Energetics of oxygen-octahedra rotations in perovskite oxides from first principles

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We use first-principles methods to investigate the energetics of oxygen-octahedra rotations in $\text{ABO}_3$ perovskite oxides. We focus on the short-period, perfectly antiphase or in-phase, tilt patterns that characterize the structure of most compounds and control their physical (e.g., conductive, magnetic) properties. Based on an analytical form of the relevant potential energy surface, we discuss the conditions for the stability of various polymorphs presenting different rotation patterns, and obtain numerical results for a collection of thirty-five representative materials. Our results reveal the mechanisms responsible for the frequent occurrence of a particular structure that combines antiphase and in-phase rotations, i.e., the orthorhombic $Pbnm$ phase displayed by about half of all perovskite oxides, as well as by many non-oxidic perovskites. In essence, the $Pbnm$ phase benefits from the simultaneous occurrence of antiphase and in-phase tilt patterns that compete with each other, but not as strongly as to be mutually exclusive. We also find that secondary antipolar modes, involving the $A$ cations, contribute to weaken the competition between tilts of different types, and thus play a key role in the stabilization of the $Pbnm$ structure. Our results thus confirm and better explain previous observations for particular compounds in the literature. Interestingly, we also find that strain effects, which are known to be a major factor governing phase competition in related (e.g., ferroelectric) perovskite oxides, play no essential role as regards the relative stability of different rotational polymorphs. Further, we discuss why the $Pbnm$ structure stops being the ground state in two opposite limits—namely, for large and small $A$ cations—, showing that very different effects become relevant in each case. Our work thus provides a comprehensive discussion and reference data on these all-important and abundant materials, which will be useful to better understand existing compounds as well as to identify new strategies for materials engineering.

I. INTRODUCTION

Most $\text{ABO}_3$ perovskite oxides present structures that are distorted versions of the ideal cubic phase. In the vast majority of compounds, this distortion is characterized by concerted, short-period rotations of the $\text{O}_6$ oxygen octahedra that constitute the basic building block of the perovskite lattice.\textsuperscript{1,2} The most common rotation patterns can be described as being exactly antiphase [usually denoted with a “$-$” sign, see Fig. 1(a)] or in-phase [“$+$”, see Fig. 1(b)], and often appear together. Indeed, about half of the perovskide oxides present the so-called GdFeO$_3$-type structure\textsuperscript{3} an orthorhombic polymorph with $Pbnm$ space group characterized by antiphase rotations about the [110] pseudo-cubic axis and in-phase rotations about [001]. This structure is usually termed “$a^-a^-c^+$” in the notation introduced by Glazer\textsuperscript{4} which is self-explanatory. Other structures present only antiphase tilts, and typically adopt tetragonal ($a^-b^0b^0$, $I4/mcm$ space group) and rhombohedral ($a^-a^-a^-$, $R3c$ space group) symmetries.\textsuperscript{5} All these purely-rotational phases are sometimes called antiferrodistortive (AFD), and all are ferroelastic.\textsuperscript{5,6} The $O_6$ rotations sometimes coexist with other primary distortions, as e.g. cation off-centerings that give rise to ferroelectricity.\textsuperscript{6,7} Notably, this is the case of materials like room-temperature multiferroic BiFeO$_3$.\textsuperscript{7} Such a coexistence is rare, though, as the ferroelectric (FE) and AFD instabilities are known to compete against each other in the most typical situations.\textsuperscript{8–11} Hence, most FE perovskites (e.g., BaTiO$_3$, PbTiO$_3$, KNbO$_3$) do not present any $O_6$ tilts at all.

The tendency of perovskites to display $O_6$ rotations is usually explained in terms of the so-called tolerance factor\textsuperscript{12}

$$
t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)},$$

where $R_A$, $R_B$, and $R_O$ are the nominal ionic radii of the $A$, $B$, and $O$ species, respectively. (Which we typically take from Ref.\textsuperscript{13}) This quantity is defined so that $t = 1$ corresponds to the ideal case in which rigid spheres with
the tilting distortion is known to be the key structural factor controlling the electronic properties of all these compounds, as it determines the overlap between the orbitals of the anion and B-site cation (often a transition metal in perovskite oxides). Hence, today there is a great interest in understanding the details of such distortions, and in exploring new possibilities to tune them, as illustrated by many recent works on epitaxial oxide thin films.

Additionally, it has been recently demonstrated that tilted structures provide an unconventional, and in some respects advantageous, strategy to obtain polar, potentially ferroelectric, materials. This so-called *hybrid improper ferroelectricity* \[23,24\] has been predicted in short-period superlattices based on \(Pbnm\) compounds, \[27,29\] and could be a convenient route to obtain elusive effects such as room-temperature magnetoelectricity. \[30,32\] Experimental demonstrations of this exotic form of ferroelectricity are starting to appear, \[33,34\] and highlight once again the importance of understanding \(O_6\) rotational patterns in perovskites, even in contexts where their relevance was difficult to anticipate *a priori*.

Given the obvious interest of these tilting distortions, it is surprising to note that they remain relatively poorly studied, especially when compared with the FE instabilities of compounds like BaTiO\(_3\) or PbTiO\(_3\). For example, while there is an exhaustive crystallographic literature on \(O_6\)-rotational patterns \[1,35–38\] there are very few phenomenological works discussing the energetics and phase transitions of materials with tilted phases. Historically, this is probably related to the fact that these structures (especially those with the \(Pbnm\) space group) tend to be very stable in wide ranges of temperature and pressure, including ambient conditions, which renders them a relatively uninteresting subject of study *a priori*. First-principles theory is somewhat underdeveloped as well. Admittedly, there are a number of recent works on how to control \(O_6\) rotations by epitaxial strain in thin films of specific compounds, \[27\] and tilts are the focus of other investigations in various contexts. Yet, in our view we are still missing a thorough first-principles study of these instabilities, and of why some rotational polymorphs prevail over others. For the sake of comparison, in the case of ferroelectric perovskites, the basic first-principles works at the origin of our current understanding, which enabled much of the later progress in FE thin films and strain engineering, were laid out in the early 90’s.\[39,41\] In our view, especially relevant were seminal contributions as that of King-Smith and Vanderbilt in Ref. \[40\]: these authors ran a comparative study of a group of representative compounds, and quantified trends in the framework of a simple energy model, which allowed them to rationalize the factors controlling why apparently similar materials present different ferroelectric phases. Our purpose in this work is to provide the same kind of description and insights in what regards octahedral tilts in perovskite oxides.

The paper is organized as follows. In Section \[11\] we
introduce the formalism that allows us to model the potential energy surface (PES) of a perovskite, around the reference cubic structure, as a function of antiphase and in-phase \( O_6 \) rotations and cell strains. We discuss the relevant critical points of the PES and their stability. In Section \( \text{III} \) we describe our first-principles computational approach, and justify the choice of the materials considered in this investigation. In Section \( \text{IV} \) we present and discuss our computational results. Finally, in Section \( \text{V} \) we summarize our conclusions.

II. FORMALISM

In this Section we introduce a general model to describe the PES of any perovskite, around the ideal cubic phase, as a function of short-period rotations of the oxygen octahedra and macroscopic strains. This approach is a direct application to rotational distortions of the methodology described in Ref. [40] and our derivations are essentially identical to those described in Ref. [42] within an investigation of CaTiO\( _3 \).

The formalism below applies to the idealized case of an infinite, periodic crystal that is free of defects. Further, some important physical effects are not treated in our theory. For example, we ignore the possibility of having spin-ordering transitions – as occurring, e.g., in the considered orthoferrites and orthochromites\( ^{18,43} \) – and the way those could affect the energetics of the tilting distortions; in fact, we implicitly assume that the materials always remain in their magnetic ground state. Thus, while these simplifications are acceptable for the present study, one should bear in mind that, in order to address more complex phenomena, the present models would need to be extended. (See Refs. [12] and [20] for examples of models including magnetostructural couplings.)

A. Relevant potential energy surface

We express the energy as a Taylor series, in terms of the relevant structural distortions, around a reference cubic structure. More precisely, we write:

\[
E = E_0 + E_s(\{\eta_\alpha\}) + E_r(\{r_\alpha\}) + E_m(\{m_\beta\}) + E_{\text{int}}(\{r_\alpha\}; \{m_\beta\}) + E_{\text{sp}}(\{\eta_\alpha\}, \{r_\alpha\}, \{m_\beta\}),
\]

where \( E_0 \) is the energy of the ideal perovskite cubic phase with a 5-atom periodically-repeated cell, as obtained from a symmetry-constrained first-principles structural relaxation; \( E_s \) is the elastic energy as a function of the homogeneous strains \( \eta_\alpha \), with \( a = 1, ..., 6 \) in Voigt notation\( ^{22} \); \( E_r \) is the energy associated to antiphase rotations of the oxygen octahedra about the \( \alpha = x, y, z \) pseudo-cubic axes, as quantified by \( r_\alpha \); \( E_m \) is the analogous function for the in-phase \( O_6 \) rotations, as given by \( m_\beta \) with \( \beta = x, y, z \); \( E_{\text{int}} \) gathers the anharmonic interactions between antiphase and in-phase tilts; finally, \( E_{\text{sp}} \) – where “sp” stands for strain-phonon – accounts for the coupling between AFD modes and strains. Let us note that the rotation amplitudes \( r_\alpha \) and \( m_\beta \) are associated to distortion patterns as those indicated in Figs. \( \text{IIa} \) and \( \text{IIIb} \), respectively. Note also that our choice of notation for the antiphase \( (r_\alpha) \) and in-phase \( (m_\beta) \) rotations reflects the fact that these distortions are respectively associated with the \( R \) \( \{\mathbf{q}_R = \pi/a(1,1,1)\} \) and \( M \) \( \{\mathbf{q}_M = \pi/a(1,1,0)\} \) for in-phase rotations about the \( z \) axis \( q \)-points of the Brillouin zone corresponding to the ideal 5-atom perovskite cell. Note that \( \mathbf{q}_R \) and \( \mathbf{q}_M \) are zone-boundary wave vectors, and \( a \) is the lattice constant of the 5-atom elemental cell as obtained from a symmetry-constrained relaxation of the cubic reference structure.

This energy must be invariant with respect to the symmetry operations of the cubic phase, which greatly simplifies its form. In the following we write the various terms, truncating the Taylor series at the lowest order that makes it possible to discuss the structural instabilities and their most relevant couplings. Thus, for example, for the elastic energy we have

\[
E_s = \frac{1}{2} C_{11}(\eta_x^2 + \eta_y^2 + \eta_z^2) + C_{12}(\eta_x \eta_y + \eta_y \eta_z + \eta_z \eta_x) + \frac{1}{2} C_{44}(\eta_x^2 + \eta_y^2 + \eta_z^2),
\]

where \( C_{ab} \) parameters are the usual elastic constants. Note that, because of the cubic symmetry, we have \( C_{11} = C_{22} = C_{33} \), etc., which allows us to write \( E_s \) in a very compact way.

Similarly, it is possible to show that the energy changes associated to antiphase rotations are given by

\[
E_r = \kappa_r r^2 + \alpha_r r^4 + \gamma_r (r_x^2 r_y^2 + r_y^2 r_z^2 + r_z^2 r_x^2),
\]

where \( r = |\mathbf{r}| \) and \( \mathbf{r} = (r_x, r_y, r_z) \). Note that the existence of antiphase rotational instabilities of the cubic structure translates into a negative value of \( \kappa_r \), which requires us to consider fourth-order terms so that \( E_r \) can be bounded from below and the low-symmetry minima well defined. Note also that the term associated to \( \alpha_r \) only depends on the modulus \( r \), and is therefore isotropic; in contrast, \( \gamma_r \) captures the anisotropy energy, and its sign will determine the preferred alignment of the antiphase rotation axis.

Interestingly, the expression for \( E_r \) is formally identical to the one corresponding to the energy change as a function of a three dimensional polarization vector\( ^{22} \). Further, it can be shown that also \( E_m \) has the same functional form; we have

\[
E_m = \kappa_m m^2 + \alpha_m m^4 + \gamma_m (m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2),
\]

where \( m = |\mathbf{m}| \) and \( \mathbf{m} = (m_x, m_y, m_z) \).

As regards the interactions between \( \mathbf{r} \) and \( \mathbf{m} \), we will restrict ourselves to the lowest-order couplings, which are
given by
\[ E_{\text{int}} = \alpha_{\text{int}} r^2 m^2 + \beta_{\text{int}} (r_x^2 m_x^2 + r_y^2 m_y^2 + r_z^2 m_z^2) . \] (6)

Note that this lowest-order interaction term is anharmonic; the antiphase and in-phase rotations are decoupled at the harmonic level, which is a direct consequence of their being associated to different \( q \)-points.

