Interplay between breathing and polar instabilities in transition metal perovskites with active A-sites

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(Received 21 November 2019; accepted 25 February 2020; published 18 March 2020)

Active A-site cations like Bi or Pb in ABO_3 perovskites are known for their valence-skipping nature as well as for the stereochemical activities connected to lone pairs. While the former gives rise to breathing distortions in compounds like $BiNiO_3$ or $PbCrO_3$, the latter has been held responsible for ferroelectric, polar distortions in compounds like $BiFeO_3$ or $PbVO_3$. The microscopic origins of both distortions have been argued to stem from the hybridization between Bi(Pb) and O. Employing first-principles calculations, together with a variational solution of the first-principles-inspired model Hamiltonian, we investigate the interplay of two types of distortion instabilities in Bi/Pb-based transition metal perovskites. Our study reveals that in the absence of orbital degeneracy of the B site, the preference of one over the other is dictated by the relative positioning of O $2p$ level with respect to the A-site $6p$ level. Closeness of the two levels favors polar distortion over the breathing and vice versa, level positioning of O $2p$ being dictated by the strength of B-O hybridization.

DOI: [10.1103/PhysRevResearch.2.013333](https://doi.org/10.1103/PhysRevResearch.2.013333)

I. INTRODUCTION

The physical properties [1] of transition metal (TM) perovskites of general formula ABO_3 , are believed to be dictated by the B-site TM d electrons and the O p electrons. A-sites play the passive role of spectators, providing cohesion in the structure, introducing the size effect through a tolerance factor and ensuring charge neutrality. This conventional viewpoint gets modified when the A-sites are occupied by cations like Bi or Pb. As an example, $BiNiO_3$ at ambient condition exhibits insulating behavior [2], while $LaNiO_3$, with La^{3+} having a similar size as Bi^{3+} , is a metal [3]. This is suggestive of the active role of Bi compared to the passive role of La. This curious behavior has been recently explained [4] in terms of strong hybridization between extended $6s$ orbital of Bi and O $2p$ orbital, forming a ligand hole at the O site, that permits a Bi-O breathing mode instability and resultant checkerboard pattern of compressed and expanded BiO_{12} polyhedra [cf. Fig. 1(a)]. The Bi cation in compressed polyhedra is associated with two holes ($Bi^{3+}\underline{L}^2$) and the Bi cation in expanded polyhedra has a negligible hole component, thereby fixing the occupancy of Ni e_g states at half-filling and driving the Mott insulating state. On the other hand, with the valence configuration of Bi being $6s^2 6p^3$, the formally trivalent Bi in ABO_3 perovskite ideally contains a lone pair of $6s^2$ electrons. The $6s^2$ lone pair has been implicated for the ferroelectric properties [5] of $BiFeO_3$ [6] or $BiCoO_3$ [7], through their

stereochemical activity, which manifests itself in off-centric polar movement of the A-cation within the AO_{12} cage [cf. Fig. 1(b)]. Microscopic origin of this phenomena has been also traced to strong Bi-O hybridization [8,9].

This makes the situation curious. Since the driving mechanisms of both distortions appear to be propelled by the Bi-O hybridization effect, it provokes the question whether there exists a common platform describing both distortions or whether there are important differences. Interestingly, a parallel almost exists between Bi and Pb compounds; $PbCrO_3$ shows breathing distortion of alternate expansion and compression of PbO_{12} polyhedra [10], while compounds like $PbVO_3$ or $PbTiO_3$ show ferroelectric distortions [11,12].

