nominal ionization charge. Analogously, the displacement of the O atoms towards the Ti has a dynamical charge of $-5.77e$ associated to it, almost tripling the nominal value of $-2e$. It is well-known that this effect is related with a partial covalent character of the Ti–O bond, and an increased hybridization of the O-2p and Ti-3d orbitals as the Ti and O atoms approach.$^{12}$ Thus, given this chemical origin, the effective charges become less anomalous once the FE distortion freezes in: according to the results in Table V, Ti’s charge of 7.31e gets reduced to 5.83e, while O’s charge of $-5.77e$ falls to $-4.79e$.

As apparent from Table IV, some Ti and O atoms in LTO also present anomalously large effective charges that reach values similar to those obtained for BTO. In the case of the Ti atoms, the computed $Z^*$ tensors are rather isotropic, with the maximum $Z^*$ values [i.e., 6.91e for Ti(1) and 7.45e for Ti(2)] corresponding to displacements along the in-layer directions $x$ and $z$. In the case of the O atoms, O(6) and O(7) clearly present the largest values, which exceed $-5e$ as in BTO. Such giant dynamical charges corresponds to displacements along the $x$ direction, for which LTO presents infinite chains of TiO$_6$ octahedra (see Figs. 1 and 2) as those in the ideal perovskite structure. Hence, as regards their polarizability properties, the results for the Ti and O atoms in LTO are strongly reminiscent of the behavior that is well-known for BTO.

Do such anomalous effective charges lead to FE instabilities in LTO? In accordance with the above discussion, the answer to this question is a negative one: the Cmcm phase presents only two $\Gamma$-point instabilities (i.e., the already discussed $\xi_1$ and $\xi_2$) and the Cmce21 is stable against $\Gamma$-point perturbations$^{23}$ Nevertheless, by inspecting the $K$-eigenmodes of the Cmcm phase, it is easy to find several low-energy FE modes that are BTO-like, i.e., they involve the displacement of the Ti atoms away from the center of nearly undistorted O$_6$ octahedra$^{24,45}$ For example, we found a marginally stable and strongly polar mode for which we computed $\kappa_s = 0.26$ eV/Å$^2$ and $\tilde{Z}_{s,x} = 21.7e$ (this distortion is $x$-polarized and has $B_{33\alpha}$ symmetry): this mode gives an enormous contribution to the $e_{xx}$ dielectric response$^{26}$ the obtained value exceeds 600. Interestingly, these BTO-like modes become stiffer in the Cmce21 phase; thus, they do not give raise to any anomalously large contribution to the dielectric response reported in Table III.

In conclusion, our analysis shows that LTO presents obvious traces of the FE instabilities of BTO. Such a transferability of instabilities was demonstrated by one of us in an hexagonal polymorph of BTO.$^{25}$ In that case, the FE phase transition was shown to be driven by soft modes that are an almost perfect match of the usual BTO-like FE instability. In LTO, such modes are very low in energy, but still stable; further, they clearly compete with the dominating AFD-like instability, and become stiffer once the Cmcm-to-Cmce21 transition occurs. Nevertheless, noting that BTO-like FE distortions tend to be very sensitive to cell strains, our results suggest the possibility that such instabilities might be induced in LTO by suitable strain engineering or chemical substitution, or that they might occur spontaneously in similar layered perovskites.
F. Implications for work on magnetoelectrics

Finding materials that display large magnetoelectric (ME) effects (i.e., a large magnetic reaction to an applied electric field) at room temperature is a major challenge that remains to be successfully tackled. The difficulties involved in the design of good magnetoelectrics have been discussed elsewhere. At present, the strategies that seem most promising rely on finding systems that satisfy the following two conditions: (1) their atomic structure must react strongly to an applied electric field (i.e., we are looking for good dielectrics), and (2) the field-induced distortions must have a large effect on the magnetic interactions (as emphasized in Refs. [48] and [49]).