Finally, we consider only the lowest-order terms of the interaction between AFD patterns and strain, which are
\[ E_{\text{sp}} = B_{r1xx}(\eta_1 r_x^2 + \eta_2 r_y^2 + \eta_3 r_z^2) + B_{r1yy}(\eta_1 r_y^2 + \eta_2 r_x^2 + \eta_3 r_z^2) + B_{r1zz}(\eta_1 r_z^2 + \eta_2 r_y^2 + \eta_3 r_x^2) \]
\[ + B_{r1xy}(\eta_3 r_x r_y + \eta_3 r_y r_x + \eta_3 r_x r_y) \]
\[ + B_{r2xx}(\eta_1 m_x^2 + \eta_2 m_y^2 + \eta_3 m_z^2) + B_{r2yy}(\eta_1 m_y^2 + \eta_2 m_x^2 + \eta_3 m_z^2) \]
\[ + B_{r2zz}(\eta_1 m_z^2 + \eta_2 m_y^2 + \eta_3 m_x^2) + \eta_3 (m_x^2 + m_y^2) \] .
(7)

Note that the form of the strain-phonon couplings is slightly different for antiphase and in-phase tilts, as the former present a low-order coupling with the shear strains while the latter do not. Indeed, coupling terms of the type \( \eta_4 m_y m_z \) are not invariant under the translations of the cubic lattice, which can be immediately seen by noting that the \( m_y \) and \( m_z \) tilts are associated, respectively to the \( \pi/a(1,1,0) \) and \( \pi/a(1,1,0) \) \( q \)-points, while the shear strain is a zone-center distortion. (Some authors include in the expression for the energy the coupling that we would denote \( B_{r4yz} \) in our notation yet, such a coupling is identically null by symmetry.)

Our expression for the PES of perovskite compounds with \( O_h \)-rotational instabilities is thus complete. Note that, thanks to the cubic symmetry of the reference structure, the list of independent couplings controlling the behavior of these materials is relatively short. We have three in \( E_s \), three in \( E_r \), three in \( E_m \), two in \( E_{\text{int}} \), and five in \( E_{\text{sp}} \).

### B. Strain-renormalized energy function

The cubic phase of simple \( ABO_3 \) perovskites tends to be stable against homogeneous strain deformations, so that \( E_s \) is always positive. (More precisely, this implies that \( C_{11} - C_{12} > 0 \), \( C_{11} + 2C_{12} > 0 \), and \( C_{44} > 0 \).) Hence, typically we can treat strains as secondary distortions that simply follow the primary order parameters \( \mathbf{r} \) and \( \mathbf{m} \). Mathematically, such equilibrium strains \( \{ \eta_{\text{eq}} \} \) can be obtained by imposing the conditions
\[ \frac{\partial E}{\partial \eta_a} \bigg|_{\text{eq}} = 0 , \] (8)
for \( a = 1, \ldots, 6 \). These translate into the set of linear equations
\[ \sum_{b} C_{ab} \eta_b^{\text{eq}} = - \sum_{\alpha \beta} B_{r\alpha \beta} r_{\alpha r_{\beta}} - \sum_{\alpha \beta} B_{m\alpha \beta} m_{\alpha m_{\beta}} , \] (9)
which can be trivially resolved by inverting the \( C_{ab} \) matrix:
\[ \eta_{\text{eq}}^a = - \sum_{b} (C^{-1})_{ab} (B_{rb} + B_{mb}) , \] (10)
where
\[ B_{rb} = \sum_{\alpha \beta} B_{r\alpha \beta} r_{\alpha} r_{\beta} \] (11)
and
\[ B_{mb} = \sum_{\alpha \beta} B_{m\alpha \beta} m_{\alpha} m_{\beta} . \] (12)

Without going into details, let us emphasize that the equilibrium strains \( \{ \eta_{\text{eq}}^a \} \) depend quadratically on the tilt amplitudes. Hence, if substitute Eq. (10) in Eq. (2), we obtain a simplified expression for a strain-renormalized energy,
\[ \tilde{E}(\mathbf{r}, \mathbf{m}) = E_0 + \tilde{E}_r(\mathbf{r}) + \tilde{E}_m(\mathbf{m}) + \tilde{E}_{\text{int}}(\mathbf{r}, \mathbf{m}) , \] (13)
where the barred energy terms are formally identical to the unbarred ones described above, but contain modified anharmonic couplings. More precisely, the strain terms in \( E_s \) will lead to renormalized \( \tilde{E}_r \) and \( \tilde{E}_m \) interactions (coming from the part of \( \eta_{\text{eq}}^a \) that is proportional to \( B_{r\alpha \beta} \)), renormalized \( \tilde{E}_s \) and \( \tilde{E}_m \) interactions (coming from the part of \( \eta_{\text{eq}}^a \) that is proportional to \( B_{m\alpha \beta} \)) and renormalized \( \tilde{E}_{\text{int}} \) and \( \tilde{E}_{\text{sp}} \) couplings (coming from the crossed products between the \( O(r^2) \) and \( O(m^2) \) contributions to \( \eta_{\text{eq}}^a \)). As for the \( E_{sp} \) term, it is linear in the strain and quadratic in the rotation amplitudes; hence, by imposing \( \eta_a = \eta_{\text{eq}}^a \), we again obtain additional contributions to the fourth-order couplings in \( E_r \), \( E_m \), and \( E_{\text{int}} \). As a result, the energies \( \tilde{E}_r \), \( \tilde{E}_m \), and \( \tilde{E}_{\text{int}} \) in Eq. (13) have exactly the same functional form as their respective counterparts in Eq. (2), but with renormalized fourth-order couplings.

Note that it is possible to solve this problem analytically, as done in the Appendix A of Ref. 44 for an analogous case. Let us also mention that the previous derivation is essentially identical to the stress-free boundary conditions discussed in the Appendix of Ref. 42, where explicit expressions for the renormalized coefficients are given.

### C. Main singular points of the energy surface

Let us now discuss the most important structures that may constitute minima or saddle points of the renormalized energy in Eq. (13). We leave strains out of the following discussion for simplicity, noting that it is always possible to obtain them from the rotation amplitudes by using Eq. (10).
1. Structures with antiphase rotations

First, let us consider phases characterized by antiphase rotations alone. As done in Ref. [4] for the formally similar case of the electric polarization, let us distinguish three different types of solutions:

\( a^{-b^0b^0} \) structures. We can have phases with \( \mathbf{r} = \mathbf{r}(1,0,0) \), denoted \( a^{-b^0b^0} \) in Glazer’s notation. Note that, equivalently, \( \mathbf{r} \) could be (anti)parallel to the [010] or [001] pseudo-cubic directions; hence, we have six symmetry-equivalent states of this kind. Such structures have tetragonal symmetry with space group \( I4/mcm \), the low-temperature phase of \( \text{SrTiO}_3 \) being a representative example. By substitution in Eq. (13), we find that the energy of such a state is given by

\[
\hat{E} = E_0 + \kappa_r r^2 + \bar{\alpha}_r r^4,
\]

which can be minimized to render a singular point characterized by

\[
r_{\text{tet}} = \left( -\frac{\kappa_r}{2\bar{\alpha}_r} \right)^{1/2}
\]

and

\[
E_{\text{r}}^{\text{tet}} = E_0 - \frac{\kappa_r^2}{4\bar{\alpha}_r}.
\]

Note that here we are assuming \( \kappa_r < 0 \), so that the antiphase \( O_6 \) rotations constitute a structural instability of the cubic perovskite phase. We also assume \( \bar{\alpha}_r > 0 \), so that there exists an optimum rotation amplitude that minimizes the energy. Finally, note that we do not mark \( E_{\text{r}}^{\text{tet}} \) with a bar, as this is the actual energy of the strain-relaxed \( a^{-b^0b^0} \) state, i.e., it is exactly the same result we would obtain by working with Eq. (2).

The stability of this solution can be readily analyzed by computing the Hessian matrix for \( \hat{E} \) at \( \mathbf{r} = r_{\text{tet}} \) and \( \mathbf{m} = \mathbf{0} \). Let us consider states given by \( \mathbf{r} = r_{\text{tet}}(1,0,0) + \delta \mathbf{r} \) and \( \mathbf{m} = \delta \mathbf{m} \). The 6-dimensional Hessian associated to the \( \delta \mathbf{r} \) and \( \delta \mathbf{m} \) perturbations has the diagonal form

\[
H_{\text{r}}^{\text{tet}} = \begin{bmatrix}
\kappa_{r_{\|}}^{\text{tet}} & 0 & 0 & 0 & 0 & 0 \\
0 & \kappa_{r_{\perp}}^{\text{tet}} & 0 & 0 & 0 & 0 \\
0 & 0 & \kappa_{r_{\perp}}^{\text{tet}} & 0 & 0 & 0 \\
0 & 0 & 0 & \kappa_{\text{m}_{\perp}}^{\text{tet}} & 0 & 0 \\
0 & 0 & 0 & 0 & \kappa_{\text{m}_{\perp}}^{\text{tet}} & 0 \\
0 & 0 & 0 & 0 & 0 & \kappa_{\text{m}_{\perp}}^{\text{tet}}
\end{bmatrix},
\]

where

\[
\kappa_{r_{\|}}^{\text{tet}} = -4\kappa_r,
\]

\[
\kappa_{r_{\perp}}^{\text{tet}} = -\frac{\bar{\gamma}_r}{\bar{\alpha}_r},
\]

\[
kappa_{\text{m}_{\perp}}^{\text{tet}} = -2\left( \kappa_m - \frac{\bar{\alpha}_\text{int} + \bar{\beta}_\text{int}}{2\bar{\alpha}_r} \right),
\]

\[
kappa_{\text{m}_{\perp}}^{\text{tet}} = -2\left( \kappa_m - \frac{\bar{\alpha}_\text{int}}{2\bar{\alpha}_r} \right).
\]

From these results, a few interesting conclusions immediately follow. As regards the antiphase rotations, we naturally have that \( \mathbf{r} = r_{\text{tet}} \) state is stable against parallel perturbations, since \( \kappa_{r_{\|}}^{\text{tet}} > 0 \). In contrast, the stability with respect to transversal perturbations depends on the sign of \( \bar{\gamma}_r \): a positive value indicates that the tetragonal phase is stable against such distortions (\( \kappa_{r_{\perp}}^{\text{tet}} > 0 \)), but a negative \( \bar{\gamma}_r \) implies we have a saddle point (\( \kappa_{r_{\perp}}^{\text{tet}} < 0 \)).

As regards the in-phase rotations, the \( \mathbf{r} = r_{\text{tet}} \) solution will be stable against them whenever we have a large enough \( \kappa_m > 0 \). A more interesting (and more typical) situation occurs if \( \kappa_m < 0 \), i.e., whenever the in-phase tilts are instabilities of the cubic phase. In such a case, the sign of \( \kappa_{\text{m}_{\perp}}^{\text{tet}} \) will be positive provided that

\[
|\kappa_m| < \left| \frac{\bar{\alpha}_\text{int}}{2\bar{\alpha}_r} \right|. \tag{19}
\]

This would be a situation in which the competition between antiphase and in-phase rotations, as quantified by the coupling \( \bar{\alpha}_\text{int} > 0 \), is large enough so that the presence of the former prevents the occurrence of the latter. Note that \( \bar{\alpha}_\text{int} \) only accounts for an isotropic competition between different tilt types, while \( \bar{\beta}_\text{int} \) – which appears in \( \kappa_{\text{m}_{\perp}}^{\text{tet}} \) but not in \( \kappa_{\text{m}_{\perp}}^{\text{tet}} \) – also includes a directional contribution.

Finally, note that for \( \bar{\alpha}_\text{int} < 0 \) or \( \bar{\alpha}_\text{int} + \bar{\beta}_\text{int} < 0 \) we would have a cooperation between different rotational patterns. In such a case the \( a^{-b^0b^0} \) state would not be an energy minimum, unless the in-phase tilt is robustly stable (i.e., \( \kappa_m > 0 \) and large enough).

