First-principles predictions of low-energy phases of multiferroic BiFeO$_3$

Oswaldo Diéguez, O.E. González-Vázquez, Jacek C. Wojdel, and Jorge Íñiguez
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

We used first-principles methods to perform a systematic search for potentially-stable phases of multiferroic BiFeO$_3$. We considered a simulation cell compatible with the atomic distortions that are most common among perovskite oxides, and found a large number of local minima of the energy within 100 meV/f.u. of the ferroelectric ground state. We discuss the variety of low-symmetry structures discovered, as well as the implications of these findings as regards current experimental (e.g., on thin films displaying super-tetragonal phases) and theoretical (on models for BiFeO$_3$’s structural phase transitions) work on this compound.

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I. INTRODUCTION

Perovskite oxide BiFeO$_3$ (BFO) continues to reveal itself as one of the most intriguing materials of the day. Not only does it remain the most promising magnetoelectric multiferroic for applications at room temperature, but it also has been shown recently to display a variety of novel fundamental effects. Such findings range from an increased conductivity at specific ferroelectric domain walls to new structural phases in thin films with potentially useful response properties.

The present work originated from our on-going research on enhancing the properties of BFO by forming solid solutions such as BiFe$_{1-x}$Co$_x$O$_3$ and Bi$_{1-x}$RE$_x$FeO$_3$ with RE = La, Sm, Dy. While investigating the chemically induced structural transitions, it became clear we needed to have a thorough and unbiased strategy to search for possible structural phases beyond those reported in the literature. Interestingly, when we applied such a scheme to BFO itself, we found plenty of low-symmetry phases that are local minima of the energy. Here we describe the lowest-energy structures that we discovered, i.e., those most likely to be observed experimentally. We discuss the origin of the large variety of distortions found in the calculations, and the possibility of capturing BFO’s structural richness within simple models. Further, we comment on the implications of our findings as regards current experimental work on BFO in both bulk and thin film forms.

II. METHODOLOGY

For the simulations we used the local density (LDA) and generalized gradient (PBE and PBEsol) approximations to density functional theory (DFT) as implemented in the vasp package. A “Hubbard-U” scheme with $U = 4$ eV was used for a better treatment of iron’s 3$d$ electrons; the corrected DFT functionals will thus be referred to as LDA+$U$, PBE+$U$, and PBEsol+$U$. We used the “projector augmented wave” method to represent the ionic cores, solving for the following electrons: Fe’s 3$s$, 3$p$, 3$d$, and 4$s$; Bi’s 5$d$, 6$s$, and 6$p$; and O’s 2$s$ and 2$p$. (We checked that qualitatively correct results can be obtained without considering semi-core electrons.) Wave functions were represented in a plane-wave basis truncated at 500 eV, and a $2 \times 2 \times 2$ $k$-point grid was used for integrations within the Brillouin zone (BZ) corresponding to the 40-atom cell of Fig. 1. The calculation conditions were checked to render converged results.

We worked with the 40-atom cell depicted in Fig. 1.
which is obtained by doubling the 5-atom cell of the ideal perovskite structure along the three Cartesian directions, denoted by $x$, $y$, and $z$ in the following. This cell is compatible with the structural distortions that characterize the low-symmetry phases of many perovskite oxides\cite{15} (1) ferroelectric (FE) patterns corresponding to any combination of in-phase ($M^+ \chi_3$) and anti-phase ($R^+ \chi_3$) rotations of the $O_6$ octahedra around the Cartesian axes. This cell is also compatible with the anti-ferromagnetic (AFM) spin arrangements known to be most relevant for BFO, i.e., the C-AFM and G-AFM orders sketched in Figs. 1(b) and 1(c), respectively.

To explore all these possibilities we considered a large number of starting configurations for our structural relaxations. Specifically, we considered: (1) all AFM patterns consisting of either an in-phase or an anti-phase rotation around each Cartesian axis (i.e., those expressible in Glazer’s notation\cite{17}); (2) various FE and AFE patterns constructed by off-centering the Bi cations; (3) cells with a cubic, tetragonal, and orthorhombic shapes; (4) G- and C-AFM orders as well as a few attempts with other spin arrangements. This added up to more than 300 starting configurations. In all cases, we first ran a short molecular dynamics simulation with random initial velocities (thus breaking all symmetries), and then performed a full structural relaxation. We used the PBE+$U$ functional for this structural search. The lowest-energy configurations obtained were confirmed to be minima by checking their stability against ionic and cell distortions.

### III. RESULTS

#### A. Lowest-energy phases found

Our search led to a wealth of local minima with energies in a range up to 200 meV/f.u. above BFO’s ground state. Table I lists the lowest-lying solutions; we show their PBE+$U$ energy directly obtained from our structure search, as well as the energies obtained by relaxing the PBE+$U$ structure using the PBEsol+$U$ and LDA+$U$ functionals. Note that the energy differences between phases are strongly dependent on the DFT functional; we will address this issue below. Table I also includes a short description of the phases found, which we label by their atomic space group and type of AFM order (e.g., R3c-G for the ground state); the complete structural information and computed polarization values are given in Tables II and III. Let us note that our work with BFO and other compounds confirms that PBEsol is more accurate than PBE and LDA for predicting the atomic structure of individual phases\cite{18}. Thus, the crystallographic data reported here correspond to PBEsol+$U$-relaxed structures.

Finally, Fig. 2 shows sketches of the structures obtained, and the most relevant distortion modes are depicted in Fig. 3.

All the functionals correctly predict the R3c phase with G-AFM spin order as the ground state of BFO. This phase displays a spontaneous polarization along the [111] Cartesian direction, and anti-phase $O_6$ rotations around the same axis ($a^-a^-a^-$ in Glazer’s notation).

We also found two orthorhombic phases that are similar to R3c-G in that they involve a relatively small distortion of the ideal cubic cell and favor the G-AFM order: Pnma-G and Pna21-G.

The Pnma-G structure is paraelectric (PE). As shown in Table I, it is characterized by an $O_6$ rotation pattern ($a^-a^-b^+$) that involves anti-phase rotations around [110] and in-phase rotations around [001]. This phase is the ground state of many perovskites, LaFeO$_3$ being the most relevant one for the current discussion. Interestingly, BFO’s Pnma-G phase can be aptly described as AFE, because the Bi cations present large anti-polar displacements in the (001) plane (associated with the $X^0_\chi_2$ mode of Table I and Fig. 3); the computed off-centering of the Bi cations is about 0.3 Å. (Such an AFE pattern is allowed by symmetry in LaFeO$_3$ too; in that case we obtain La off-centers by about 0.2 Å.)