While there are well-known strategies to comply with the first condition, satisfying the second one is proving much more difficult. In fact, the existing quantitative studies indicate that the dielectric response of ME multiferroics like BiFeO$_3$ is dominated by modes that have small magnetostructural couplings associated to them. It is thus interesting to consider the alternative approach adopted by Benedek and Fenici. These authors noted that modes involving O$_6$ rotations are likely to be strongly coupled with the magnetism of perovskite oxides, as such AFD-like distortions usually control the nature and magnitude of the main magnetic interactions (e.g., the metal–oxygen–metal super-exchange and Dzyaloshinskii-Moriya couplings). Hence, they looked for materials in which AFD-like distortions are related with (or lead to) ferroelectricity, as in such cases one could use an electric field to act upon the O$_6$ rotations. Note that the linked connection between AFD-like distortions and ferroelectricity is an exotic one, since the O$_6$-rotational modes are strictly non-polar in compounds with the ideal perovskite structure (see Section III.B). Accordingly, ferroelectricity-related O$_6$-rotational modes have been found in non-ideal perovskites, e.g., in the PbTiO$_3$/SrTiO$_3$ artificial superlattices and the layered compound Ca$_3$Mn$_2$O$_7$. In both cases, ferroelectricity has an improper character, and a combination of various AFD-like modes must occur for an spontaneous polarization to appear.

There is no need to emphasize the importance of our findings for LTO in the context of magnetoelectrics. In LTO’s case, the FE soft mode is AFD-like already; hence, it can freeze in and give raise to a sizeable spontaneous polarization by itself, without the need of any accompanying distortion. Further, LTO’s O$_6$ rotations couple directly (bi-linearly) with an applied electric field, which might prove advantageous for the purpose of obtaining large ME effects. (In improper ferroelectrics, the coupling between an applied field and the AFD-like modes will typically be a higher-order effect.) Indeed, the proper ferroelectricity driven by O$_6$ rotations that occurs in LTO seems to be the dreamed FE instability from the viewpoint of ME applications.

One would thus like to obtain LTO-like ferroelectricity in a magnetic material. The most obvious possibility is to consider the substitution of Ti by Mn in LTO, so as to form La$_2$Mn$_2$O$_7$, a crystal that we have not found described in the literature. In La$_2$Mn$_2$O$_7$ we would have manganese in the Mn$^{4+}$ ionization state, most likely in the high spin $t^3_{2g}e^0_g$ electronic configuration; thus, we can expect this crystal to be insulating. Further, since the Ti–O chemistry does not seem to play any relevant role in LTO’s FE instability, we can expect La$_2$Mn$_2$O$_7$ to present a FE transition analogous to LTO’s. Hence, this material seems an excellent candidate to satisfy the condition (2) mentioned above and thus display large ME effects. Additionally, one would like the FE transition to occur near room temperature, so as to benefit from the enhancement of the functional responses near $T_C$ [in the spirit of the condition (1) mentioned above]. In this sense, it may be useful to note that materials like Sr$_2$Ta$_2$O$_7$ or Sr$_2$Nb$_2$O$_7$ present FE transitions that seem similar to LTO’s but occur at lower $T_C$’s: 166 K and 1615 K, respectively. This suggests that exploring alternative compositions is a promising route to tune the temperature of the O$_6$-rotational FE transition.

IV. SUMMARY AND CONCLUSIONS

We used first-principles methods to study the origin of ferroelectricity in the layered perovskite La$_2$Ti$_2$O$_7$ (LTO), one of the materials with highest Curie temperature known ($T_C = 1770$ K). To do so, we carried out for LTO a research program that has been repeatedly and successfully applied to the investigation of displacive phase transitions in ferroelectric (FE) oxides with the perovskite structure. Our results allowed us to characterize LTO’s high-temperature FE transition, which was found to present very peculiar features.

We found that ferroelectricity in LTO is very different from what occurs in the well-known FE oxides with the ideal perovskite structure, such as BaTiO$_3$ (BTO) or PbZr$_{1-x}$Ti$_x$O$_3$ (PZT). Indeed, the dominant FE instability of this compound has little in common with the textbook picture of positive charges moving against negative charges in an ionic insulator; instead, it involves concerted rotations of the oxygen octahedra that form the perovskite framework. Hence, LTO’s high-temperature structural transition is reminiscent of the behavior of simple perovskite oxides, but not the FE ones: LTO’s FE distortion is much alike the O$_6$ rotational soft modes that drive the anti-ferrodistortive phase transitions of SrTiO$_3$, LaAlO$_3$, LaMnO$_3$, and many other non-polar perovskite crystals.