\( a^{-a^{-a}} \) structures. Another important case corresponds to rhombohedral structures like those of \( \text{LaAlO}_3 \) and \( \text{LaNiO}_3 \), with space group \( R3c \), displaying antiphase rotations of equal amplitude about the three pseudo-cubic axes. Equivalently, we can think of a single rotation about [111]. (Note that there are eight symmetry-equivalent states of this type.) The corresponding singular point is given by \( \mathbf{r} = r_{\text{r}^\text{ho}} = r_{\text{r}^\text{ho}}(1,1,1) \) and \( \mathbf{m} = \mathbf{0} \) with

\[
E_{\text{r}}^{\text{r}^\text{ho}} = \left( \frac{\kappa_r}{6\bar{\alpha}_r + 2\bar{\gamma}_r} \right)^{1/2}, \tag{20}
\]

and

\[
E_{\mathbf{r}}^{\text{r}^\text{ho}} = E_0 - \frac{\kappa_r^2}{4\left(\bar{\alpha}_r + \frac{2}{3}\bar{\gamma}_r\right)}. \tag{21}
\]

Here we assume that \( \kappa_r < 0 \) and \( \bar{\alpha}_r + 2\bar{\gamma}_r > 0 \) (with \( \bar{\alpha}_r > 0 \), as mentioned above), so that \( r_{\text{r}^\text{ho}} \) is well defined. As above, we can study the stability of this solution by computing the corresponding Hessian matrix. We thus consider states given by \( \mathbf{r} = r_{\text{r}^\text{ho}}(1,1,1) + \delta \mathbf{r} \) and \( \mathbf{m} = \delta \mathbf{m} \), and work with symmetry-adapted distortions so that

\[
\delta \mathbf{r} = \frac{\delta r_{\|}}{\sqrt{3}}(1,1,1) + \frac{\delta r_{\perp}}{\sqrt{2}}(1,\bar{1},0) + \frac{\delta r_{\perp}}{\sqrt{6}}(1,1,\bar{2}),
\]

\[
\delta \mathbf{m} = \frac{\delta m_{\|}}{\sqrt{3}}(1,1,1) + \frac{\delta m_{\perp}}{\sqrt{2}}(1,\bar{1},0) + \frac{\delta m_{\perp}}{\sqrt{6}}(1,1,\bar{2}).
\]
It can be proved that the Hessian matrix is diagonal in this basis; we have

\[
H^{\text{rho}} = \begin{bmatrix}
\kappa_{r,\parallel} & 0 & 0 & 0 & 0 \\
0 & \kappa_{r,\perp} & 0 & 0 & 0 \\
0 & 0 & \kappa_{r,\perp} & 0 & 0 \\
0 & 0 & 0 & \kappa_{m} & 0 \\
0 & 0 & 0 & 0 & \kappa_{m}^{\text{tet}}
\end{bmatrix},
\tag{23}
\]

where

\[
\begin{align*}
\kappa_{r,\parallel} &= -4\kappa_r, \\
\kappa_{r,\perp} &= 2\kappa_r \frac{\gamma_r}{3\alpha_r + \gamma_r}, \\
\kappa_{m}^{\text{tet}} &= 2 \left( \kappa_m - \kappa_r \frac{3\alpha_{\text{int}} + \beta_{\text{int}}}{6\alpha_r + 2\gamma_{\text{int}}} \right).
\end{align*}
\tag{24}
\]

This result bears obvious similarities with what we obtained above for the \(a^-b^0b^0\) state. One interesting observation is that \(\kappa_{r,\parallel}\) and \(\kappa_{r,\perp}\) must necessarily have opposite signs. This implies that, in our fourth-order PES, the \(a^-b^0b^0\) and \(a^-a^-a^-\) states cannot be energy minima simultaneously, and their relative stability is controlled by the sign of the \(\gamma_r\) parameter. Note that this observation is consistent with the discussion in Ref. [47] on the conditions for having multiple stable states in potential energy surfaces of the same type as \(E_r\).

\(a^-a^-c^0\) structures. – Finally, the last structure of this series is the orthorhombic phase with space group \(I\text{mcn}\) and antiphase rotations of equal amplitude about two pseudo-cubic axes. (This amounts to a rotation about a \((110)\) direction. Note that there are twelve symmetry-equivalent structures of this type.) The corresponding stationary point is defined by \(\mathbf{r} = \mathbf{r}_\text{ort} = \mathbf{r}_\text{ort}(1,1,0)\) and \(\mathbf{m} = 0\) with

\[
\mathbf{r}_\text{ort} = \left( \frac{\kappa_r}{4\alpha_r + \gamma_r} \right)^{1/2},
\tag{25}
\]

and

\[
E_r^\text{ort} = E_0 - \frac{\kappa_r^2}{4\alpha_r + \gamma_r},
\tag{26}
\]

where, as above, we assume that \(\kappa_r < 0\) and \(4\alpha_r + \gamma_r > 0\) with \(\alpha_r > 0\), so that \(r^\text{ort}\) is a real number. To study the stability of the solution, we consider states given by \(\mathbf{r} = \mathbf{r}_\text{ort}(1,1,0) + \delta\mathbf{r}\) and \(\mathbf{m} = \delta\mathbf{m}\), and work with symmetry-adapted distortions defined as

\[
\begin{align*}
\delta\mathbf{r} &= \frac{\delta r}{\sqrt{2}}(1,1,0) + \frac{\delta r_{\perp \perp}}{\sqrt{2}}(1,1,0) + \delta r_{\perp \perp}(0,0,1) \\
\delta\mathbf{m} &= \frac{\delta m}{\sqrt{2}}(1,1,0) + \frac{\delta m_{\perp \perp}}{\sqrt{2}}(1,1,0) + \delta m_{\perp \perp}(0,0,1)
\end{align*}
\tag{27}
\]

In this basis, the Hessian is diagonal and has the form

\[
H^\text{ort} = \begin{bmatrix}
\kappa_{r,\parallel}^\text{ort} & 0 & 0 & 0 & 0 \\
0 & \kappa_{r,\perp}^\text{ort} & 0 & 0 & 0 \\
0 & 0 & \kappa_{r,\perp}^\text{ort} & 0 & 0 \\
0 & 0 & 0 & \kappa_m^\text{ort} & 0 \\
0 & 0 & 0 & 0 & \kappa_m^\text{ort}
\end{bmatrix},
\tag{28}
\]

where

\[
\begin{align*}
\kappa_{r,\parallel}^\text{ort} &= -4\kappa_r, \\
\kappa_{r,\perp}^\text{ort} &= 6\kappa_r \frac{\gamma_r}{4\alpha_r + \gamma_r}, \\
\kappa_m^\text{ort} &= 2 \left( \kappa_m - \kappa_r \frac{2\alpha_{\text{int}} + \beta_{\text{int}}}{4\alpha_r + \gamma_r} \right),
\end{align*}
\tag{29}
\]

As compared to the two cases above, the main peculiarity of this result lies on the fact that \(\kappa_{r,\perp}^\text{ort}\) and \(\kappa_m^\text{ort}\) must necessarily have opposite signs, which implies that the orthorhombic \(a^-a^-c^0\) solution cannot be a minimum of the energy in our fourth-order PES.

\section{Structures with in-phase rotations}

As regards the states in which only in-phase rotations are condensed – denoted by \(a^+b^0b^0\), \(a^+a^+b^0\), and \(a^+a^-a^-\), respectively –, the situation is exactly analogous to that of the purely antiphase structures. Indeed, since \(E_\mathbf{r}(\mathbf{r})\) and \(E_\mathbf{m}(\mathbf{m})\) have the same functional form, our previous discussion can be directly applied to the phases with pure in-phase tilts by simply making the substitution \(r \rightarrow m\).

\subsection{The \(a^-a^-c^+\) structure}

Finally, let us discuss the case of the orthorhombic \(P\text{bnm}\) phase that combines antiphase tilts about \([110]\) with in-phase tilts about \([001]\). (There are twenty-four symmetry-equivalent structures of this type.) In this case the distortion has the form \(r = r(1,1,0)\) and \(\mathbf{m} = m(0,0,1)\), and the energy is

\[
E = E_0 + 2\kappa_r r^2 + (4\alpha_r + \gamma_r) r^4
+ \kappa_m m^2 + \alpha_m m^4 + 2\alpha_{\text{int}} r^2 m^2.
\tag{30}
\]

For simplicity, in the following we use \(\alpha^* = 4\alpha + \gamma\). Minimizing this energy renders a structure given by

\[
(r^C)^2 = \frac{-\kappa_r}{\alpha_r^* - \alpha_{\text{int}} / \alpha_m} + \frac{\alpha_{\text{int}} \kappa_m}{2(\alpha_r^* \alpha_m - \alpha_{\text{int}}^2)},
\tag{31}
\]
and
\[(m^O)^2 = \frac{-\kappa_m}{2(\alpha_m - \alpha^2_m/\alpha^*_m)} + \frac{\alpha_{\text{int}}\kappa_r}{\alpha^*_m\alpha_m - \alpha^2_{\text{int}}},\] (32)
where we use the notation \( O \) to distinguish this orthorhombic \((a^{-a} c^+)^\perp\) phase from the simpler “ort” tilt patterns \((a^{-a} c^0)^\perp\) discussed above. The energy for this state is
\[E^O = E_0 - \frac{\kappa^2_r}{\alpha^2_r - \alpha^2_{\text{int}}/\alpha_m} - \frac{\kappa^2_m}{4(\alpha_m - \alpha^2_m/\alpha^*_m)} + \frac{\kappa_{r\text{int}}\alpha_{\text{int}}}{\alpha^*_m\alpha_m - \alpha^2_{\text{int}}} \] (33)
From the previous expressions, it is obvious that in absence of interaction between antiphase and in-phase rotations – i.e., for \( \alpha_{\text{int}} = 0 \) – the \( O \) phase reduces to a trivial combination of the orthorhombic \( r = r^{\text{ort}} \) and tetragonal \( m = m^{\text{tet}} \) states described above. It is also possible to prove that, for the \( O \) solution to exist, at least one of the rotational modes must be an instability of the cubic phase, i.e., either \( \kappa_r \) or \( \kappa_m \), or both of them, must be negative. Indeed, if we have \( \kappa_r, \kappa_m > 0 \) – and given that \( \alpha_r, \alpha_m > 0 \) as required for the energy to be bounded from below –, there is no choice of \( \alpha_{\text{int}} \) that can yield a well-defined \( O \) state.

To study the stability of this solution, we consider the structures given by \( r = r^O + \delta r \) and \( m = m^O + \delta m \), and work with symmetry-adapted distortions defined by
\[\delta r = \frac{\delta r\perp}{\sqrt{2}}(1,1,0) + \frac{\delta r\parallel}{\sqrt{2}}(0,0,1)\]
\[\delta m = \frac{\delta m\perp}{\sqrt{2}}(1,1,0) + \frac{\delta m\parallel}{\sqrt{2}}(0,0,1) \] (34)
In this basis, the Hessian has the form
\[H^O = \begin{bmatrix}
\kappa^O_{r\perp} & 0 & 0 & 0 & \kappa^O_{r\parallel} & 0 \\
0 & \kappa^O_{m\parallel} & 0 & 0 & 0 & 0 \\
0 & 0 & \kappa^O_{m\perp} & 0 & 0 & 0 \\
0 & 0 & 0 & \kappa^O_{m\perp} & 0 & 0 \\
0 & 0 & 0 & 0 & \kappa^O_{r\parallel} & 0 \\
0 & 0 & 0 & 0 & 0 & \kappa^O_{r\perp}
\end{bmatrix},\] (35)
where
\[\kappa^O_{r\perp} = 2\kappa_r + 6(r^O)^2\alpha^*_r + 2(m^O)^2\alpha_{\text{int}},\]
\[\kappa^O_{r\parallel} = 2\kappa_r + 4(r^O)^2(2\alpha_r + \gamma_r) + 2(m^O)^2\alpha_{\text{int}},\]
\[\kappa^O_{m\perp} = 2\kappa_r + 4(r^O)^2(2\alpha_r - \gamma_r) + 2(m^O)^2\alpha_{\text{int}},\]
\[\kappa^O_{m\parallel} = 2\kappa_m + 2(m^O)^2(2\alpha_m + \gamma_m) + 2(\alpha^2_m/\alpha^*_m)\alpha_{\text{int}},\]
\[\kappa^O_{m\parallel} = 2\kappa_m + 12(m^O)^2\alpha_m + 4(\alpha^2_r)\alpha_{\text{int}},\]
\[\kappa^O_{r\parallel} = 2\kappa_m + 2(m^O)^2(2\alpha_m + \gamma_m) + 2(\alpha^2_m/\alpha^*_m)\alpha_{\text{int}},\]
\[\kappa^O_{r\parallel} = 4\sqrt{2}\kappa_m^O m^O \alpha_{\text{int}}.\] (36)

Note that, at variance with the Hessian matrices introduced above, this one is not diagonal. Indeed, because both \( \delta r\perp \) and \( \delta m\parallel \) correspond to fully symmetric distortions in the \( O \) phase, there is a non-zero off-diagonal coupling between them. Naturally, by construction, the \( O \) phase is stable against such distortions, and this part of the Hessian is positive definite. The stability of the \( O \) phase thus relies on the parameters \( \kappa^O_{r\parallel} \), \( \kappa^O_{m\parallel} \), \( \kappa^O_{r\perp} \), and \( \kappa^O_{m\perp} \), which should all be positive. It is clear that this will depend on the relative values of the \( \alpha \) and \( \gamma \) anharmonic couplings affecting individual tilt patterns (e.g., a positive \( \gamma \) favoring the \( \alpha^+-\alpha^-0^+\) configuration over \( \alpha^+-\alpha^-0^-\) will obviously be helpful), and on the strength of the competing/cooperative interactions between different tilt types (thus, e.g., a positive \( \beta_{\text{int}} \) will be generally beneficial for the stability of the \( O \) phase). It is worth noting that the existence of the \( a^-a^-c^+ \) pattern as the ground state also requires that its energy \( E^O \) be lower than that of competing polymorphs (\( E^{\text{cubic}} \), etc.), which imposes additional conditions on the coupling parameters.