The Pna21-G phase is similar to Pnma-G, but with an additional FE distortion along the axis of the in-phase rotations. As compared with that of Pnma-G, the 40-atom cell of the Pna21-G phase is elongated along the polarization direction; this reflects the usual coupling between the FE distortion and strain observed in perovskite oxides.

Regarding magnetism, the R3c-G, Pnma-G, and Pna21-G phases display strong AFM exchange couplings between neighboring Fe ions, as evidenced by a large energy splitting of more than 200 meV/f.u. between the G-AFM and ferromagnetic (FM) configurations. This is consistent with the high magnetic ordering temperature observed in bulk BFO.

In addition, we found a number of phases that involve a large stretching of the ideal cubic cell along the z direction, with $c/a$ aspect ratios approaching 1.3. In the following we will generically refer to such structures as super-tetragonal or $T$ phases. They all favor the C-AFM order (see Fig. 1), the parallel spin alignment occurring along the stretched lattice vector. The magnetic interactions along $z$ are weak, as evidenced by an energy splitting of about 5 meV/f.u. between the C- and G-AFM orders; accordingly, the ordering temperatures will be relatively low. Three of these phases are monoclinic (Cc-C, Cm-C, and Pc-C) and one is orthorhombic (Pna21-C); all of them are ferroelectric with a very large polarization component along [001] (see computed values in Table II).

More specifically, the Cc-C phase presents a polarization in the (110) plane, as well as relatively small AFD distortions. This type of monoclinic phase is usually termed $M_A$; a similar phase has been studied theoretically in connection with the super-tetragonal structures
versions of the ideal super-tetragonal

the in-phase rotations.

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observed experimentally in BFO films.

The Pc-C phase is very similar to Cc-C as regards the

polar distortion (thus, it is also \( M_\alpha \)), but it displays a

different \( O_6 \)-rotation pattern.

The Cm-C phase displays a polarization in the (100)

plane, and the cell is significantly distorted in the \( xy \)

plane; such a monoclinic phase is termed \( M_C \).

The Pna21-C phase is very similar to the Pna21-G

structure discussed above, the stretching of the cell and

development of polarization coinciding with the axis of

the in-phase rotations.

Note that all these \( T \) phases can be viewed as distorted

versions of the ideal super-tetragonal \( P4mm-C \) structure

listed in Table I. Interestingly, we found that this \( P4mm-C \)

phase, which is the ground state of BiCoO\(_3\),\(^{24}\) is a saddle

point in BFO’s energy landscape.

Our results thus reveal an intricate energy landscape,

especially regarding structures with a large \( c/a \) ratio.

In this sense, it is interesting to note that some of the

phases reported here are small distortions of higher-
symmetry structures. For example, the Cm-C phase can

be shown to be a \( Pm- \) structure distorted by the \( M_5^\perp-\)

\([0, y, 0]\) mode listed in Table I; by moving from the \( Pm-C \)
saddle point to the Cm-C minimum, BFO gains about

1 meV/\( \text{f.u.} \). Similarly, the reported \( Pc-C \) phase is

connected with a higher-symmetry Cm-C structure via a

observed experimentally in BFO films.\(^{3,10,13,20}\)

The \( Pc-C \) phase is very similar to \( Cc-C \) as regards the

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The \( Cm-C \) phase displays a polarization in the (100)

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plane; such a monoclinic phase is termed \( M_C \).

The \( Pna21-C \) phase is very similar to the \( Pna21-G \)

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development of polarization coinciding with the axis of

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TABLE I. Energies and distortions of the most stable energy minima found, as well as a few saddle points (six bottom phases) included for reference. Columns 2-4: Energies obtained with different DFT functionals. Note \( Pna21-G \) goes to \( Pnma-G \) when relaxed with PBEsol+U and LDA+U. Columns 5-8: Distortions from the ideal cubic perovskite structure (\( Pm3m \)) that characterize the phases. In all cases the FE and AFD modes fully determine the symmetry breaking. A generic \([x, y, z]\) FE (AFD) distortion involves displacements \((O_6 \) rotations\) along (around) the \( x, y, \) and \( z \) Cartesian axes. We indicate the dominant FE and AFD distortions in bold. Column 8 includes other modes with a significant contribution (at least 10% of largest one). The mode analysis was done with the ISODISPLACE software;\(^{20}\) note that \( q \)-points indicated in symmetry labels constitute default choices and do not always correspond to the actual distortion modulation (e.g., the \( X_5^\perp \) FE modes in Table I; by moving from the \( Pm-C \) saddle point to the Cm-C minimum, BFO gains about 1 meV/\( \text{f.u.} \). Similarly, the reported \( Pc-C \) phase is

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1 meV/\( \text{f.u.} \). Similarly, the reported \( Pc-C \) phase is

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TABLE II. Computed PBEsol+U lattice parameters (corresponding to the 40-atom cell of Fig. 1) and polarization values for the six stable phases of BFO listed in Table I. The polarization direction is given in a Cartesian reference that corresponds almost exactly with the 40-atom cell vectors. For comparison, we also include the result for the \( P4mm-C \) structure.

| Phase | \( a \) (\( \text{Å} \)) | \( b \) (\( \text{Å} \)) | \( c \) (\( \text{Å} \)) | \( \alpha \) (\( ^\circ \)) | \( \beta \) (\( ^\circ \)) | \( \gamma \) (\( ^\circ \)) | Magnitude (\( \text{C}/\text{m}^2 \)) | Direction |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------|
| \( Pc-C \) | 7.500 | 7.500 | 9.489 | 88.1 | 88.1 | 89.7 | 1.20 | \((0.29, 0.29, 0.92)\) |
| \( Cm-C \) | 7.380 | 7.608 | 9.533 | 86.6 | 90.0 | 90.0 | 1.50 | \((0.00, 0.30, 0.95)\) |
| \( Pna21-C \) | 7.515 | 7.515 | 9.452 | 90.0 | 90.0 | 90.0 | 1.39 | \((0.00, 0.00, 1.00)\) |
| \( Cc-C \) | 7.527 | 7.527 | 9.444 | 88.0 | 88.0 | 90.0 | 1.45 | \((0.23, 0.23, 0.94)\) |
| \( Pnma-G \) | 7.830 | 7.830 | 7.770 | 90.0 | 90.0 | 87.6 | 0.91 | \((0.58, 0.58, 0.58)\) |
| \( R3c-G \) | 7.893 | 7.893 | 7.893 | 89.5 | 89.5 | 89.5 | 1.52 | \((0.00, 0.00, 1.00)\) |
| \( P4mm-C \) | 7.414 | 7.414 | 9.526 | 90.0 | 90.0 | 90.0 | 1.52 | \((0.00, 0.00, 1.00)\) |
M$_3^+$-[0, 0, z] distortion. Given BFO’s manifest complexity, we tend to view the phases of Table I as a probably incomplete list, just indicative of the rich variety of stable structures that this compound can present.