Hence, we found that the existence of ferroelectricity in LTO at record-high temperatures is the result of structural distortions as those occurring in many perovskite oxides that are not ferroelectric. As discussed here, the solution to this puzzle has to do with LTO’s layered structure: Because the lattice of oxygen octahedra is truncated in this compound, the O$_6$-rotations acquire a polar character and give raise to a macroscopic polarization.
We can thus describe LTO as a topological ferroelectric, since it owes its spontaneous polarization to the layered topology of its structure. Note that such a peculiar topology does not seem essential for LTO’s high-temperature transition to occur, but it is critical for it to have a ferroelectric character.

We quantified energetics of LTO’s FE transformation, the results being consistent with the very high temperature at which it happens. Most remarkably, we found that the structural distortion connecting the PE (Cmcm) and FE (Cmcm2) phases presents large contributions from two modes, namely, the above-mentioned strong instability consisting of $O_6$ rotations, and an isosymmetric weakly-unstable mode that involves deformations of the oxygen octahedra. Further, we found that the large energy change associated to the Cmcm-to-Cmcm21 transition depends crucially on the simultaneous occurrence of both modes. We were able to describe such effects in terms of a very strong and cooperative anharmonic coupling, and briefly discussed the possibility of constructing a phenomenological theory of such a two-mode transition. Interestingly, LTO’s behavior is in strong contrast with what (to the best of our knowledge) is most common among perovskite oxides, where structural instabilities tend to compete and suppress each other.

We calculated the polarization and response properties of LTO’s FE phase, obtaining results that are consistent with related experimental information. Interestingly, the computed electric properties revealed clear similarities between LTO and prototype ferroelectric BTO. For example, we obtained anomalously large Born effective charges for some Ti and O atoms in LTO, a feature that is known to be the fingerprint of the FE instabilities in compounds like BTO and PZT. Further, our results showed that LTO presents nearly-unstable modes that are strongly polar and involve atomic distortions that essentially match BTO’s FE instabilities. Such traces of BTO-like behavior in LTO suggest the intriguing possibility that conventional ferroelectricity might be induced in this compound upon suitable modifications (e.g., strain engineering or chemical substitutions), or that such a behavior might occur spontaneously in similar materials.

Finally, let us emphasize the implications that our findings have for the design of new magnetoelectric multiferroics. In the context of magnetoelectric perovskite oxides, it would be ideal to have proper ferroelectricity driven by $O_6$-rotational modes, so that an electric field can be used to tune the structural distortions (e.g., metal–oxygen–metal angles) that control the main magnetic interactions (i.e., super-exchange and Dzyaloshinskii-Moriya). That is exactly the kind of ferroelectricity that we have found in LTO. Here we have briefly discussed how to obtain such an effect in a magnetic perovskite, proposing La$_2$Mn$_2$O$_7$ as the most promising candidate material.

In conclusion, our theoretical study of La$_2$Ti$_2$O$_7$ has revealed a wealth of interesting effects, some of which may have important implications for current work on multifunctional oxides. We thus hope this study will stimulate further investigation of these layered perovskites and the novel functionalities that they may offer.

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36 In the usual perovskite oxides, the coupling between the FE modes and strain tends to be stronger than the AFD-strain coupling. For example, Fig. 1 of Ref. 3 illustrates these effects as computed for CaMnO$_3$: the FE-strain coupling is very significant, while the AFD-strain interaction is almost negligible. These couplings have been quantified in detail for SrTiO$_3$: King-Smith and Vanderbilt$^{24}$ computed FE-strain couplings of about 0.0036 Hartree/bohr$^3$, while Sai and Vanderbilt$^{25}$ obtained AFD-strain couplings of about 0.0002 Hartree/bohr$^3$.

37 The fourth-order expression in Eq. (2) may not be good description of the energy for arbitrary values of $u_1$ and $u_2$; e.g., distortions with $u_1 = u_2$ are unbounded from below for the fitted parameter values. An acceptable description of the full $E(u_1, u_2)$ energy landscape would probably require including higher order terms.

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