We will not analyze here all the possibilities and parameter combinations that may result in the stabilization of the \( Pbnm \) phase. Instead, below we will focus on discussing the parameter values that are typical of actual materials displaying the \( a^-a^-c^+ \) ground state. As we will see, all the investigated \( Pbnm \) compounds present a rather similar behavior, and a very clear physical picture emerges.

### III. Computational Approach

We use first-principles simulation methods to investigate thirty-five representative perovskite oxides with low-energy structures characterized by \( \text{O}_6 \) rotations. The chosen compounds tend to have small tolerance factors ranging between \( t = 0.81 \) (\( \text{ZnSnO}_3 \)) and \( t = 1.00 \) (\( \text{BaZrO}_3 \)). In some cases, we consider various members of significant materials families – as e.g. for the \( AFeO_3 \) orthoferrites –, so that trends as a function of \( t \) can be more clearly identified. Note that all the considered compounds are simple \( \text{ABO}_3 \) perovskites with uniquely defined \( A \) and \( B \) cations. Nevertheless, since the structural properties of perovskite solid solutions of the form \((A,A')(B,B')_3\) tend to depend smoothly on composition (Vegard’s law), we believe that our conclusions should be applicable to such more complex compounds, at least as regards trends dominated by cation size or steric effects.

Note that some of the considered compounds – especially small-\( t \) ones – may display (anti)pol (anti)pol instabilities of their cubic phase, in addition to the AFD soft modes. In such cases, a complete PES model should include, on top of the description of the tilting modes, an explicit theory of the most important polar order parameters, which would complicate the treatment considerably and remains for future work. Here, all such degrees of freedom are treated implicitly, and they are
assumed to follow the primary AFD order parameters in what concerns the discussion of the tilted structures. We should note that, in a few cases, the actual ground state of such materials may be FE, or may combine FE and AFD distortions. However, for the purpose of the present discussion, we will only consider structures in which the AFD modes are the primary order. For example, ZnSnO$_3$ has the $R3c$ ground state structure that is typical of LiNbO$_3$. Further, ZnTiO$_3$ and ZnGeO$_3$ have an ilmenite-type ground state. The present discussion does not consider such structures and, thus, is not intended to be a complete investigation of these compounds. Yet, we include them among our studied materials, as they provide us with valuable information on the behavior for very small tolerance factors.

To obtain information about the PES, we run symmetry-constrained structural relaxations corresponding to the following tilt systems: $a^{-}a^{-}c^{+}$, $a^{-}a^{-}a^{-}$, $a^{-}b^{0}b^{0}$, $a^{+}a^{-}a^{+}$, and $a^{+}b^{0}b^{0}$. We also optimize the cubic structure to obtain the reference energy $E_0$, and calculate the elastic constants $C_{ab}$ from the response of this phase to small strains. Further, we run structural relaxations under several constraints — e.g., by imposing the cell optimized for the cubic structure (i.e., $\eta_a = 0 \alpha a$), by disallowing the off-centering displacements of the A cations — to further test the behavior of the investigated materials. Such special situations are described in detail below.

We fit the bare coupling parameters [Eqs. (2)–(4)] by imposing that our models reproduce the AFD amplitudes, strains, and energies obtained for the relaxed structures. More precisely, the $\kappa_r$, $\alpha_r$, and $\gamma_r$ parameters are obtained so as to reproduce exactly $E_{\text{ vib}}$ and $E_{\text{ vib}}$, as well as the zero-derivative condition at the relaxed $a^{-}b^{0}b^{0}$ state. Similarly, $\kappa_m$, $\alpha_m$, and $\gamma_m$ are fitted to reproduce $E_{\text{ vib}}$ and $E_{\text{ vib}}$, and the zero-derivative condition at the $a^{+}b^{0}b^{0}$ phase. The $B_{1rxx}$, $B_{1ryyy}$, and $B_{1ryz}$ couplings are obtained by fitting the the $\eta_1$-derivatives of the energy evaluated at the $a^{-}a^{-}a^{-}$ and $a^{-}b^{0}b^{0}$ phases, as well as the $\eta_4$ derivative of the energy for the $a^{-}a^{-}a^{-}$ structure. Similarly, $B_{1rxx}$ and $B_{1ryyy}$ are obtained from the $\eta_1$-derivatives of the energy evaluated at the $a^{+}a^{-}a^{+}$ and $a^{+}b^{0}b^{0}$ structures. Finally, we fit $\alpha_{\text{int}}$ so that we reproduce the energy and zero-derivative conditions of the O phase as well as possible. Additionally, we consider a $a^{-}a^{-}a^{-}$ structure which we distort by hand, imposing a small in-phase rotation about the [100] pseudo-cubic axis, as needed to compute the coupling $\beta_{\text{int}}$.

As for the strain-renormalized parameters, we follow essentially the same procedure as above, demanding that the energy given by Eq. (3) reproduces all the features of the relaxed stationary structures, except the strains. We find that the assumed fourth-order polynomial energy is sufficient to obtain a satisfactory description of the key polymorphs mentioned above for all the materials considered. Most importantly, the interaction parameters $\alpha_{\text{int}}$ and $\alpha_{\text{int}}$ are sufficient to capture the key $\mathbf{r} \cdot \mathbf{m}$ coupling, and our models yield $E_0 = 0$ values that deviate from the first-principles result by about 2%, typically. Then, as we will see in Section [IV E], obtaining a quantitatively (very) accurate description of additional polymorphs (e.g., $a^{-}b^{-}b^{+}$) may require consideration of higher-order interaction terms; however, this detail is not relevant for our present discussion.

For the first-principles calculations, we use density functional theory (DFT) within the generalized gradient approximation adapted for solids (the so-called “PBEsol”$^{22}$ as implemented in the simulation package VASP$^{23,50}$). In the case of the considered ferrites, we use a Hubbard-$U$ correction of the energy functional, for a better description of iron’s 3$d$ electrons$^{50}$ choosing $U_{\text{eff}} = 3.8$ eV which is known to work well for these compounds$^{19,61,62}$ we also assume the iron spins are in an anti-ferromagnetic arrangement, with antiparallel first-nearest neighbors, mimicking their well-known ground-state magnetic structure. For SrRuO$_3$ and LaNiO$_3$, we do not use any Hubbard-$U$ correction, and consider a trivial ferromagnetic spin arrangement as starting point of our simulations; for SrRuO$_3$ this yields the magnetic solution that has been obtained in previous DFT investigations of this compound, and basically coincides with the experimental state for LaNiO$_3$ our simulations yield a non-magnetic configuration, thus reproducing previous calculations and agreeing well with the experimental result.$^{64,65}$ Nevertheless, one should keep in mind that the adequacy of a simple DFT treatment is questionable for such challenging compounds and, hence, our quantitative results for SrRuO$_3$ and LaNiO$_3$ should be regarded with some caution. The interaction between core and valence electrons is treated using the projector augmented wave (PAW) method$^{66}$ solving explicitly for the following electrons: O’s 2$s$ and 2$p$; Na’s 2$s$ and 2$p$; and 3$s$; Al’s 3$s$ and 3$p$; Ca’s 3$s$, 3$p$, and 4$s$; Ti’s 3$p$, 4$s$, and 3$d$; Cr’s 3$p$, 4$s$, and 3$d$; Fe’s 3$p$, 4$s$, and 3$d$; Ni’s 3$p$, 4$s$, and 3$d$; Zn’s 4$s$ and 3$d$; Ga’s 4$s$, 3$d$, and 4$p$; Ge’s 4$s$, 3$d$, and 4$p$; Sr’s 4$s$, 4$p$, and 5$s$; Y’s 4$s$, 4$p$, 5$s$, and 4$d$; Zr’s 4$s$, 4$p$, 5$s$, and 4$d$; Ru’s 4$s$, 4$p$, 5$s$, and 4$d$; Sn’s 5$s$ and 5$p$; Ba’s 5$s$, 5$p$, and 6$s$; La’s 5$s$, 5$p$, 6$s$, and 5$d$; Pr’s 5$s$, 6$s$, 5$p$, and 5$d$; Nd’s 5$s$, 6$s$, 5$p$, and 5$d$; Sm’s 5$s$, 6$s$, 5$p$, and 5$d$; Gd’s 6$s$, 5$p$, and 5$d$; Dy’s 6$s$, 5$p$, and 5$d$; Yb’s 6$s$, 5$p$, and 5$d$; Hf’s 6$s$, 6$d$, and 5$d$; Ta’s 6$s$ and 5$d$. Electronic wave functions are described in a plane wave basis cut off at 500 eV. All the investigated structures are treated using the same 40-atom Glazer cell, which can be viewed as a $2 \times 2 \times 2$ multiple of the elemental 5-atom perovskite unit and is compatible with all the AFD patterns of interest here. Brillouin zone integrals corresponding to this cell are computed using a $\Gamma$-centered $3 \times 3 \times 3$ grid of $k$-points. (Note that except for SrRuO$_3$ and LaNiO$_3$ — for which a grid of $9 \times 9 \times 9$ $k$-points is used – all the considered materials are insulators.) Structural relaxations are stopped when residual forces and stresses are below 0.01 eV/Å and 0.2 GPa, respectively. We checked that these calculation conditions are well-converged and sufficient for our current purposes.

Our results are in reasonable agreement with previ-
ous first-principles calculations in the literature. Representative of this are the elastic constants, for which there is plenty of published data for some compounds. For example, for CaTiO$_3$ we obtain $C_{11} = 373$ GPa, $C_{12} = 103$ GPa, and $C_{44} = 99$ GPa from our PBEsol calculations (see Table I). In contrast, a work$^{67}$ based on a different generalized-gradient approximation$^{68}$ reports values of 331 GPa, 96 GPa, and 95 GPa, respectively; while the authors of Ref. 42 obtained 403 GPa, 107 GPa, and 100 GPa, respectively, when using a local-density approximation$^{69}$ to DFT. Hence, our numerical results fall within the accuracy that can be expected from first-principles calculations that, besides other technical details, depend significantly on the choice of density functional.

Finally, let us mention some important details for the calculation of structural parameters and coupling constants. As mentioned above, $\mathbf{r}$ and $\mathbf{m}$ are the amplitudes of the antiphase and in-phase AFD order parameters, respectively (see Fig. 1). Then, let $\{r_{i\alpha}\}$ be the atomic positions corresponding to an arbitrary configuration of our periodically-repeated Glazer cell; here, $l$ labels the individual 5-atom cells inside our 40-atom supercell, $\{R_{l\beta}\}$ being the corresponding lattice vectors; $\kappa$ labels the atoms inside a 5-atom cell, whose positions in the cubic reference structure are given by $\tau_{\kappa\beta}$; $\alpha$ and $\beta$ label the Cartesian axes, which coincide with the pseudo-cubic directions of the perovskite structure. Then, such a configuration can be expressed as

$$ r_{i\kappa\alpha} = \sum_{\beta} (\delta_{\alpha\beta} + \eta_{\alpha\beta})(R_{l\beta} + \tau_{\kappa\beta}) + u_{i\kappa\alpha} , \quad (37) $$

where we have written the strains $\eta_{\alpha\beta}$ in their full tensor form, avoiding the compact Voigt notation. More importantly, Eq. (37) introduces the quantities $\{u_{i\kappa\alpha}\}$, i.e., the atomic distortions with respect to the strained reference structure. From these distortions, we obtain the amplitudes $\mathbf{r}$ and $\mathbf{m}$ by projecting onto six symmetry-adapted modes associated to each of the three antiphase and three in-phase octahedral rotations. We use modes that are normalized to unity when we sum over atoms in the 40-atom cell. The resulting amplitudes $\mathbf{r}$ and $\mathbf{m}$ thus have units of length (we use Å throughout). Hence, the harmonic constants $\kappa_r$ and $\kappa_m$ in our energy function are given in eV/Å$^2$, the 4th-order couplings ($\alpha_r$, $\beta_r$, $\alpha_{int}$, etc.) are in eV/Å$^4$, and the 6th-order correction $\gamma_{int}$ in eV/Å$^6$. As usual, the strains are adimensional, so that the elastic constants are given in eV and the strain-phonon couplings ($B_{1rxx}$, etc.) in eV/Å$^2$. Finally, note that all the parameters are normalized so that the functions $E(\mathbf{r}, \mathbf{m}, \{\eta_{\alpha}\})$ and $\bar{E}(\mathbf{r}, \mathbf{m})$ give energy per 40-atom cell.

IV. RESULTS AND DISCUSSION

In the following we present our results and discuss their implications, paying especial attention to the reasons why the $Pbnnm$ structure is the ground state of most perovskite oxides.

A. Raw first-principles results

Figure 2 summarizes our raw results, from which many conclusions can be directly drawn. Let us go over them in an orderly manner, and in the next Section we will see how each of them is reflected in (and explained by) the parameters of our energy function.