Finally, let us stress we explicitly checked that all the above phases are local minima of the energy, a fact that is remarkable since some of them (e.g., the pairs formed by Pnma-G and Pnma21-G, or Ce-C and Pc-C) are rather close structurally. It is also interesting to note that monoclinic phases with such small primitive cells may be energy minima by themselves, i.e., without the need of any stabilizing (electric, stress) fields. Note that, to the best of our knowledge, monoclinic phases in bulk perovskite oxides tend to be associated with complex solid solutions or large unit cells. Examples of the former are the monoclinic $M_A$ phase that occurs in prototype piezoelectric PbZr$_{1-x}$Ti$_x$O$_3$ and the monoclinic $M_C$ phase of relaxor PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$. Examples of the latter occur in BiMnO$_3$ and BiScO$_3$; see the discussion in Ref. [27]. It was thus unexpected to discover that bulk BFO presents such a collection of simple low-symmetry minima of the energy.

B. Energy differences between phases

The relative stability of the phases discussed above is quantified by the energy differences between them. Disturbingly, Table I shows that such energy differences are strongly dependent on the DFT functional used to compute them. By switching functional we obtained changes in relative stability — e.g., Pnma-G is more stable than

![Energy minimum configurations obtained. (a)-(d) C-AFM super-tetragonal phases; in the left (right) image the c axis is perpendicular (parallel) to the page. (e)-(f) G-AFM phases; two pseudo-cubic axis are equivalent in (e), with the left (right) figure having the non-equivalent axis perpendicular (parallel) to the page; the three pseudo-cubic axis are equivalent in (f). The atomic species can be identified as in Fig. 1.](image-url)
FIG. 3. Illustration of atomic displacements for different symmetry modes of BFO: (a) soft FE mode, (b)-(f) secondary modes mentioned in Table I. Only displacement directions, not magnitudes, are indicated; for the (a) case, the PBEsol+U computed atomic displacements are quoted in the caption of Fig. 7. White, grey, and black circles represent Bi, Fe, and O atoms, respectively.

TABLE III. Energy minima structures of Table I as obtained from PBEsol+U calculations. In the case of the Pna21-G phase, the PBE+U result is given (see text).

| Phase | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|-------|-------|-------|-------|-------|-------|-------|
| Pbc-C | 7.291 | 5.291 | 5.315 | 90    | 139.46| 90    |
| Cm-C  | 9.534 | 7.380 | 3.804 | 90    | 86.60 | 90    |
| Pna21-C| 5.314 | 5.314 | 9.452 | 90    | 90    | 90    |
| Cc-C  | 10.604| 5.322 | 5.323 | 90    | 62.80 | 90    |

One would like to address this issue by resorting to a higher-level first-principles theory. However, performing quantum Monte Carlo calculations, which are the reference for accuracy in this context, is well beyond the scope of this work. Simpler schemes like the so-called hybrid functionals, which are usually considered to be more accurate than DFT for insulators like BFO, are not well tested for quantifying relative stabilities in cases like this one. Moreover, structural predictions with hybrids have been shown to depend strongly on the underlying generalized gradient approximation, which invalidates them for the present purposes.

Nevertheless, we were able to make a couple of mean-
Table III. (contd.)

| Structure  | a (Å) | b (Å) | c (Å) | \(\alpha = \beta = \gamma = 90^\circ\) |
|------------|-------|-------|-------|----------------------------------|
| Pnma-G     | 5.650 | 7.770 | 5.421 |                                  |
| \(\alpha = \beta = \gamma = 90^\circ\) | |

| Atom | Wyc. | x     | y     | z     |
|------|------|-------|-------|-------|
| Bi   | 4c   | 0.0523| 1/4   | 0.0100|
| Fe   | 4b   | 0     | 0     | 1/2   |
| O    | 4c   | 0.9722| 1/4   | 0.5946|
| O    | 8d   | 0.2998| 0.0461| 0.3037|

| Structure  | a (Å) | b (Å) | c (Å) | \(\alpha = \beta = \gamma = 90^\circ\) |
|------------|-------|-------|-------|----------------------------------|
| Pnma-G     | 5.559 | 13.782| 5.507 |                                  |
| \(\alpha = \beta = \gamma = 90^\circ\) | |

| Atom | Wyc. | x     | y     | z     |
|------|------|-------|-------|-------|
| Bi   | 6a   | 0     | 0     | 0.0000|
| Fe   | 6a   | 0     | 0     | 0.7236|
| O    | 18b  | 0.3156| 0.2294| 0.1238|

| Structure  | a (Å) | b (Å) | c (Å) | \(\alpha = \beta = \gamma = 90^\circ\) |
|------------|-------|-------|-------|----------------------------------|
| Pnma-G     | 5.702 | 5.507 | 8.036 |                                  |
| \(\alpha = \beta = \gamma = 90^\circ\) | |

| Atom | Wyc. | x     | y     | z     |
|------|------|-------|-------|-------|
| Bi   | 4a   | 0.4435| 0.0016| 0.2194|
| Fe   | 4a   | 0.5015| 0.5007| 0.4943|
| O    | 4a   | 0.2137| 0.7074| 0.0519|
| O    | 4b   | 0.1848| 0.6876| 0.4796|
| O    | 4a   | 0.5302| 0.4171| 0.2532|

We obtained (see Fig. 4) transition pressures of about 2 GPa for LDA+U, 3 GPa for PBEsol+U, and 5 GPa for PBE+U. Room-temperature experiments by Haumont et al.\cite{34} showed that at 3.5 GPa the \(R3c\)-G phase transforms into a monoclinic \(C2/m\) structure with a large cell (made of 12 formula units), and that a second transition at 10 GPa leads to the \(Pnma\)-G phase. These results suggest that the \(R3c\)-G and \(Pnma\)-G phases revert their relative stability at a pressure between 3.5 GPa and 10 GPa, a bracket that can be shifted to 5–14 GPa if the transition lines are extrapolated to 0 K.\cite{34} Thus, this comparison seems to indicate that the PBE+U is the most accurate theory for relative stability calculations, and that the LDA+U should not be used for these purposes. We have reached similar conclusions in our work with BiFe\(_1-x\)Co\(_x\)O\(_3\) solid solutions.\cite{35} In that case, the LDA+U predicts a \(R3c\)-to-\(Pnma\) transition for a La content that is clearly too small to be compatible with the experiments.