In this communication, we investigate this intriguing scenario within the framework of density functional theory (DFT), along with solution of model Hamiltonian, constructed based on DFT essentials. This important problem is difficult due to various influencing factors. Given the complexity of the problem, the paper has been organized in the following manner. First, the trend of O $2p$ level position with respect to A-site $6s$ and $6p$ positions is demonstrated in terms of band centers, on site energies, Wannier functions, and crystal orbital Hamiltonian population, considering four compounds: $BiFeO_3$, $BiNiO_3$, $PbVO_3$, and $PbCrO_3$. This tendency toward polar instability versus the breathing instability can be described within a common framework of A-site $6s$ and $6p$ orbitals hybridizing with O $2p$ orbitals. The breathing versus polar instability is decided by the relative positioning of $6s$ versus $6p$ with respect to O $2p$ states. As shown, this trend is strongly manifested for $BiFeO_3$, and $BiNiO_3$ and less pronounced for $PbVO_3$ and $PbCrO_3$. Second, the role of B site (Fe in $BiFeO_3$ versus Ni in $BiNiO_3$) to tune the O $2p$ level position is discussed. Against this backdrop, with DFT essentials, a model Hamiltonian calculation is carried out which confirms the trend discussed on the basis of DFT results. This scenario,

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FIG. 1. (a) Breathing distortion of AO_{12} polyhedra in compounds like BiNiO_3 or PbCrO_3 , exhibiting alternately expanded (marked in blue [dark gray]) and compressed (marked in light green [light gray]) AO_{12} polyhedra. (b) Off-centric, polar distortion of A cations within the AO_{12} cage of ferroelectric compounds like BiFeO_3 , along the specified direction of polarization. The B-site atoms have been omitted from the pictures for clarity.

however, is complex for perovskites, which have B-sites with orbital degeneracy, in which case the off-centric movement of the B-site, in addition to the A-site, contributes to polar distortions, and disentangling the two is difficult. We close the paper with discussion on such compounds. Our study paves a way to understanding an important yet difficult problem which needs future attention.

II. NON-SPIN-POLARIZED ELECTRONIC STRUCTURE

We start our discussion with DFT non-spin-polarized density of states (DOS). The DFT electronic structure calculations have been carried out in pseudopotential plane-wave basis with generalized gradient approximation (GGA) [13] and projected augmented wave potentials (PAW) [14] as implemented within the Vienna *ab initio* Simulation Package (VASP) [15]. The results have been validated in terms of all-electron augmented plane-wave calculations [16]; see the Supplemental Material (SM) for details [17].

The DOS projected to Bi(Pb) 6s, 6p, and O 2p characters of BiFeO_3 (BFO), BiNiO_3 (BNO), PbVO_3 (PVO), and PbCrO_3 (PCO), at their respective undistorted phases, are shown in Figs. 2(a) and 2(b). The undistorted phases of BNO [2] and those of PVO [18] and PCO [10] are undisputed to be orthorhombic and cubic, respectively. However, the symmetry of the high-temperature nonpolar phase of BFO is controversial (cf. Fig. 1 in Ref. [19]), with cubic ($Pm\bar{3}m$) [20], monoclinic ($P2_1/m$) [21], orthorhombic ($Pbnm$) [22], as well as centrosymmetric rhombohedral ($R\bar{3}c$) [23] symmetries suggested as different possibilities. While most results reported in the following [Figs. 2 and 3(a)] for BFO have been carried out assuming the cubic symmetry for the high-temperature phase, we have also carried out calculations considering the monoclinic, orthorhombic, and rhombohedral symmetries [17]. Some of these results are included in the relevant figures [Fig. 3(b)].

The band centers and bandwidths of the respective bands, predominantly contributed by Bi(Pb) 6s, 6p and O 2p characters, extracted from the DOS plots, are shown in Fig. 2(c). The large mass of Bi and Pb separates the energies of 6s and 6p by several eVs, about 11 eV for Bi and 10 eV for Pb. As is

FIG. 2. (a) Non-spin-polarized density of states of BFO and BNO, projected onto A 6s (black), O 2p (cyan [gray]), and A 6p (brown [gray shaded]) characters. The zero of the energy is set at Fermi level. (b) Same as panel (a), but shown for PVO and PCO. (c) The band centers (A 6s, circles; O 2p, squares; A 6p, triangles) and band widths (vertical lines) of A 6s, O 2p, and A 6p of BFO, BNO, PVO, and PCO. The brackets show the differences of band centers between A-sites 6s and 6p and O-site 2p.