First, the energy difference between the reference cubic structure and the lowest-energy (ground state) configuration varies strongly with the tolerance factor, from about 3.5 eV/f.u. for ZnSnO$_3$ to less than 5 meV/f.u. for BaZrO$_3$. Correspondingly, there is a decrease of the AFD distortion amplitudes for increasing $t$, although not as drastic; for example, we have 2.3 Å for each of the three components of $\mathbf{r}$ in the $a^-a^-a^-$ state of ZnSnO$_3$, while we obtain $r_x \approx 0.8$ Å in the $a^-b^0b^0$ state of BaZrO$_3$. (These distortion amplitudes may seem unrealistically large; this is a consequence of our choice for the normalization of the associated symmetry-adapted vectors, described above.) Note that the mentioned energy gap – and, to a lesser extent, the distortion amplitudes – are expected to correlate with the temperature at which the cubic phase would transform into the low-symmetry structure, bigger energy differences – or bigger distortions – corresponding to higher-temperature transitions. Our results are consistent with the experimental observations in this regard. For example, intermediate-$t$ compound CaTiO$_3$ remains tilted up to about 1500 K, while LaFeO$_3$ is estimated to become cubic above 2000 K (provided it does not melt first). In contrast, the cubic phase of our materials with $t \approx 1$ is stable at rather low temperatures, e.g., down to 110 K in SrTiO$_3$ (Refs. 72 and 74) and down to essentially 0 K in BaZrO$_3$, for which the symmetry-breaking distortions are probably suppressed by quantum fluctuations. Finally, let us note that, as a consequence of the weaker AFD instabilities, the energy differences between tilt polymorphs become very small for large-$t$ compounds; generally, this should result in a greater structural tunability (e.g., by means of epitaxial strain imposed on thin films) in these materials.

Second, for all the investigated compounds, the antiphase O$_6$ rotations render stronger structural instabilities than their in-phase counterparts. Both instability types behave in a much correlated manner, becoming simultaneously stronger, or weaker, as a function of $t$. Interestingly, for $t \lesssim 1$, we find compounds in which the $\mathbf{r}$-tilts are still a (weak) instability of the cubic structure while the $\mathbf{m}$-tilts are not. Examples of this are LaAlO$_3$ and BaZrO$_3$, for which we find it impossible to relax $a^+b^0b^0$ or $a^+a^+a^+$ phases. (In those simulations the compounds relax back to the cubic reference structure; the corresponding results are missing in Fig. 2) It is not our task here to investigate the atomistic reasons for the gen-
FIG. 2. Summary of our first-principles results. Panel (a) shows the energies of the different tilt phases considered, given in eV per formula unit (f.u.). We take the result for the $a^-a^-a^-$ structure as zero of energy. The insets display zooms of the results for the materials that do not present the $a^-a^-c^+$ ground state (energies in meV/f.u.). The case of SrGeO$_3$ is not visible even in the inset; for this compound we obtain an $a^-b^0b^0$ ground state that is only 0.025 meV/f.u. below the $a^-a^-a^-$ structure.

Panel (b) shows the tolerance factor $t$ of the considered compounds. Note that the compounds are ordered from left to right as follows: We place together all the materials that share the same $A$ cation, and the ionic radius of $A$ grows as we move to the right. Compounds sharing the same $A$ cation are ordered so that the ionic radius of the $B$ cation decreases as we move to the right. All in all, the tolerance factor roughly grows when we move from left to right. Panels (c)–(g) show the antiphase and in-phase rotation components (Å) corresponding to the relaxed structures. The chemical formulas are given following a color code, red corresponding to compounds with $A^{3+}B^{3+}O_2^-$ nominal ionizations, blue to $A^{2+}B^{4+}O_2^-$, and black to $A^{1+}B^{5+}O_2^-$. General – albeit slight – prevalence of antiphase tilt patterns over in-phase ones; let us note, though, that a discussion of this matter can be found in Ref. 11.

Third, the $O$ phase $a^-a^-c^+$ is not obtained as a distinct solution for two materials, namely, LaAlO$_3$ and BaZrO$_3$. In such cases, during the structural relaxation of the $O$ phase — for which we use a typical $a^-a^-c^+$ configuration as starting point — we observe a progressive decrease of the in-phase $m_z$ rotation, until the $a^-a^-c^0$ solution is obtained as final result. Note that these are exactly the same two compounds for which we cannot stabilize structures with only in-phase tilts.

Fourth, the $O$ phase is the most stable structure (i.e., the ground state) of the majority of studied materials. On one hand, while our batch of crystals is obviously a limited one, this observation is consistent with reality. Indeed, it is well-known that the $O$ phase is dominant among perovskite oxides and, in particular, the number of compounds displaying tilt structures other than $a^-a^-c^+$ is comparatively small. On the other hand, if we take into account the points made above, this is somewhat surprising result. Indeed, our calculations show the preeminence of antiphase tilts over their in-phase counterparts, which suggests that purely antiphase patterns should be dominant over purely in-phase ones (as is indeed the case) and over antiphase/in-phase combinations as well (obviously not the case). Then, to explain why the $O$ phase is generally preferred, it would be most natural to imagine some sort of cooperative interaction between antiphase and in-phase rotations, which would drive their simultaneous occurrence. However, our results clearly suggest that, for the $Pbnm$ state to exist, the in-phase...
tilts must be a native instability of the cubic structure, which seems at odds with the cooperation hypothesis. Further, if the \( r \) and \( m \) rotations were to cooperate, we would expect to see an enhancement of their amplitudes when they appear combined in the \( O \) phase; however, this is not observed in our results. Hence, the dominance of the \( Pbnm \) ground state is a surprise that we cannot explain from the results presented thus far.

Finally, if we look at the compounds that present lowest-energy structures other than \( Pbnm \), they clearly belong to two different classes. On one hand, we have a group of large-\( t \) materials in which the in-phase tilts are either a weak instability of the cubic phase (\( \text{NdAlO}_3 \), \( \text{PrAlO}_3 \), \( \text{LaNiO}_3 \), \( \text{SrTiO}_3 \), and \( \text{SrGeO}_3 \)) or not unstable at all (\( \text{LaAlO}_3 \) and \( \text{BaZrO}_3 \)). This clearly suggests that relatively strong in-phase tilts are necessary to obtain a \( Pbnm \) ground state. On the other hand, we have small-\( t \) compounds (\( \text{ZnSnO}_3 \), \( \text{ZnTiO}_3 \), and \( \text{ZnGeO}_3 \)) for which all considered AFD distortions are very strong instabilities of the cubic phase. However, for such materials the \( a^- a^a^- a^a^- \) state lies lower in energy than \( a^- a^- c^+ \). Naturally, the reasons behind these results in the small-\( t \) limit must be quite different from those relevant to large-\( t \) materials like \( \text{SrTiO}_3 \) or \( \text{BaZrO}_3 \). In particular, it is interesting to note that, as mentioned above, the considered small-\( t \) Zn-based compounds are not perovskites in reality; thus, one may wonder whether their predilection for other crystalline lattices (\( \text{LiNbO}_3 \)-like and ilmenite) may be related to their preference for \( a^- a^- a^- \) over \( a^- a^- c^+ \).

### B. Modeling the relevant potential energy surface

Next, we use the results described above to fit the parameters defining the relevant PES, following the guidelines given in Section III. Table I shows the results obtained for the parameters entering the energy of Eq. (2), where strains are explicitly considered. In contrast, in Table II we present the results obtained for the parameters that implicitly capture the strain relaxations that follow the primary orders \( r \) and \( m \), corresponding to Eq. (3). Finally, Fig. 3 displays the key couplings in a way that makes it easier to appreciate trends as a function of the tolerance factor. For simplicity, in this Section we focus on the strain-renormalized results to discuss the main features of the PES. The computed parameters reflect and explain the conclusions drawn above by direct inspection of our raw first-principles results, and also yield a number of additional insights.

First, the strength of the AFD instabilities for small-\( t \) compounds is reflected in the large negative values of \( \kappa_r \) and \( \kappa_m \), which get closer to zero (and eventually become positive) as the tolerance factor increases. Note that, in principle, a large energy difference between the AFD phases and the cubic reference might also originate from small anharmonic couplings \( \bar{\alpha}_r \) and \( \bar{\gamma}_m \) [see Eqs. (10), (21), (26), and (53)]. However, these parameters do not present any marked or systematic variation with \( t \), and remain in the range between 0.1 eV/Å\(^4\) and 0.5 eV/Å\(^4\) for all investigated compounds.

Second, we find \( \kappa_r < \kappa_m \) for all the investigated materials, reflecting the fact that the antiphase rotations constitute stronger structural instabilities of the cubic phase than their in-phase counterparts. Describing the anharmonic couplings is not as straightforward. Roughly, we find that the isotropic coupling constants \( \bar{\alpha}_r \) and \( \bar{\gamma}_m \) are similar for all the considered compounds, and that we generally have \( \bar{\alpha}_r \geq \bar{\gamma}_m > 0 \). In contrast, we tend to have \( \bar{\gamma}_r < \bar{\gamma}_m < 0 \), which is consistent with the dominance of the \( a^- a^- c^+ \) solution over purely in-phase or other purely antiphase states.

Third, while we obtain \( \kappa_r < 0 \) for all the investigated compounds, we find two materials (\( \text{LaAlO}_3 \) and \( \text{BaZrO}_3 \)) for which \( \kappa_m \geq 0 \). In such cases the in-phase tilts are not instabilities of the cubic phase, and it is thus natural that structures with only in-phase tilts cannot be stabilized, as mentioned above. Hence, our usual fitting procedure does not allow us to compute \( \kappa_m \) for these compounds; instead, we obtain it by diagonalizing the Hessian matrix — of second derivatives of the energy — corresponding to the cubic reference structure. Also, as can be seen in the Tables, for \( \text{LaAlO}_3 \) and \( \text{BaZrO}_3 \) we do not compute any anharmonic terms involving in-phase tilts, or the couplings with strains.

Fourth, our calculated parameters allow us to discuss in detail the reasons why the \( O \) phase turns out to be the ground state of most perovskite oxides. As already mentioned, for all the considered compounds, antiphase tilts render more stable structures than in-phase rotations. Further, our fitted PES clearly indicates that the antiphase and in-phase modes compete with each other, as we get \( \bar{\alpha}_{int} \leq \bar{\beta}_{int} > 0 \) for all studied materials. Hence, it is now clear that the \( a^- a^- c^+ \) ground state, which combines antiphase and in-phase tilts, does not emerge because of a cooperation between the two types of AFD modes. Rather, the \( O \) phase prevails in spite of the fact that these two distortions compete and tend to cancel each other.

Let us emphasize this point. Our results clearly show that there is no such thing as a driving force for the simultaneous occurrence of antiphase and in-phase tilts in \( \text{ABO}_3 \) perovskites. Instead, the reason why they appear together in most compounds is somewhat mundane. Indeed, all the investigated \( Pbnm \) materials share the feature that \( \kappa_r \lesssim \kappa_m < 0 \), i.e., they possess similarly strong antiphase and in-phase instabilities of the high-symmetry cubic structure. Thus, in principle such distortions should occur simultaneously, unless their competition is large enough for the strongest (\( r \)) to suppress the weakest (\( m \)). Our results show that the \( r-m \) competition is not as strong, and thus the two tilt types coexist.