Second, we computed the relative stabilities of these phases as a function of an epitaxial strain corresponding to a square substrate in the (001) plane, so as to determine the lattice mismatch needed to stabilize the large-\(c/a\) structures.\cite{33} As shown in Fig. 5, we obtained strain values of \(-2.3\%\), \(-4.0\%\), and \(-4.5\%\) for PBE+U, PBEsol+U, and LDA+U, respectively. Experimentally it is known that a BFO-(001) thin film grown on SrTiO\(_3\) (\(-1.5\%\) misfit strain) displays a monoclinic structure that is an epitaxially-distorted version of the \(R3c\) phase (such a phase is believed to be monoclinic \(M_A\) with the \(Cc\) space group\cite{33}); we will denote this phase by \(R\) in the following. In contrast, when LaAlO\(_3\) substrates (\(-4.8\%\) misfit strain) are used, a super-tetragonal \(T\) phase whose symmetry remains unclear\cite{33} or a co-existence of the \(R\) and \(T\) phases\cite{33} has been observed. These results suggest that the energies of the \(R\) and \(T\) phases cross at an epitaxial compression close to \(-4.8\%\). Hence, according to this criterion, and assuming that our large-\(c/a\) phases are good candidates to be the observed \(T\) phase, the PBE+U curves would be the least reliable ones. We have reached similar conclusions in our work with BiFe\(_1-x\)Co\(_x\)O\(_3\) solid solutions, where PBE+U predicts an \(R\)-to-\(T\) transition for a Co content that is too small to be compatible with experiment. Further, these observations seem consistent with a well-known failure of the PBE approximation: it tends to render too large tetragonal distortions in ferroelectric perovskites.\cite{33,34,35}

In conclusion, while the PBE+U and LDA+U approaches seem to be rather accurate in some cases, they also render clearly wrong predictions in others. In this respect, PBEsol+U seems to be a reasonable compromise, as it constitutes the overall most accurate DFT theory available to us. Nevertheless, because PBE+U performs well as regards the relative stability of the \(R3c\)-G and \(Pnma\)-G phases, we believe that the PBE+U prediction of the new ferroelectric phase \(Pnma\)-G, structurally very similar to \(Pnma\)-G, deserves some attention. Finally, let us note that the choice of \(U\) also has an effect on the energy differences of Table I. Yet, for \(U\) values in the 3–5 eV range, such effects are small as compared with the
IV. DISCUSSION

Our results have direct implications for current experimental work on the structural characterization and phase transitions in BFO, especially regarding the epitaxially compressed films in which super-tetragonal phases were discovered. Further, they also provide us with information that is relevant to the effective modeling of BFO’s structural transitions, at both the macroscopic (Landau-type theories) and atomistic (effective Hamiltonians) levels. In the following we discuss all these aspects. To conclude this Section, we comment on Bi’s ability to form very different and stable coordination complexes with oxygen, as this seems to be the factor responsible for the observed structural richness of BFO.

A. Implications for experimental work

1. Super-tetragonal phases in BiFeO$_3$ films

The recent works by Béa et al. and Zeches et al. have shown that it is possible to obtain a novel phase of BFO if thin films are grown on strongly compressive substrates like LaAlO$_3$-(001). Experimentally, this T phase presents a very large c/a ratio of about 1.23, and an out-of-plane polarization $P_2 \approx 0.8$ C/m$^2$. First-principles studies have identified the T phase with a monoclinic $Cc$ structure for which LDA+$U$ calculations predict $c/a \approx 1.23$ and $P_2 \approx 1.5$ C/m$^2$. Thus, there is a large quantitative discrepancy between theory and experiment as regards the value of $P_2$, which suggests that the identification of the simulated and experimental phases may be incorrect.

Our present results show that there are many possible T phases – e.g., the low-energy $Pc$-C, $Cm$-C, $Pna2_1$-C, and $Cc$-C structures that we found – that might correspond to the one experimentally realized in the BFO films. Indeed, as shown in Fig. 5, all our large-c/a phases are essentially degenerate in energy for values of the epitaxial strain corresponding to a LaAlO$_3$ substrate. Moreover, at the PBEsol+$U$ level – which we have adopted as the DFT flavor of choice for BFO –, all these phases have their energy minimum at a misfit strain of about $-4.8\%$, implying that any of them can form a stable BFO film under such epitaxial conditions.

Because our T phases are an almost perfect epitaxial match with the LaAlO$_3$ substrate, the structural and polarization data in Tables II and III can be compared with the experimental results directly. Most remarkably, our results show that phases with very similar c/a ratios can display rather different polarization values. Indeed, the $Pc$-C phase (with a c/a of 1.27) presents $P_2 \approx 1.1$ C/m$^2$, while the $Cm$-C and $Pna2_1$-C phases (with c/a’s of 1.26 and 1.25, respectively) present $P_2 \approx 1.4$ C/m$^2$. Hence, our $Pc$-C structure seems to be the best candidate to represent the T phase realized in the BFO films investigated experimentally; the quantitative disagreement between the measured and predicted $P_2$’s would be below 40%, a clear improvement upon the previously reported 90% difference.

Let us also note that, because our T phases are so close in energy, the question of which one is realized experimentally may depend on subtle details not considered in this work. Thus, for example, two of these phases ($Pc$-C and $Cm$-C) present no tilts (i.e., rotations around the [100] and [010] axes) of the O$_8$ octahedra, which may make them preferable if the BFO films are grown on (001) substrates that clamp such distortions strongly. Similarly, a rectangular substrate might favor the $Cm$-C phase, whose cell tends to distort in the xy plane, etc.