FIG. 3. (a) Absolute value of Bi 6s-O 2p COHP (left axis) and its cumulative sum, ICOHP (right axis), plotted as a function of energy, with zero of energy set at Fermi level for BNO (black) and BFO (brown [gray]). (b) Same as panel (a), but plotted for Bi 6p-O 2p. The values of COHP and ICOHP in panel (b) have been divided by three, to make them comparable with that of Bi 6s-O 2p. Insets show the constant amplitude surface of O-p Wannier functions for BNO (left inset) and BFO (right inset). Yellow (light gray) and magenta (dark gray) colors indicate opposite signs. The weights at Bi sites are encircled. (c) Calculated energy level positions of Bi-s, O-p, and B (Ni/Fe)-d in BNO and BFO. The zero of the energy is set at the average on-site energy of O p.

seen for BFO, the primarily empty Bi $6p$ states are close to O $2p$ bands, strongly hybridizing and overlapping the respective bandwidths, while localized Bi $6s$ states are situated about 11 eV below Fermi energy (E_F). Replacing Fe by Ni at B-site moves the Bi $6s$ state closer to O $2p$ states by a eV or so, while the Bi $6p$ states gets pushed away from O $2p$ states by couple of eV, significantly weakening the Bi $6p$ -O $2p$ admixture. A similar trend is observed between PVO and PCO, though less pronounced. As judged by the positions of band centers, the Bi(Pb) $6s$ state is moved closer to O $2p$ states by about 0.5 (0.5) eV in the case of BNO (PCO) compared to BFO (PVO), while the Bi (Pb) $6p$ states in BNO (PCO) are moved away from O $2p$ states by about 2.0 (0.7) eV, compared to that in BFO (PVO). We thus conclude that while Bi/Pb $6p$ -O $2p$ covalency contributes in a significant manner in Bi/Pb-O hybridization in BFO or PVO compounds, i.e., those showing polar distortions, it is relatively weaker in compounds like BNO or PCO, i.e., those exhibiting breathing distortion. The hybridization in the latter cases is mostly governed by Bi/Pb $6s$ -O $2p$ covalency. As a passing comment, the change in hybridization is primarily governed by the change in on-site energies, with the change in hopping integrals being less important. The O- p to Bi- p energy separation between BNO and BCO changes by about 2.2 eV, which is about 50%, while the Bi-O bond length changes only by 1%, resulting in a change in Bi $6p$ -O $2p$ hopping ($t_{pp\sigma}$) of only 1.05%. In the paper, we thus focus primarily on the on-site energy differences. It is to be further noted that although the above analysis considers non-spin-polarized electronic structure results, inclusion of magnetism at the B site through spin-polarized calculations is found to keep the trend intact, as presented in the Supplemental Material. This confirms the robustness of the trend.

In order to ascertain the nature of A-O covalency on a quantitative level, we computed crystal orbital Hamiltonian population (COHP), which provides energy-resolved analysis of hybridization between a pair of atoms [24]. Figure 3(a) shows Bi $6s$ -O $2p$ COHP in the left panel and Bi $6p$ -O $2p$ COHP in the right panel, for BNO in comparison to that for BFO. We plot the absolute magnitudes of COHP, since we are primarily interested in the strength of the covalency. Integrated COHP (ICOHP) shows that its value at Fermi level (E_F) for Bi $6s$ -O $2p$ covalency is about two times larger in BNO than in BFO, while for Bi $6p$ -O $2p$ covalency it is about 0.65 times smaller in BNO compared to BFO. A similar trend in COHP/ICOHP between PCO and PVO is found (see the Supplemental Material), though less pronounced. The weakening of $6p$ - $2p$ hybridization in BNO compared to BFO is further evident in the plots of Wannier functions in oxygen p -only Hamiltonian for BNO (left inset, Fig. 3) and BFO (right inset, Fig. 3), constructed using N th-order muffin-tin orbital (NMTO) downfolding technique [17,25,26] by retaining only O- p degrees of freedom in the basis, with the rest including Ni/Fe- d and Bi- s, p degrees of freedom being downfolded. As is seen from the plots, while the central part of the Wannier functions of oxygen p -only basis is shaped according to oxygen p symmetry, the tails extending to Ni/Fe and Bi are shaped according to integrated out Ni/Fe- d and Bi degrees of freedom, reflecting the covalency. Significant amount of weights of the tails are found at the Bi sites (see encircled parts). Bi $6s$ -O $2p$ mixed state further bonds to the