To gain additional insight, and to understand why the antiphase and in-phase tilts appear in the specific \( a^- a^- c^+ \) combination, let us turn our attention to Fig. 4. The diagram shows the relative stability, with respect to the cubic (\( a^0 a^0 a^0 \)) phase, of different AFD polymorphs...
| Compound       | $\kappa_m$ | $\alpha_m$ | $\gamma_m$ | $\alpha_{int}$ | $\beta_{int}$ | $B_{1rrxx}$ | $B_{1rryy}$ | $B_{1rryz}$ | $B_{1rxyz}$ | $C_{12}$ | $\alpha$ |
|----------------|-----------|------------|------------|----------------|---------------|-------------|-------------|-------------|-------------|----------|-----------|
| ZnSnO₃         | 0.1738    | 0.1395     | 0.0933     | 0.1725         | 0.0676        | 0.1228      | 0.0025      | -0.1914     | 0.9977      | 0.1893   | 3.235     |
| YSnO₃          | 0.1846    | 0.1323     | 0.1039     | 0.1323         | 0.1039        | 0.1323      | 0.1039      | 0.1323      | 0.1039      | 0.1323   | 3.235     |
| ZnTiO₃         | 0.1955    | 0.1210     | 0.0901     | 0.1955         | 0.0901        | 0.1955      | 0.0901      | 0.1955      | 0.0901      | 0.1955   | 3.235     |
| ZnGeO₃         | 0.2063    | 0.1181     | 0.0871     | 0.2063         | 0.0871        | 0.2063      | 0.0871      | 0.2063      | 0.0871      | 0.2063   | 3.235     |
| ZnGeO₃         | 0.2171    | 0.1148     | 0.0849     | 0.2171         | 0.0849        | 0.2171      | 0.0849      | 0.2171      | 0.0849      | 0.2171   | 3.235     |
| ZnGeO₃         | 0.2279    | 0.1116     | 0.0827     | 0.2279         | 0.0827        | 0.2279      | 0.0827      | 0.2279      | 0.0827      | 0.2279   | 3.235     |
| ZnGeO₃         | 0.2388    | 0.1083     | 0.0805     | 0.2388         | 0.0805        | 0.2388      | 0.0805      | 0.2388      | 0.0805      | 0.2388   | 3.235     |
| ZnGeO₃         | 0.2496    | 0.1052     | 0.0783     | 0.2496         | 0.0783        | 0.2496      | 0.0783      | 0.2496      | 0.0783      | 0.2496   | 3.235     |

See Section III for more details on the units and normalization used. For compounds in which the in-plane tilt is not instabilities of the cubic phase ($\kappa_m > 0$), the corresponding anharmonic and strain-photon couplings are not given.
the in-phase tilts are not instabilities of the cubic phase (κa compounds in which the
Section IV E 1) is in eV/Å.

\[
\begin{array}{cccccccc}
\kappa_r & \alpha_r & \gamma_r & \alpha_{int} & B_{1xx} & B_{1yy} & B_{1xy} & \bar{C}_{12} \\
-0.8050 & 0.1487 & -0.0538 & 0.1411 & -0.4475 & 5.9698 & 0.7210 & 266.54 \\
-0.6982 & 0.1471 & -0.0335 & 0.8377 & -1.2223 & 5.8840 & 1306.46 & 290.66 \\
-0.9135 & 0.1511 & -0.0722 & 0.1008 & -2.3470 & 3.5175 & 1.3626 & 288.47 \\
-0.7916 & 0.1443 & -0.0350 & 0.9393 & -3.1308 & 3.2244 & 1068.14 & 285.23 \\
-0.9559 & 0.2509 & -0.0953 & 0.2353 & -3.0008 & 2.0584 & 2.4588 & 334.02 \\
-0.8691 & 0.2466 & 0.0428 & 1.3700 & -4.2993 & 0.9725 & 1025.70 & 218.88 \\
-0.1882 & 0.1865 & -0.0242 & 0.1393 & -3.1262 & 4.3840 & 1.8653 & 312.45 \\
-0.0215 & 0.1842 & 0.0614 & 1.3014 & -4.5659 & 4.8710 & 1054.96 & 337.56 \\
-0.2585 & 0.4252 & -0.1934 & 0.0827 & -9.6994 & 1.4051 & 4.2523 & 299.63 \\
-0.0928 & 0.6012 & 0.2004 & 3.6661 & -12.8138 & 0.6900 & 858.38 & 415.25 \\
-0.1135 & 0.1013 & -0.0288 & --- & -2.0365 & 4.2014 & 1.2545 & 303.73 \\
BaZrO3 & 0.1226 & --- & --- & --- & --- & --- & 1224.42 & 315.85 \\
\end{array}
\]

TABLE II. Calculated parameters for the energy \( E(\mathbf{r}, \mathbf{m}) \) of Eq. (13). The harmonic constants \( \kappa_r \) and \( \kappa_m \) are given in eV/Å². The anharmonic couplings \( \bar{\alpha}_r, \bar{\alpha}_m, \bar{\gamma}_r, \bar{\gamma}_m, \bar{\alpha}_{int}, \) and \( \bar{\beta}_{int} \) are in eV/Å⁴. The 6th-order correction \( \bar{\gamma}_{int} \) (introduced in Section \[\text{IV.E.1}\]) is in eV/Å⁶. See Table III for more details on the units and normalization used. For compounds in which the in-phase tilts are not instabilities of the cubic phase (\( \kappa_m > 0 \)), the corresponding anharmonic couplings are not given. For compounds in which the \( a⁺b⁻a⁺ \) phase is not a local energy minimum, the \( \bar{\gamma}_{int} \) coupling is not given.
for the representative case of GdFeO$_3$. The dominant antiphase-tilted phase is $a^-a^-a^-$, closely followed by the $a^-a^-a^0$ structure, which lies about 50 meV/f.u. above it. The structures with only in-phase tilts are about 300 meV/f.u. above the corresponding antiphase-tilted ones, and the energy gap between the most ($a^+a^+a^+$) and least ($a^-b^0b^0$) stable one is about 35 meV/f.u. Now, for the sake of the argument, let us imagine that the r and m tilts do not interact. In that case, hybrid r-m states like those indicated in Fig. 3—namely, “$a^-b^0b^0+a^+b^0b^0$” and “$a^-a^-c^0+a^0d^0e^++$” could potentially be the ground state of the material. Indeed, in absence of r-m interactions, these two structures can be viewed as a simple combination of antiphase and in-phase distortions, and their energies with respect to the cubic reference would be $E_{tet} + E_{tet} - 2E_0$ and $E_{ort} + E_{tet} - 2E_0$, respectively. As shown in Fig. 4 for GdFeO$_3$ this yields energies well below that of the $a^-a^-a^-$ phase, simply because the energy gain associated to the condensation of an in-phase tilt ($E_{tet} - E_0$ in these examples, which is about 630 meV/f.u.) is much greater than the energy cost of rotating the antiphase-tilt axis (i.e., the anisotropy for r, as given by $E_{tet} - E_{ort} \approx 200$ meV/f.u., is comparatively small). As long as such a condition is met, having a ground state combining r and m tilts is in principle possible.

However, antiphase and in-phase tilts do interact repulsively ($\tilde{\alpha}_{int}, \tilde{\beta}_{int} > 0$), which will increase the energy of our hypothetical hybrid configurations. The “$a^-b^0b^0+a^+b^0b^0$” structure will be most strongly affected, as the occurrence of r and m tilts about the same axis is much penalized by the large coupling $\tilde{\beta}_{int}$.

In Fig. 4 we show the energy of such a phase once the r-m interactions are considered; the result, which we denote $a^\pm b^0b^0$, is obviously not competitive with other polymorphs. In contrast, for “$a^-a^-c^0+a^0d^0e^+$” the active r-m interaction is given by the relatively small $\tilde{\alpha}_{int}$ coupling, and the resulting structure (a’ $a^-c^-$) is obviously competitive with the other low-lying polymorphs. In fact, this is the Pbnm ground state in the case of GdFeO$_3$.

By inspecting the parameters computed in the present investigation, it is apparent that the above picture applies to all the compounds with a Pbnm ground state considered in this work. Hence, we think this picture is likely to be valid for most Pbnm perovskite oxides.

Finally, let us turn our attention to the materials that do not present a Pbnm ground state. In the case of the large-t compounds, the situation is quite obvious from the above description. Whenever $\kappa_m > 0$ (LaAlO$_3$, BaZrO$_3$), there is actually no driving force for the occurrence of in-phase tilts, and the Pbnm polymorph does not exist. Whenever we have a negative but small $\kappa_m$, we get a Pbnm polymorph that barely differs from a $a^-a^-c^0$ structure [see Fig. 2 g)]. In such cases, the repulsion $\tilde{\alpha}_{int}$ is often able to push up the energy of the O phase and yield a purely antiphase-tilted ground state. We should note that the result may depend on very tiny energy differences in some limit cases; see e.g. the occurrence of a Pbnm ground state in NaTaO$_3$ ($\kappa_m = -0.4708$ eV/Å$^2$, for the representative case of GdFeO$_3$. The dominant antiphase-tilted phase is $a^-a^-a^-$, closely followed by the $a^-a^-a^0$ structure, which lies about 50 meV/f.u. above it. The structures with only in-phase tilts are about 300 meV/f.u. above the corresponding antiphase-tilted ones, and the energy gap between the most ($a^+a^+a^+$) and least ($a^-b^0b^0$) stable one is about 35 meV/f.u. Now, for the sake of the argument, let us imagine that the r and m tilts do not interact. In that case, hybrid r-m states like those indicated in Fig. 3—namely, “$a^-b^0b^0+a^+b^0b^0$” and “$a^-a^-c^0+a^0d^0e^+$” could potentially be the ground state of the material. Indeed, in absence of r-m interactions, these two structures can be viewed as a simple combination of antiphase and in-phase distortions, and their energies with respect to the cubic reference would be $E_{tet} + E_{tet} - 2E_0$ and $E_{ort} + E_{tet} - 2E_0$, respectively. As shown in Fig. 4 for GdFeO$_3$ this yields energies well below that of the $a^-a^-a^-$ phase, simply because the energy gain associated to the condensation of an in-phase tilt ($E_{tet} - E_0$ in these examples, which is about 630 meV/f.u.) is much greater than the energy cost of rotating the antiphase-tilt axis (i.e., the anisotropy for r, as given by $E_{tet} - E_{ort} \approx 200$ meV/f.u., is comparatively small). As long as such a condition is met, having a ground state combining r and m tilts is in principle possible.

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and the actual parameters obtained for specific materials. For example, it is straightforward to check why the energy of the \( O \) phase \([E^O, \text{ Eq. } (53)]\) will be generally lower than that of competing polymorphs: it benefits from the contributions from both antiphase and in-phase distortions, while \( \alpha_{\text{int}} \) is relatively small. It is also easy to understand why the \( Pbnm \) solution is a minimum of the energy \([\text{Eq. } (56)]\), as this is essentially guaranteed by the positive interaction terms \( \alpha_{\text{int}} \) and \( \beta_{\text{int}} \). Further, it can be readily seen that, whenever \( \kappa_m > 0 \), the possible existence of the \( O \) phase as a singular point is unclear, as we would typically have \( (m^2)^2 < 0 \) in \( \text{Eq. } (52) \) if all the other parameters have values as those computed here. It is true that, from \( \text{Eq. } (32) \), one might imagine alternative ways to stabilize the \( O \) phase even if \( \kappa_m \) is positive; for example, we might have a strong cooperative interaction \( \alpha_{\text{int}} \leq 0 \), while keeping \( \kappa_r \leq 0 \) as the main driving force for the structural instability. Nevertheless, according to our DFT results, all the investigated compounds are far from such alternative scenarios, which thus seem to be highly unlikely.

### C. Strain effects

Let us now turn our attention to the elastic energy \( (E_s) \) and the coupling of strains with the tilt modes \( (E_{sp}) \). The corresponding parameters are given in Table 1 as obtained from the fit of all the bare coupling constants in \( \text{Eq. } (2) \).

As regards \( E_s \), the behavior of the investigated materials is standard, the cubic phase being stable against strains. It is interesting to note that there is no clear dependence of the elastic constants on the tolerance factor, suggesting that chemical considerations – as opposed to steric – should be most relevant in this case.

As regards the coupling between strains and AFD modes, we find that the constants \( B_{1xx}, B_{1yy}, B_{m1xx}, \) and \( B_{m1yy} \) are positive for some compounds and negative for others. Thus, for example, LaAlO\(_3\) presents negative values of \( B_{1xx} \) and \( B_{1yy} \), implying that negative strains \( \eta_1, \eta_2, \eta_3 < 0 \) – i.e., a smaller cell volume – will tend to weaken the \( r \) instabilities; this is compatible with the known behavior of LaAlO\(_3\), as it is experimentally and computationally observed that an hydrostatic compression results in a transition from the usual tilted phase of the compound \((R3c, a\ a\ a^-)\) to a non-tilted structure \((\text{cubic } Pm3m)\). In contrast, positive values of these strain-tilt couplings imply the opposite effect, that is, an enhancement of the rotational instabilities upon compression; this is the most common behavior, as discussed at length by some of us in Ref. [77]. In addition, we find that the coupling constant between shear strains and antiphase rotations \((B_{1xyz})\) varies sign depending on the compound. Finally, it seems all but impossible to identify clear trends of the strain-phonon coupling parameters as a function of tolerance factor, which suggests that other (chemical) factors must play a role in determining their

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\( \alpha_{\text{int}} = 0.0693 \text{ eV/Å}^4 \), and its absence in NdAlO\(_3\) \((\kappa_m = -0.3255 \text{ eV/Å}^4, \alpha_{\text{int}} = 0.1203 \text{ eV/Å}^4) \). Yet, the general trends are clear.

In the case of the large-\( t \) Zn-based compounds, the reasons why we obtain a lowest-lying \( a^- a^- a^- \) state, instead of the fully developed \( a^- a^- c^+ \) polymorph, are totally different. Indeed, by inspecting the parameters in Table 1 we find that these materials display the following distinct features affecting the \( a^- a^- a^- \) vs \( a^- a^- c^+ \) competition. On one hand, they present very strong \( r-m \) repulsive interactions, featuring record values for \( \alpha_{\text{int}} \) in the case of ZnTiO\(_3\) and ZnGeO\(_3\). On the other hand, they display, by far, the strongest anisotropies among the investigated compounds, as quantified by \( \gamma_r \) and \( \gamma_m \). As a result, antiphase tilts about \( \langle 110 \rangle \) and \( \langle 100 \rangle \) axes are strongly penalized compared to the \( a^- a^- a^- \) state. The combination of these two factors, particularly the latter, explains why these materials prefer the \( R3c \) polymorph. Interestingly, a \((p)\) antiphase rotation with \( r \parallel [111] \) constitutes the structural path connecting the perovskite and LiNbO\(_3\)-type structures. Further, we know that, in reality, the considered Zn-based compounds crystallize in the LiNbO\(_3\)-type phase or the \((\text{related}) \) ilmenite structure. Hence, our present results in the small-\( t \) limit – featuring \( \kappa_r \ll 0 \) and \( \gamma_r \ll 0 \) – reflect the well-known tendency to abandon the perovskite lattice and move towards a LiNbO\(_3\)-like structure. As a by-product of sorts, the \( O \) phase loses its predominance in this limit.