Finally, we have very recently become aware of new results[21,23] showing that both $M_C$ and $M_A$ monoclinic phases with large-c/a ratios can be realized in epitaxially compressed BFO-(001) films. Such findings further support the physical relevance of the present study.

2. Structural transitions in bulk BiFeO$_3$

Our calculations were restricted to the limit of low temperatures, and do not allow for a conclusive discussion of temperature-driven effects and transitions in BFO. Nevertheless, a few comments can be made based on the obtained (large) energy differences between some relevant phases. Indeed, our results seem consistent with experiment[21,23] showing that, as a function of increasing temperature, BFO’s ferroelectric $R3c$ phase transforms into an orthorhombic $Pmma$ structure at $T \approx 1100$ K, to then become cubic $Pm3m$ at $T \approx 1200$ K. More specifically, the PBEsol+$U$ results of Table I show...
that the $R3c$-G and $Pnma$-G minima are very close in energy and constitute strong instabilities of the prototype $Pm\bar{3}m$ structure, which lies about 900 meV/f.u. above them, as consistent with the fact that BFO's cubic phase can be observed only at very high temperatures. Moreover, $R3c$-G and $Pnma$-G constitute BFO's most stable phases, with a large margin over other structures (e.g., the ferroelectric $R\bar{3}m$-G and $Amnm2$-G, or paraelectric $R3c$-G and $I\bar{4}/mcm$-G, listed in Table I) that are common among perovskite oxides. Hence, our results seem incompatible with the $R3c \rightarrow I\bar{4}/mcm \rightarrow Pm\bar{3}m$ transition sequence obtained by Kornev et al.\textsuperscript{26} from Monte Carlo simulations of first-principles-derived effective Hamiltonians; we found that the $I\bar{4}/mcm$ structure has a relatively high energy and is thus unlikely to occur instead of $Pnma$.

As regards pressure-driven transitions, our results confirm that under compression BFO's $R3c$-G phase loses stability in favor of the $Pnma$-G structure.\textsuperscript{27,28} Additionally, it is worth noting that, at the PBE+U level, we found a $Pn2_1$-G phase (see Table I) whose stability is also favored by compression and which nearly becomes the ground state in the pressure range in which $R3c$-G and $Pnma$-G revert their relative stability (results not shown here). Given that PBE+U seems the most accurate DFT flavor for the description of these pressure-induced transformations (see Section III.B), it seems wise to bear in mind the possibility that such a $Pn2_1$-G structure might occur, especially considering that the nature of the phase intermediate between $R3c$-G and $Pnma$-G remains unclear.\textsuperscript{27}

### B. Implications for modeling work

Our results clearly demonstrate that, in spite of its apparent simplicity, BiFeO$_3$ is extraordinarily complex from the structural point of view. In the following sections we will quantify such a complexity, adopting the perspective of someone who is interested in determining the simplest possible model, either macroscopic or atomistic, that captures accurately BFO’s structural diversity. Our analysis shows that BFO is much more challenging to model than traditional ferroelectric perovskites like BaTiO$_3$, PbTiO$_3$, or even PbZr$_{1-x}$Ti$_x$O$_3$.

1. **Primary and secondary distortions in BiFeO$_3$**

By analyzing the BFO phases described in Table I, it is possible to identify three primary distortion types (or primary order parameters) whose occurrence can explain all the symmetry reductions of interest and which must be considered in any theory of BFO’s structural phase transitions: A polar distortion that can in principle be oriented along any spatial direction ($\Gamma^{-}_4$ symmetry), and in-phase ($M^{+}_4$) and anti-phase ($R^{+}_2$) $O_6$ rotations around the three Cartesian axes. The atomic displacements associated with the two AFD order parameters (i.e., the oxygen-octahedra rotations) are uniquely defined by symmetry; hence, these modes are trivial in this sense. In contrast, the polar distortions are not determined by symmetry: any combination of $\Gamma^{-}_4$-like displacements of the Bi, Fe, and O sub-lattices is in principle valid. Following the usual first-principles approach to simple ferroelectric perovskites like BaTiO$_3$ or PbTiO$_3$,\textsuperscript{10} one would determine the specific atomic displacements that define the FE order parameter by computing the unstable (soft) polar mode of the cubic phase of the compound; the result thus obtained for BFO is depicted in Fig. 3(a). In materials like BaTiO$_3$, such a soft mode captures very accurately the atomic distortions associated to the relevant FE phases, e.g., tetragonal $P4mm$ and rhombohedral $R3m$. It is not obvious that the same will be true for BFO, where we would like to describe simultaneously super-tetragonal phases, which imply a very large distortion of the cubic cell, and the rhombohedral ground state, where the polar distortion coexists with very large $O_6$ rotations. Interestingly, we were able to demonstrate that the traditional approach works well for BFO: We performed a mode-by-mode decomposition of the atomic distortions connecting the prototype $Pm\bar{3}m$-G phase with the $P4mm$-C (as representative of our large-$c/a$ phases) and $R3c$-G structures, and checked that the $\Gamma^{-}_4$-like component is captured very accurately by the soft FE mode of the cubic phase (to within a 93% for $P4mm$-C and 99% for $R3c$-G). We can thus conclude that it is possible to describe all the FE phases of BFO with relatively simple theories that include only one polar mode.

The three primary order parameters described above are clearly the driving force for the structural transitions in BFO. For a given phase of the material, the occurrence of a particular combination of such primary distortions involves a specific breaking of the $Pm\bar{3}m$ symmetry of the cubic perovskite structure, which in turn results in the activation of secondary order parameters that become allowed in the low-symmetry phase. The most significant secondary distortions that we found in our BFO’s phases are listed in the last column of Table I and sketched in Fig. 3. There is a considerable number of such secondary modes; the ones involving the largest atomic displacements can be easily grouped in two categories: AFE patterns (see (c) to (f) modes in Fig. 3) and twisting modes of the $O_6$ octahedra ((b) in Fig. 3). In this sense, BFO is very different from ferroelectrics like BaTiO$_3$ or PbTiO$_3$, where the relevant FE phases do not present any secondary modes (note the absence of additional distortions for the $P4mm$, $Amnm2$, and $R3m$ symmetries listed in Table I, which are the relevant ones for BaTiO$_3$ and PbTiO$_3$). One thus needs to wonder: How important are these secondary distortions? Do they play a role in determining the energetics and relative stability of BFO’s phases, or can they be ignored in an effective theory of BFO’s structural phase transitions?\textsuperscript{11}