empty Bi $6p$ state, lowering the energy of the system, as is seen in the presence of Bi $6p$ -like shapes in the tails at Bi sites. Interestingly, the $6p$ character in the Bi tail is weak in BNO, being more of Bi $6s$, while the contribution of Bi $6p$ character is relatively stronger in BFO (estimated to be 15% in BNO compared to 30% in BFO). As argued by Watson *et al.* [9], the stereochemical activity of lone pairs is driven by the important contribution of mixing with Bi/Pb $6p$ states. The Bi $6s$ -O $2p$ interaction does not lead to energetic gain since both Bi $6s$ and O $2p$ are positioned below E_F . Energy gain happens through hybridization of these states with unoccupied $6p$ states, which effectively moves O $2p$, positioned at E_F due to Bi $6s$ -O $2p$ interaction, away from E_F . In the event of weakening the $6p$ contribution, as in the case of BNO, the contribution of Bi $6s$ -O $2p$ mixed state at E_F leads to formation of ligand hole, triggering the disproportionate charge-assisted breathing distortion of the A-O lattice [4].

Another useful way of looking at the stereochemical activity of the lone pair is considering its degree of localization around the atomic framework. Higher localization corresponds to higher asymmetry, which results in division of O-coordination around the A-site into two coordination spheres, as discussed in Ref. [27]. In order to estimate the degree of localization of the lone pair in a quantitative manner, we computed the spread of effective Pb or Bi $6s$ Wannier function, obtained in a massive downfolding calculation by integrating out everything else other than A-site s . By construction, this takes into account the hybridization between A $6s$, A $6p$, and O $2p$. The spread of such effective orbital for BFO is found to be about 22-27% smaller than that of BNO, suggestive of the localized and directional nature of the lone pair in BFO compared to the delocalized and symmetric one in BNO. See the Supplemental Material.

III. ROLE OF B-SITE

What decides the positioning of O $2p$ within the the Bi/Pb $6s$ - $6p$ energy window? Figure 3(b) shows the Bi- s , TM- d , and O- p energy level positions in BFO averaged over possible nonpolar phases in comparison to those of BNO, obtained from the tight-binding representation of the Hamiltonian in the Bi $6sp$, Ni/Fe $3d$, and O $2p$ basis within the NMTO-downfolding calculations [25,28]. As is seen, moving across the third row of the periodic table from Fe to Ni, the TM d energy level position gets closer to the oxygen p energy level, resulting in stronger d - p interaction between the B-site and oxygen in BNO compared to BFO. The bonding oxygen p level, renormalized by the TM d -O p hybridization, gets pushed down, thus being positioned farther from Bi p in BNO compared to BFO. The position of the oxygen p level, being tuned by B-site-O hybridization, thus decides the fate of the active A-site, exhibiting breathing or polar distortion.

IV. MODEL STUDY

In order to capture the competition between the two instabilities within a general framework, we considered variational calculation of a DFT-inspired model Hamiltonian, consisting of A-site s , p , and O p . Interestingly enough, it was found that competition between breathing and polar distortion at the