Note that the above observations can be confirmed by considering the formulae in Section 1 and the actual parameters obtained for specific materials. For example, it is straightforward to check why the energy of the \( O \) phase \([E^O, \text{ Eq. } (53)]\) will be generally lower than that of competing polymorphs: it benefits from the contributions from both antiphase and in-phase distortions, while \( \alpha_{\text{int}} \) is relatively small. It is also easy to understand why the \( Pbnm \) solution is a minimum of the energy \([\text{Eq. } (56)]\), as this is essentially guaranteed by the positive interaction terms \( \alpha_{\text{int}} \) and \( \beta_{\text{int}} \). Further, it can be readily seen that, whenever \( \kappa_m > 0 \), the possible existence of the \( O \) phase as a singular point is unclear, as we would typically have \( (m^2)^2 < 0 \) in \( \text{Eq. } (52) \) if all the other parameters have values as those computed here. It is true that, from \( \text{Eq. } (32) \), one might imagine alternative ways to stabilize the \( O \) phase even if \( \kappa_m \) is positive; for example, we might have a strong cooperative interaction \( \alpha_{\text{int}} \leq 0 \), while keeping \( \kappa_r \leq 0 \) as the main driving force for the structural instability. Nevertheless, according to our DFT results, all the investigated compounds are far from such alternative scenarios, which thus seem to be highly unlikely.
value. This issue, which is the focus of ongoing studies by some of us, falls beyond the scope of this work and will not be pursued here.

Rather, our present interest is to understand how strain affects the relative stability of the tilt phases. To gain insight into this question, we show in Fig. 5 the most important bare parameters [e.g., $\alpha_r$, $\gamma_r$, etc., obtained by fitting Eq. (2) to our DFT results] together with their strain-renormalized counterparts [e.g., $\alpha_r$, $\gamma_r$, etc., obtained by fitting Eq. (13)]. Note that a difference between bare and strain-renormalized couplings is indicative of a strain relaxation. Our main findings are as follows.

First, for the harmonic parameters $\kappa_r$ and $\kappa_m$, we obtain essentially the same values from the two fitting procedures, for all investigated compounds. This is the expected result because, provided our fourth-order series is an accurate representation of the relevant PES, we should not have any strain renormalization of the harmonic constants (see Section 11.1). Second, the strain renormalization is also negligible for the interaction couplings, so that we have $\bar{\alpha}_{\text{int}} \approx \alpha_{\text{int}}$ and $\bar{\beta}_{\text{int}} \approx \beta_{\text{int}}$. This result is not obvious a priori, and indicates that, for the investigated compounds, strain does not play any significant role in the competition between antiphase and in-phase rotations. Third, there is a sizeable renormalization of the $\alpha_r$ and $\alpha_m$ parameters for some of the compounds studied (e.g., NaTaO$_3$), although the effect has no qualitative significance. Note that we always have $0 < \bar{\alpha}_r \lesssim \alpha_r$ and $0 < \bar{\alpha}_m \lesssim \alpha_m$, i.e., the strain results in larger tilt distortions by weakening the anharmonic (repulsive) interaction. This is easy to understand: For given values of $\mathbf{r}$ and $\mathbf{m}$, the energy for fixed (zero) strains will be higher than the one obtained if we allow the strains to relax in response to the tilts. The former case is captured by the bare couplings, and the latter by the strain-renormalized ones; the mentioned energy reduction corresponds to having $\bar{\alpha}_r$ and $\bar{\alpha}_m$ strictly smaller than $\alpha_r$ and $\alpha_m$, respectively. Finally, the anisotropy terms $\gamma_r$ and $\gamma_m$ also exhibit a significant strain renormalization for some compounds, although the effect is generally small. In this case, we have no definite expectations on the behavior of the renormalized parameters and, indeed, our findings do not show any obvious systematics. It is worth noting that, in cases in which $\gamma_r$ or $\gamma_m$ is close to zero, the strain relaxation may cause the coupling to change sign, and thus reverse the relative stability of the tetragonal (e.g., $a^-b^0c^0$) and rhombohedral (e.g., $a^-a^-a^-$) structures (see Section 11.1). According to our results, SrGeO$_3$ presents this behavior ($\gamma_r = -0.193$ eV/Å$^4$, $\gamma_m = 0.004$ eV/Å$^4$), and NdAlO$_3$ and PrAlO$_3$ are borderline cases. This extreme sensitivity to strain is best characterized theoretically in ferroelectric PbTiO$_3$[10,16] and our results here provide an AFD analogue of such an effect.

Hence, while strains do have some impact on our investigated PES, the effects are of little importance to the central question here, i.e., the preeminence of the $Pbnm$ structure among perovskites. Indeed, strain effects – which are negligible for the interacting constants $\alpha_{\text{int}}$ and $\beta_{\text{int}}$ – are largely irrelevant in that respect. Let us note that we corroborated this conclusion by repeating the computational investigation of our thirty-five compounds, considering all the AFD polymorphs mentioned above, under the constraint of zero strains. (We thus impose that the lattice vectors be fixed at the values obtained from the symmetry-constrained relaxation of the cubic structure.) By fitting Eq. (13) to the DFT data thus computed, we obtain parameters that are qualitatively identical, and quantitatively very similar, to our strain-renormalized results in Table 11. Hence, strains will not be further considered here.

### D. A-site antipolar distortions

Antipolar displacements of the A cations, as those shown in Fig. 4, have been found to play an important role in stabilizing the $a^-a^-c^+$ structure over competing polymorphs in some compounds.[52,62,63] In this Section we discuss how such modes can be treated, and their effect quantified and analyzed, within our present scheme.

Let us first test the importance of the antipolar distortions by performing the following computational experiment: For all the materials considered here, we repeat the relaxation of the $Pbnm$ structure under the constraint that the A-cations be frozen in their high-symmetry positions. In other words, we impose null antipolar distortions and thus preclude the possibility that the A-cations may move off-center to optimize the energy of the O phase. In the following we will refer to such a constraint as “frozen-A”, and the quantities computed in frozen-A conditions will be primed. Figure 5 summarizes our findings, showing how the energy difference between the $a^-a^-c^+$ and $a^-a^-a^-$ structures varies depending on whether the antipolar modes are allowed or not. The results are crystal clear: We observe that, for most of the considered compounds, the $Pbnm$ and $R3c$ phases become nearly degenerate in frozen-A conditions. Further, we typically have $E_r^{\text{fro}} \lesssim E_r^{O^r}$, so that the $R3c$ structure becomes the lowest-energy state. Hence, previous observations in the literature get confirmed: the antipolar A-cation distortions are essential for the preeminence of the $Pbnm$ ground state among perovskite oxides. In their absence, most compounds would present an $a^-a^-a^-$ ground state.

These antipolar distortions can be thought of as secondary modes that follow the primary $\mathbf{r}$ and $\mathbf{m}$ order parameters in the same way that strain does. Hence, the antipolar modes are naturally present whenever we relax the $Pbnm$ phase for any of the considered compounds; they couple to the octahedral tilts and strains, and thus contribute to the resulting structure and energy of the O phase. Consequently, the effect of these modes is implicitly captured when we fit the parameters describing the relevant PES to DFT data. Note that this interpretation of the antipolar distortions as secondary modes is strictly...
correct only for compounds that do not present antipolar instabilities of the cubic phase, as is the case of the majority of materials here considered (see discussion in Section III and below). It is also important to realize that, from all the AFD polymorphs discussed above, such antipolar distortions appear only in the $a^-a^-c^+$ structure; in fact, it can be checked that none of the simpler phases considered here, for which we have either $\mathbf{m} = \mathbf{0}$ or $\mathbf{r} = \mathbf{0}$, presents any secondary distortions besides strain.

Since the antipolar distortions are treated implicitly in our PES description, we can view our calculated parameters in Tables III and IV as being renormalized by these modes. Nevertheless, we can go further and explicitly study such a renormalization by recalling the relevant couplings between antipolar and AFD modes, which have been discussed elsewhere. For simplicity, in the following we consider the particular $a^-a^-c^+$ variant of the O phase, noting that the results for other, equivalent structures – e.g., the one described by $a^-b^+a^-$ – can be obtained directly by suitable symmetry transformations.

There are two antipolar modes associated to off-centering displacements of the A-cations. In the following we discuss at length the first and most relevant of them, which yields the largest structural distortions and associated energy reductions. We will briefly discuss the second one at the end of the Section.

The first antipolar mode features movements of the A cations along the [110] pseudo-cubic direction, spatially modulated according to the $\mathbf{q}_Z = \pi/a(0,0,1)$ wave vector [see Fig. III(c)]. This mode involves an homogeneous pattern of [110]-oriented dipoles in a given (001) plane, and the reversal of such dipoles as we move by one elemental cell along the [001] direction. Let $Z_{xy}$ be the amplitude of this distortion. Following Ref. 28, one can prove that its lowest-order coupling with the AFD modes has the form

$$E_{\text{int}} Z_{xy} = \beta_{\text{int}} Z_{xy} r_{xy} m_z ,$$

where $\beta_{\text{int}}$ is a material-dependent constant and we assume that the $a^-a^-c^+$ state is characterized by

$$\mathbf{r} = r_{xy}(1,1,0) \quad \mathbf{m} = m_z (0,0,1) .$$

Let the energy associated to this antipolar mode be given by

$$E_Z = \kappa_z Z_{xy}^2$$

with $\kappa_z > 0$, as it corresponds to a regular distortion that is not an instability of the cubic phase. [If $\kappa_z$ were negative, we would need to introduce $O(Z_{xy}^4)$ terms in $E_Z$.] We can add $E_Z$ and $E_{\text{int}} Z_{xy}$ to the energy in Eq. 22 and, in analogy to our treatment for the strain in Section II B, impose the equilibrium condition

$$\frac{\partial E}{\partial Z_{xy}} \bigg|_{\text{eq}} = 0 ,$$

which yields the distortion

$$Z_{xy}^{\text{eq}} = -\frac{\beta_{\text{int}} Z_{xy}}{2\kappa_z} r_{xy} m_z .$$

If we substitute this result into the above expressions for $E_Z$ and $E_{\text{int}} Z_{xy}$, we obtain

$$E_Z + E_{\text{int}} Z_{xy} = -\frac{\beta_{\text{int}}^2 Z_{xy}^2}{4\kappa_z} r_{xy}^2 m_z^2 ,$$

where there is no explicit dependence on the antipolar mode amplitude. Now, by recalling the form of the energy for an $a^-a^-c^+$ state [Eq. 20], we can see that the coupling term stemming from $E_Z + E_{\text{int}} Z_{xy}$ contributes exclusively to the anharmonic interaction constant $\phi_{\text{int}}$. If we work with the full expression for the energy (Eq. 22), we trivially find that the renormalized anharmonic coupling

FIG. 5. Energy difference (meV/f.u.) between the $Pbnm$ and $R3c$ phases, as obtained in usual (filled circles, $E^O - E^{\rhoho}$) and frozen-A (open squares, $E^{\rhoho} - E^{\rhoho}$) conditions. A negative energy difference implies that the $Pbnm$ phase is more stable. The color code for the chemical formulas is as in Fig. 2.
is $\alpha_{\text{int}}$. Further, if we write the full symmetry invariant for the trilinear $Z \cdot r \cdot m$ coupling, we obtain a renormalization term proportional to $r^2 m^2$, which contributes to $\alpha_{\text{int}}$ in Eq. (2).

It is important to note that this contribution to $\alpha_{\text{int}}$ is negative. In other words, the $Z_{xy}$ relaxation favors an attractive, cooperative anharmonic interaction between antiphase and in-phase tilts. As a consequence, it tends to stabilize structures that combine both types of tilts about certain specific axes (e.g., $r \parallel [110]$ and $m \parallel [001]$ in our case), and will result in larger tilt amplitudes and a lower energy $E^0$.

We can test this theoretical prediction numerically. As mentioned above, we have DFT results for relaxed $O$ phases in absence of antipolar distortions (frozen-A conditions). Hence, we can use those data, together with our DFT results for the simpler only-antiphase and only-in-phase AFD states, to compute the coupling constants that describe the corresponding PES. The main outcome of this exercise is shown in Fig. 3 where the effect of the antipolar renormalization on the $\alpha_{\text{int}}$ parameters is clearly visible. (We get no significant difference for the other coupling constants, in agreement with the theoretical expectations.) Indeed, for all compounds we find $\alpha_{\text{int}} > 0$, where a larger $\alpha_{\text{int}}$ implies a greater $r \cdot m$ competition. As shown in Fig. 3 such a competition can become strong enough as to yield an $a^- a^- a^-$ ground state.