We quantified the importance of the secondary modes
in the following approximate manner: We considered the PBEsol+U equilibrium structures of all the relevant phases, artificially set to zero the secondary atomic distortions, and computed the energy of the modified structures. The obtained energy increments with respect to the actual equilibrium phases are very significant: they range from tens of meV/f.u. for the monoclinic (Pc-C, Cm-C, and Cc-C) phases to more than a hundred for the orthorhombic (Pma21-C and Pnma-G) ones. A more exact estimate can easily be performed for Pnma-G, as we found that in this case the most relevant secondary modes are clearly associated to Bi displacements: By fixing the Bi ions at their high-symmetry positions and relaxing all other structural parameters, we obtained an energy increase of 125 meV/f.u. with respect to the fully-relaxed Pnma-G structure. Thus, our results show that the energy changes associated to the secondary modes are of the same magnitude as the energy differences between different phases, which implies that these modes play a key role in determining BFO’s phase diagram. In particular, the large effects obtained for the orthorhombic phases indicate that their stability depends crucially on occurrence of the AFE patterns associated to Bi’s off-centering. We can thus conclude that an effective theory of BFO’s structural transitions must account for the effect of these secondary modes.

2. Phenomenological theories

The Devonshire-Landau phenomenological approach to phase transitions in bulk ferroelectrics and its extension to epitaxially-constrained films constitutes the simplest, yet powerful, theory that one might try to use to model BFO. Working out such a theory for BFO – i.e., determining the simplest possible Landau potential and temperature dependence of the parameters – constitutes a great challenge that, as far as we know, remains to be tackled. In the following we discuss what our results imply as regards the Landau theory of BFO.

In order to describe all the known phases of this compound, the corresponding Landau potential should be written in terms of a three-dimensional FE polarization \( P \) (which would correspond to the atomic distortions discussed in Section IV.B.1), as well as two AFD order parameters associated, respectively, to in-phase and anti-phase O\(_6\)-octahedra rotations. The cross terms between these three three-dimensional primary order parameters, and the additional terms that will appear if a non-zero epitaxial strain is considered, should allow us to reproduce the intricate energy landscape of BFO and its low-symmetry minima.

Indeed, in cases with several order parameters, it is possible to obtain stable low-symmetry phases from low-order Landau potentials. Imagine, for example, a FE perovskite that develops a polarization along the [1,1,1] direction as well as an in-phase O\(_6\) rotation around the [0,0,1] axis. Such instabilities can be described with a Landau potential truncated at 4th order in both the FE and AFD order parameters. The resulting phase would have a monoclinic Pc \((M_A)\) symmetry, exactly as the Pc-C structure of Table I. Hence, according to this example, it might be possible to describe all BFO’s phases with a low-order Landau theory.

However, our results show that the Landau theory for BFO would be significantly more complicated, especially in what regards the relative stability of the large-\(c/a\) phases. To illustrate this point, let us consider a simplified version of BFO in which only FE distortions and cell strains are allowed, and try to determine the order of the Landau potential \( F(P) \) required to describe ferroelectricity in such a system.

In a landmark article, Vanderbilt and Cohen analyzed the form of the Landau potential needed to describe low-symmetry phases in FE perovskites. In essence, they showed that a potential \( F(P) \) can present tetragonal or rhombohedral minima if expanded up to 4th order in \( P \); the occurrence of orthorhombic minima requires a 6th-order theory, and one needs to go up 8th order to have minima of monoclinic symmetry. This work was essential to understand which Landau potentials are needed to describe the monoclinic phases that were being found at the time in perovskite solid solutions such as PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) \((M_A\) type\) and PbZn\(_{1/3}\)Nb\(_{2/3}\)O\(_3\)-PbTiO\(_3\) \((M_C\) type\). The energy landscape associated to an 8th-order potential with a monoclinic \( M_A \) minimum is sketched in Fig. 6(a), following the convenient representation scheme introduced in Ref. 17.

We simulated our simplified (FE-only) version of BFO by forcing the material to have a 5-atom unit cell in which only polar \((\bar{1}4\bar{1})\) distortions and cell strains are allowed. (Of course, this cell was appropriately doubled to capture the G- and C-AFM spin arrangements.) If we impose such a constraint to the phases in Table I, we immediately recover the symmetries that were bro-
ken by the AFD modes: The $Pc$-C and $Cc$-C phases reduce to a single monoclinic $M_A$ structure with space group $Cm$-C; the $Cm$-C phase changes to a monoclinic $M_C$ with $Pm$-C symmetry; $R3c$-G gives us a $R3m$-G phase analogous to BaTiO$_3$’s ground state, etc. We can then consider two additional phases – namely, the super-tetragonal $P4mm$-C and orthorhombic $Amnm$-G listed in Table I, to sketch the energy landscape of Fig. 6(b). (To plot Fig. 6(b), the structural stability against T-like distortions of the $T$ and $M$ phases was explicitly checked. We have divided the diagram in two sectors to emphasize that the distortions connecting the super-tetragonal phases with the rhombohedral and orthorhombic structures are very large.) The most notable feature of this energy diagram is that it presents two inequivalent monoclinic minima, as opposed to only one as in Fig. 6(a). Further, if we follow the lowest-energy path connecting the $M_A$ and $M_C$ minima through triclinic structures, we will necessarily cross either a saddle point (case depicted in Fig. 6(b)) or a maximum. According to the analysis of Ref. [17], the existence of a triclinic saddle point requires a Landau potential of 10th order, while a 12th-order theory is needed to have a triclinic maximum. Note that Landau potentials of such a high order are unheard of among FE perovskites, even if complex solid solutions are considered. Amusingly, in their paper [17] Vanderbilt and Cohen justified the interest of discussing theories of very high order by writing that “the discovery (or synthesis) of a material having such a behavior may be challenging, but is by no means impossible.” Our analysis shows that BFO (even a simplified version of it) is such a material.