A sublattice can be captured without active involvement of B-sites. The B-site d orbitals, responsible for the insulating nature (Mott or dimerized) of the compounds, have frozen charge fluctuations. Therefore, they drop out of the problem, being included in an implicit manner and dictating the position of O p through tuning of B-O hybridization. The following convention is adopted. A-site coordinate is chosen as $\Delta \equiv (1/2, 1/2, 1/2)$, with origin set at the B-site. η 's refer to oxygen positions around a given A-site. The effect of the distortion in bond lengths is incorporated through the Harrison scaling of the hopping elements [29], while the directional nature of the s - p and p - p hopping is captured using appropriate Slater-Koster integrals in the hopping elements. The model Hamiltonian can be written as a sum of three terms: (i) on-site term H_1 , (ii) hopping term H_2 , and (iii) restoring force term for polar and breathing distortions H_3 :

$$\begin{aligned}
 H_1 &= \sum_{\mathbf{r}, \sigma, \alpha} \varepsilon_{A, \alpha} b_{\mathbf{r}+\Delta, \alpha, \sigma}^\dagger b_{\mathbf{r}+\Delta, \alpha, \sigma} \\
 &+ \sum_{\mathbf{r}, \sigma, \alpha} \varepsilon_{Ox, \alpha} s_{\mathbf{r}+\Delta+\eta, \alpha, \sigma}^\dagger s_{\mathbf{r}+\Delta+\eta, \alpha, \sigma}, \\
 H_2 &= -t^{A-O} \sum_{\mathbf{r}, \eta, \alpha, \beta, \sigma} (M_{\alpha, \beta}^\eta b_{\mathbf{r}+\Delta, \alpha, \sigma}^\dagger s_{\mathbf{r}+\Delta+\eta, \beta, \sigma} + \text{H.c.}), \\
 H_3 &= \frac{1}{2} \kappa_B \sum_{\mathbf{r}, \eta, \alpha, \beta} \delta_B^2 + \frac{1}{2} \kappa_P \sum_{\mathbf{r}, \eta, \alpha, \beta} \delta_P^2
 \end{aligned}$$

with

$$M_{\alpha, \beta}^\eta = g_{\alpha, \beta} [1 + f_{\alpha, \beta}^\eta \delta_B (-1)^{x+y+z} + p_{\alpha, \beta}^\eta \delta_P (-1)^{q(\mathbf{r})}],$$

where $b_{\mathbf{r}, \alpha, \sigma}^\dagger$ and $s_{\mathbf{r}, \alpha, \sigma}^\dagger$ create an electron in the orbital α (s , p) at the A-site and in the p orbital at an oxygen atom located at $\mathbf{r}$, respectively, and spin is denoted by σ . The A-site and the oxygen on-site energies are denoted by $\varepsilon_{A, \alpha}$ and $\varepsilon_{Ox, \alpha}$ respectively. t^{A-O} sets the overall energy scale while the prefactor $g_{\alpha, \beta}$ in $M_{\alpha, \beta}^\eta$ contains the symmetry dependency of the hopping. Breathing and polar distortions are captured in terms of modulation of hopping via distortion amplitudes δ_B and δ_P respectively. $f_{\alpha, \beta}^\eta$ and $p_{\alpha, \beta}^\eta$ encode the orbital-dependent Harrison scaling factors and the long and short bond effect resulting from polar distortion, respectively. κ_B and κ_P refer to spring constants for δ_B and δ_P , respectively. For uniform polar distortion, we choose $q(\mathbf{r}) = 0$ and along the (111) direction. Based on DFT estimates and previous literature [4], we choose $t_{sp}^{A-O} \approx t_{pp\sigma}^{A-O} = 1.5$ eV, $t_{pp\pi}^{A-O} = -0.3$ eV, setting the on-site energies for $\varepsilon_{A, s}$ and $\varepsilon_{A, p}$ to be zero and 11 eV respectively. We vary κ_B/κ_P as well as ε_{Ox} . We stress that δ_B and δ_P are variational parameters that induce phase competition between distortions of two distinct symmetries. Thus, a phase transition occurs when the ground-state energies with the two kinds of distortions cross each other as a function of ε_{Ox} and κ_B/κ_P . In this sense, one can identify δ_B and δ_P as indicators of phase transition.