In view of these findings, we can conclude that the pre-eminence of the Pbnm ground state over the R3c polymorph stems from a balance between the tendency of the material to condense both antiphase and in-phase tilts ($\kappa_r < \kappa_m < 0$) and the mutually-exclusive interaction between them ($\alpha_{\text{int}} > 0$). This balance is a delicate one. Indeed, as shown in Fig. 3 it typically involves small energy differences $|E^{(O)} - E^{(I)}| \approx 10$ meV/f.u., the $a^- a^- a^-$ phase being dominant in frozen-A conditions. Then, the extra energy reduction provided by the relaxation of antipolar modes ($E^{(O)} - E^{(I)}$) is usually enough to tip the balance and stabilize the $O$ ground state.

Finally, let us comment on the second antipolar mode occurring in the Pbnm phase [Fig. 4(d)], which involves displacements of the A-cations along the [110] pseudo-cubic direction, modulated according to the $q_R$ wave vector. Following Ref. 7, we know that the leading coupling responsible for the activation of this secondary mode has the form

$$E_{\text{intR}} = \beta_{\text{intR}} R_{x\bar{y}} r_{xy} m_\perp^2,$$

where $R_{x\bar{y}}$ is the amplitude of the $q_R$-modulated antipolar distortion and $\beta_{\text{intR}}$ is a material-dependent coupling constant. Assuming that the energy of this mode is given by

$$E_R = \kappa_R R_{x\bar{y}}^2,$$

with $\kappa_R > 0$, the tilt-dependent equilibrium value of $R_{x\bar{y}}$ is

$$\beta_{\text{intR}} = \frac{\kappa_R R_{x\bar{y}}}{2\kappa_R} r_{xy} m_\perp^2,$$

and its contribution to the energy is

$$E_R + E_{\text{intR}} = \frac{\kappa_R R_{x\bar{y}}^2}{4\kappa_R} r_{xy} m_\perp^4.$$

This result is similar to the one obtained above for the $Z_{xy}$ distortion. In fact, the qualitative effect of this second antipolar renormalization – i.e., to favor the simultaneous occurrence of antiphase and in-phase tilts – is exactly the same. There is one important difference, though: Relaxing the $R_{x\bar{y}}$ mode affects a sixth-order interaction between the tilts, a coupling that is not included in our fourth-order model of the relevant PES. Since our numerical results regarding the Pbnm vs R3c competition seem perfectly consistent with a fourth-order Taylor series, we can conclude that the effect of this second antipolar renormalization is probably small. Hence, we do not pursue this issue further in this work.

### E. Additional remarks

Let us conclude with some additional comments on our results.

#### 1. Energy landscape, sixth-order corrections

The above discussion focuses on the relative stability of the lowest-energy AFD polymorphs, i.e., the $a^- a^- a^-$ and $a^- a^- c^+$ phases. Nevertheless, from the PES given by our fitted $E(r, m)$, we have access to the full six-dimensional energy landscape and can thus explore its features. To do this, we find it convenient to implement the special stereographic projection shown in Fig. 6. We work with a three-dimensional Cartesian system, with coordinates $\psi = (\psi_x, \psi_y, \psi_z)$, in which a positive value of $m_\alpha (r_\alpha)$ correspond to a positive (negative) value of $\psi_\alpha$. We can further define the two-dimensional surface obtained by minimizing the energy along the radial coordinate $\psi = |\psi|$, and make a stereographic projection of the result. We can then inspect the PES regions in which the energy is lowest. Figure 6(a) shows the energy map thus obtained for representative compound GdFeO$_3$.

Before commenting on the features of this landscape, let us note the low-energy (dark blue) path displayed by Fig. 6(a), which connects the following string of structures: $r_x r_y m_z \rightarrow r_y m_z \rightarrow m_x r_y m_z \rightarrow m_x r_y \rightarrow m_x r_y r_z$, where we start from the $a^- a^- c^+$ (Pbnm) phase indicated with an arrow in the figure and, as we move to the right and down, end up in an equivalent $a^+ b^- b^-$ structure. According to our fitted 4th-order PES, all the structures along this path are rather low in energy; in particular, the $a^+ b^- a^-$ phase is predicted to be the second most stable
play a role. Specifically, our DFT result for the $a^+b^-a^+$-type structures can be easily reproduced by extending the model with an additional 6th-order coupling of the form

$$\Delta E_{\text{int}} = \gamma_{\text{int}}(r_x^2m_y^2m_z^2 + r_y^2m_x^2m_z^2 + r_z^2m_x^2m_y^2),$$

(48)

which has the peculiarity of having no effect at all on the energy and stability of all the polymorphs discussed above. (For the $\gamma_{\text{int}}$ coupling to be active, at least two in-phase tilt components must be different from zero.) We find that for $\gamma_{\text{int}} = 0.2706$ eV/Å$^6$, we recover the DFT result for the energy of GdFeO$_3$’s $a^+b^-a^+$ structure. The corrected energy $E_{\text{c}}$ yields the landscape shown Fig. (b). The new map is overall quite similar to that of Fig. (a), except that the $a^+b^-a^+$-like phases are relatively high-energy saddle points now.

It is apparent from this map that the $Pbnm$ and $R3c$ states both constitute energy minima, and that such minima are connected by a low-energy $a^-a^-e^0$ saddle point. Simple tetragonal structures, like those corresponding to the points marked $r_z$ and $m_z$, are relatively high-energy saddles that appear as local maxima in our projection (for such states the energy is convex only along the radial direction $|\psi|$); in contrast, the orthorhombic structures $a^-a^-e^0$ and $a^+a^+e^0$ are lower-energy saddles, reflecting that we have $\gamma_r, \gamma_m < 0$ for this material. A peculiar case is that of the $a^+b^-e^0$ state, e.g., the mid point between $m_y$ and $r_y$ in Fig. (b): Note that an $r_z$-distortion reduces the energy of such a structure, as it takes it towards the $Pbnm$ ground state; in contrast, an $m_z$-distortion increases the energy, as in this case the condensation of a new in-phase rotation ($\gamma_m < 0, \gamma_m < 0$) cannot compensate for the increase in $r-m$ repulsion ($\gamma_{\text{int}} > 0$).

In Fig. (c) we show the stereographic projection of the PES of GdFeO$_3$ obtained under the frozen-A constraint. (This PES includes a small 6th-order correction term with $\gamma_{\text{int}} = 0.0192$ eV/Å$^6$.) As compared with the actual PES [Fig. (b)], the most significant changes occur in the vicinity of the $Pbnm$ state. Indeed, the increased $\gamma_{\text{int}}$ competition results in the near disappearance of the $a^-a^-c^+$ minimum and the consolidation of the $a^-a^-a^-$ ground state. Note also that the energy of other phases involving A-cation relaxations – e.g., the $a^+b^-a^+$ and $a^+b^-e^0$ structures – increases significantly in frozen-A conditions, while, in contrast, the purely antiphase or in-phase states (e.g., $a^-a^-a^-$, $a^+b^-b^0$) remain unaltered.

Let us conclude this part by noting that the issue discussed above for GdFeO$_3$ – i.e., the exaggerated stability of the $a^+b^-a^+$ structure, as predicted by the default 4th-order model – is general among the compounds studied in this work. Indeed, we used our DFT methods to relax the $a^+b^-a^+$ phase of all investigated materials, and found that the error in the energy predicted by the 4th-order model tends to grow as the tolerance factor decreases. (It can be as large as 400 meV/f.u. for YbFeO$_3$.) This is a reasonable result: smaller-t compunds display larger tilts and, as a consequence, higher-order energy terms should become more relevant for an accurate PES.
description. Following the recipe described above, we can compute $\gamma_{\text{int}}$ for all the investigated compounds that present a stable $a^+b^--a^+$ phase; the results are given in Table 11.

These results show that our fourth-order models – which are sufficient to reproduce the low-lying PES accurately, and whose simplicity allows satisfying physical interpretations – perform poorly when it comes to predict the energies of less-favorable states. While this seems an acceptable compromise in the present study, such an inaccuracy might become a problem if, for example, these same models were used to predict the behavior of the materials under the action of fields (epitaxial stress, electric field) that can be expected to stabilize unusual phases. Indeed, our results suggest that, generally speaking, one should validate low-order potentials before using them for quantitative investigations of materials subject to significant perturbations.

2. More on the phase diagram

To conclude, let us comment on the scope of the present investigation as regards a full discussion of the phase diagram of these perovskites. In this work we compare the relative stability of different structural phases by inspection of their energies, as directly obtained from DFT simulations. We focus on discussing the character of the ground state structure, and are thus confined to the limit of very low temperatures (strictly speaking, to 0 K). Then, it is worth noting that, for the prediction of the ground state to be more accurate, one should add the zero-point contribution to our computed static energies. Yet, here we leave zero-point energies out of the discussion, essentially for two reasons: First, they are not defined for many of the considered structures, which are saddle points of the PES and thus have imaginary-frequency phonons associated to them. Second, they depend on the soft modes of the material as much as (actually, less than) they depend on the harder ones; hence, the discussion of zero-point energies has little to do with the PES of the tilt modes, which is our main focus in this work.

To these main reasons, let us add the expectation that, because all the AFD phases of a given compound share the same kind of lattice topology and chemical bonding, zero-point energies should not be strongly polymorph dependent. It is obvious, though, that we have materials in which the obtained energy gap between different phases is tiny, and in such cases zero-point effects might in principle tip the balance. Nevertheless, the general agreement between our results for the lowest-energy structure and experimental observations (we are not aware of any obvious conflict) suggests that zero-point energies do not play any important role in determining the ground state of these compounds. Let us note that this seems to be the case of most first-principles works with perovskite oxides, as zero-point corrections are seldom considered and, yet, good agreement with experiment is common.

Finally, let us briefly comment on how one could investigate the effect of temperature on the competition among different tilt polymorphs. We have two distinct situations. On one hand, whenever we have compounds with well-developed O$_6$ rotations, for which the $Pbnm$ and $R3c$ structures are local energy minima, it should be possible to account for the effect of temperature by using the well-known quasi-harmonic approximation (see, e.g., Ref. 81). This would require accurate and heavy calculations of the phonon spectrum, as a function of volume, from which the temperature-dependent free energy of the different polymorphs can be approximated. Such an approach that has been barely applied in studies of perovskite oxides. Yet, it is interesting to note that a detailed investigation of BiFeO$_3$ (Ref. 81) showed that the $a^- a^- c^+$ structure is softer than the $a^- a^- \tilde{a}^+$ polymorph (which is polar, with space group $R3c$, for this compound), and it becomes favored upon heating. Interestingly, if the occurrence of a relatively soft $Pbnm$ phase were general in the perovskite family, thermal effects would provide us with yet another reason for the prevalence of the O state. Nevertheless, this point should be explicitly verified on a case by case basis, as we do not see any general reasons for the $a^- a^- c^+$ structure to be softer (or harder) than the $a^- a^- \tilde{a}^+$ one.

On the other hand, for compounds with weak tilt instabilities, the phase diagram will probably be determined by mechanisms that are typical of displacive soft-mode transitions. Hence a theoretical discussion will require a treatment of unstable phonon bands that will be, presumably, strongly temperature dependent. To study such cases we would need to resort to effective-potential schemes like e.g. those introduced in Refs. 10, 82, and 83. The few existing studies applying such methods to AFD compounds suggest that subtle interactions control the phase diagram, which dissuades us from formulating any general expectations.

V. CONCLUSIONS

In summary, this article reports on a thorough theoretical investigation of ABO$_3$ perovskite oxides whose structure is characterized by concerted tilts of the O$_6$ octahedra that constitute the backbone of the lattice. Our results provide a clear picture of how one particular tilt polymorph (the $a^- a^- c^+$ pattern, corresponding to the orthorhombic $Pbnm$ space group) prevails over all other in most perovskite materials; indeed, we are able to identify the physical requirements for such a structure to occur – i.e., antiphase and in-phase tilts are both native instabilities of the cubic perovskite prototype, relatively small anisotropy energy of the antiphase tilts, relatively weak competition between antiphase and in-phase tilts –, which happen to occur very frequently. Our results also prove the critical role played by secondary distortions – antipolar modes involving the A cations – to weaken
the antiphase/in-phase competition and yield the $Pbnn$ ground state. Additionally, we find that the $Pbnn$ polymorph loses its preeminence in two opposite limits – essentially, for small and large $A$ cations – for completely different reasons, which we discuss in some detail. Hence, beyond corroborating some scattered observations in the literature, this work brings unprecedented insight into (and quantification of) the competition between different tilt phases in perovskite oxides, and we hope will be useful to better understand existing compounds and eventually design new ones.

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