3. Atomistic theories

Effective theories of the inter-atomic interactions in ferroelectric perovskites, with parameters computed from first-principles, were introduced in the early 90’s by Rabe and Vanderbilt [22]. Ever since, these so-called effective Hamiltonians have made it possible to perform statistical simulations of increasingly complex materials, from crystalline BaTiO$_3$ [23] to disordered PbZr$_{1−x}$Ti$_x$O$_3$ [24] successfully reproducing temperature-driven phase transitions, response properties, etc. More recently, an effective Hamiltonian for BFO has been derived by Kornev et al. [25] who thus extended the approach to incorporate magneto-structural interactions in the model. Such a groundbreaking development has led to great physical insight into BFO’s ferroelectric and magneto-electric properties [26] as well as into the material’s behavior under applied electric [27] and magnetic [28] fields. On the other hand, in view of recent experimental results, we now know that some of the model predictions (e.g., the occurrence of a $I4/mcm$ phase at high temperature) are questionable. In the following we briefly summarize what our results teach us about how to construct an accurate effective Hamiltonian for BFO, extracting the corresponding conclusions as regards the theory of Kornev et al.

The first step of the classic approach to constructing effective Hamiltonians consists in identifying the relevant local distortions that must be retained in the model, so that we can use a coarse-grained representation of the atoms in the unit cell of our compound. In the case of BFO, there are clearly two local distortions that need to be considered: (1) a polar displacement pattern compatible with the FE ($T^+_4$) soft mode of Fig. 3(a), and (2) the rotation of individual $O_8$ octahedra around an arbitrary axes, whose in-phase ($M^+_3$) and anti-phase ($R^+_3$) repetition throughout the crystal reproduces the relevant AFD modes. As shown in Section IV.B.1, it is enough to consider one local polar mode to reproduce the FE distortion of the $R3c$-G ground state and $large-c/a$ phases, which allows us to work with a relatively simple model. A first-principles effective Hamiltonian considering these two types of local variables was first constructed to study SrTiO$_3$ [23] and this was also the starting point of the work of Kornev et al. for BFO.

In Section IV.B.1 we demonstrated the importance of the secondary distortions in determining the relative stability of BFO’s phases. The most relevant secondary modes are clearly the Bi-related AFE patterns that occur in the $Pnma$-G and $Pna2_1$-C phases. Fortunately, it is possible to incorporate such effects in an effective Hamiltonian without extending or complicating the model: We can choose the above mentioned local polar modes to be centered at the Bi atoms, as sketched in Fig. 7(a), so that (i) their homogeneous repetition throughout the crystal reproduces the FE soft mode of Fig. 3(a) and (ii) the zone-boundary modulations reproduce approximately the most relevant AFE distortions of the Bi atoms. Note that, alternatively, one could think of using local polar modes centered at the Fe atoms (see Fig. 7(b)). However, while this option is valid to reproduce BFO’s FE distortions, it fails to capture Bi’s AFE patterns (a zone-boundary modulation of the Fe-centered modes results in null Bi displacements). Consequently, an effective model based on Fe-centered modes will put a considerable energy penalty on the $Pnma$-G and similar phases. Such was the approach adopted by Kornev et al., which may explain their prediction that a $I4/mcm$ structure, and not $Pnma$, occurs in the phase diagram of bulk BFO.

As regards the rest of (less important) secondary modes, it might be possible to incorporate their effect by suitably renormalizing the Hamiltonian parameters. To make this idea more precise, let us denote by $u$ (resp. $v$) the distortions that will (resp. will not) be explicitly considered in the model. The usual effective Hamiltonians $H_{eff}(u)$, which work well for materials like BaTiO$_3$ in which secondary distortions are clearly not critical, can be formally defined as:

$$H_{eff}(u) \approx E(u,v)|_{v=0},$$

where $E(u,v)$ is the first-principles energy of an arbitrary configuration of the compound. In contrast, we
FIG. 7. Examples of local polar modes that can be used as variables of an effective Hamiltonian for BFO. (a) Centered at the Bi atom. (b) Centered at the Fe atom. The quantities $\delta_I$ identify displacements of the corresponding $I$ atom in the soft FE mode of the system; they should be divided by a factor that takes into account how many cells share atom $I$. For BFO we obtained $\delta_{\text{Bi}} = 0.80$, $\delta_{\text{Fe}} = 0.06$, $\delta_{\text{O1}} = -0.42$, and $\delta_{\text{O2}} = -0.04$.

could define an effective Hamiltonian $\tilde{H}_{\text{eff}}(u)$ designed to account for the effect of secondary distortions as:

$$\tilde{H}_{\text{eff}}(u) \approx \min_v E(u, v).$$  \hspace{1cm} (2)

Such a refined approach should improve the accuracy of the models in all cases, and it might prove critical to obtain correct results for compounds as challenging as BFO. The implementation of these ideas remains for future work.

C. The role of Bismuth

The Bi cations play a key role in BFO’s structural transitions. This can be predicted already from very simple steric arguments: In BiMO$_3$ perovskites, where $M$ is a first-row transition metal, the lattice parameter is essentially determined by the ionic radii of the metal and oxygen ions. This situation, which corresponds to a small value of the so-called tolerance factor,

$$t = \frac{r_M + r_O}{\sqrt{2}(r_{\text{ion}} + r_{\text{ion}})},$$

where $r_{\text{ion}}$ is the ionic radius, tends to result in either the off-centering of the Bi$^{3+}$ cation or the occurrence of AFD modes, both of which imply the shortening of some Bi–O bonds. This is exactly what is commonly observed in BiMO$_3$ crystals, and the main reason why some of these compounds make it possible to combine ferroelectricity (related to Bi’s off-centering) and magnetism (associated with the transition metals) at high temperatures.

Beyond its relatively small size, Bi$^{3+}$ presents an electronic configuration ($6s^2p^6$) that allows for orbital rearrangements suitable to form very directional bonds with neighboring oxygen atoms. Such Bi–O bonds tend to result in a lone pair on the non-bonding side, exactly as found in BFO’s $R3c$-G phase. This can be readily visualized in an electron-localization-function (ELF) analysis of the computed electronic structure: As shown in Fig. 8(a), there is a distinct non-bonding localization domain on the side of Bi that is opposite to the three neighboring O atoms, which is the signature of a lone pair.

The occurrence of such a lone pair was discussed at length by Ravindran et al. on the basis of first-principles calculations similar to ours; our results for BFO’s $R3c$-G phase (Figs. 8(a) and 9(a)) essentially reproduce their study.