The phase diagram of breathing and polar distorted phases in the κ_B/κ_P versus ε_{Ox} (scaled by $t_{pp\sigma}$) plane is shown in Fig. 4(a). The phase boundary is constructed by following the evolution of δ_B and δ_P , as a function of ε_{Ox} , for every ratio of κ_B/κ_P explored here. Typical data, for realistic DFT estimates of $\kappa_B/\kappa_P = 1$, are shown in Fig. 3(b) and exhibit strong first-

FIG. 4. (a) Model phase diagram in κ_B/κ_P - ε_{Ox} plane. The regions in the parameter space showing polar and breathing instability have been marked. The solid line is a guide to the eye. (b) The evolution of the breathing (δ_B) and polar (δ_P) distortions amplitudes as a function of ε_{Ox} , for $\kappa_B/\kappa_P = 1$.

order transition as $\varepsilon_{Ox}/t_{pp\sigma}$ crosses 3.33 or $\varepsilon_{Ox} = 5$ eV, from a breathing mode to a polar mode phase. We find that the phase transition remains first order for all other κ_B/κ_P ratios shown in the phase diagram. This phenomenology is in good agreement with conclusions drawn from DFT calculations [cf. Fig. 2(c)], proving the robustness and generality of our conclusions.

V. COMPOUNDS WITH ASSOCIATED ORBITAL DEGENERACIES AT B-SITE

In our discussion so far, we focused on lattice instabilities arising out of only the A-site. However, the situation gets complex when the lattice instabilities associated with orbital degeneracies at the B-site also participate. A pertinent example in this context is BiCoO₃ (BCO). The B-site TM element, Co, lies in between Fe and Ni in the periodic table. The calculated energy-level diagram in BCO shows the positioning of Bi 6s and Bi 6p, relative to O 2p, to be more similar to that of BNO than that of BFO (see the Supplemental Material). This would support suppression of polar instability and promotion of breathing instability. Calculated spread of Bi s effective Wannier function also supports this idea. However, BCO is found to be ferroelectric with polar, tetragonal crystal structure [7]. This polar distortion, however, is primarily driven by the d^6 configuration of high-spin configuration Co³⁺ which prefers a large off-centric displacement of the Co³⁺. This situation may be compared to the case of PVO, which in its polar, tetragonal phase shows the off-centric vanadyl distortion of V⁴⁺ with d^1 occupancy. As pointed out before, the difference between PVO and PCO is much less obvious than BFO and BNO, making the situation indeed similar to that of BCO [30].

In this respect, BiCrO₃ with Cr in its orbitally inactive d^3 configuration is more akin to BFO, which according to phase diagram presented in Fig. 4, should show polar instability. As was found experimentally [31] as well as theoretically [32], BiCrO₃, like its counterpart BiFeO₃, is unstable in the ideal cubic perovskite phase, with a structural instability driven by the stereochemical activity of the Bi lone pair. Following the same guideline, one would expect PbFeO₃ with orbitally inactive Fe d^5 nominal state to show a disproportionate charge-driven breathing distortion at the A-site, as in the case of PCO. Such a suggestion was indeed made [33], and PbFeO₃ was

synthesized under high pressure [34], but the situation remains to be settled.

VI. CONCLUSION

In summary, analyzing the first-principles electronic structure, combined with model Hamiltonian study, we examine the instability toward polar versus breathing distortions of Bi/Pb-O sublattice in TM perovskites. Our study reveals that instability toward breathing or polar instability is dictated by relative mixing of O p states with filled A-site s state and empty A-site p states. Choice of B-site tunes the position of effective O p states by influencing the B-O hybridization.

Replacement of Fe by Ni at the B-site of BiFeO₃ thus triggers breathing distortion instead of polar. This general picture may get modified in the presence of orbital degeneracy at the B-site, which can lead to polar distortion of B-O sublattice, dominating over the instabilities at A-O sublattice.

ACKNOWLEDGMENTS

T.S.-D. thanks the Department of Science and Technology, India, for the support through Thematic Unit of Excellence. I.D. thanks the Department of Science and Technology, India, for support.

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