We computed the ELF maps for the other BFO phases found in this work. Figure 8 shows the results for two representative cases: $Cc$-C and $Pnma$-G. It is immediate to note that a lone pair forms in the super-tetragonal $Cc$-C phase, as might have been expected from Bi’s large off-centering and the anisotropic spatial distribution of its neighboring oxygens. The case of $Pnma$-G is quite different, though: As shown in Fig. 8(c), in this phase the Bi cations have four neighboring oxygens that form a rather
regular BiO$_4$ tetrahedron. The corresponding ELF plots show a very isotropic localization domain around Bi. There is no clear lone-pair formation in this case; further, such a localization domain is not typical of bonding electrons, as evidenced by the slightly smaller ELF values along the directions of the Bi–O bonds. Hence, it might be more appropriate to interpret this result as corresponding to a semi-core-like case. Interestingly, the partial density of states results shown in Fig. 9 indicate that these three phases are very similar as regards orbital occupation, even if they clearly differ in terms of Bi–O bonding and lone-pair occurrence. Hence, our results illustrate Bi’s electronic flexibility and its ability to form different coordination complexes with the neighboring oxygens.

These chemical effects are clearly the driving force for the structural transitions in BFO. Note that all the BFO phases discussed here, either ferroelectric or paraelectric, have an energy that is lower than that of the cubic structure by more than 800 meV/f.u. (see Table I). In contrast, the cubic and polar phases differ by about 15 meV/f.u. in the case of prototype ferroelectric BaTiO$_3$, where the Coulomb dipole-dipole interactions are known to be the driving force for the FE instability.[58] Noting that BFO and BaTiO$_3$ are rather similar as regards the magnitude of the dipole-dipole forces,[59] we can conclude that such an enormous difference in the strength of the structural instabilities must be associated with the dominant role of the Bi–O chemistry in BFO. Then, the relative stability of BFO’s low-energy phases is probably determined by factors that involve smaller energy differences, such as subtle competitions between different Bi–O bonding mechanisms, the build-up of dipole-dipole interactions in the FE phases, etc. Analyzing these issues in detail falls beyond the scope of the present work. We hope our findings will stimulate further theoretical studies of the chemical bond in these phases, so that the factors controlling the occurrence of AFD and/or FE distortions (especially the super-tetragonal ones) can be elucidated.

Let us conclude by noting that our results for BFO – with most phases being dominated by either AFD or FE distortions – are clearly reminiscent of the competition between AFD and FE instabilities that is well-known to occur in many perovskite oxides. Such a competition has been studied in detail in SrTiO$_3$[29] and is one of the factors responsible for the rich phase diagram of materials like PbZr$_{1-x}$Ti$_x$O$_3$. Interestingly, BFO is peculiar inasmuch its FE soft mode is driven by the B-site transition metal and PbZr$_{1-x}$Ti$_x$O$_3$ is an intermediate case. Hence, BFO may constitute a new model system for the investigation of competing-instability phenomena in perovskite oxides.

V. SUMMARY AND CONCLUSIONS

We have used first-principles methods to perform a systematic search for potentially-stable phases of multiferroic BiFeO$_3$. We worked with a 40-atom supercell (i.e., a $2 \times 2 \times 2$ repetition of the cubic perovskite cell) that is compatible with the atomic distortions that are most common among transition-metal perovskite oxides, namely, ferroelectric, anti-ferroelectric, and anti-ferrodistortive. We obtained plenty of distinct low-energy phases of the compound; here we have restricted the discussion to the most stable ones. Many of the obtained minima present complex structural distortions and very low symmetry (e.g., monoclinic $M_A$ and $M_C$ space groups) while preserving a relatively small unit cell. As far as we know, this is quite unique among perovskite oxides, as the monoclinic structures reported so far are associated to complex solid solutions (e.g., PbZr$_{1-x}$Ti$_x$O$_3$ or PbZn$_{1/2}$Nb$_{1/2}$O$_3$-PbTiO$_3$), present large unit cells (e.g., BiMnO$_3$ and BiScO$_3$), or are obtained under special conditions (e.g., thin films subject to appropriate epitaxial strains or bulk compounds under external electric fields). In contrast, our study shows that bulk BiFeO$_3$ presents per se a collection of simple low-symmetry minima of the
Our findings have a number of important implications for the research on BiFeO₃ and related materials. Maybe the most general and interesting one stems from the demonstration that BFO can form plenty of (meta-)stable structural phases, which suggests that recent puzzling observations – ranging from possible structural transitions at low temperatures to surface-specific atomic structures and strain-induced new phases – may just be reflecting BFO’s intrinsic structural richness. Additionally, our results will provide useful information to the experimental workers exploring the possibility of obtaining large functional (piezoelectric, magnetoelectric) effects in BiFeO₃ films grown on strongly-compressive substrates: We have shown that there are plenty of phases – all with large polarizations and c/a aspect ratios – that can be realized in such conditions, including possibilities with monoclinic and orthorhombic symmetries. Our results also provide new insights concerning the relative importance of the various structural distortions that can occur in BiFeO₃, stressing the key role that the so-called secondary modes play in determining the relative stability of the observed phases.

Our work also has implications for theoretical studies of BiFeO₃. First, we present a critical comparison of the various DFT schemes most commonly employed to study BiFeO₃ and related compounds, and discuss the existing difficulties to quantify the relative phase stability. Second, we draw important conclusions as regards the effective modeling of structural phase transitions in BiFeO₃, in connection with both Landau-type and atomistic theories. Our analysis shows that BiFeO₃ is rather unique, and that its modeling needs to address issues – ranging from the work with high-order Landau potentials to the accurate treatment of secondary distortions – that are unheard of in the work with classic distortions such as BaTiO₃, PbZr₁₋ₓTixO₃, or even relaxor ferroelectrics. Finally, our results provide quantitative evidence for the dominant role that the Bi–O bond formation plays in BiFeO₃’s structural instabilities. Further, our analysis suggests that some of the phases discussed here do not exhibit the “lone-pair mechanism” usually invoked to explain the Bi–O directional bonds in BiFeO₃. We take this as a new illustration of Bi’s ability to form diverse, competitive in energy, bonding complexes with its neighboring oxygens.

Finally, our results will provide useful information concerning the key role that the so-called secondary modes play in determining the relative stability of the observed phases.

In conclusion, we have used first-principles simulation methods to illustrate, quantify, and analyze in some detail the structural richness of BiFeO₃, the most relevant representative of the family of Bi-based transition-metal perovskite oxides. Our simulations have revealed a variety of novel effects, some of which have important implications for current experimental and theoretical research on this material. We thus hope this work will help clarify and further stimulate research on these ever surprising compounds.

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