Oxygen tilt driven polar superorders in BiFeO₃-based superlattices

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Ferroelectric-dielectric superlattices have attracted renewed interest for their ability to frustrate the polar order, leading to the emergence of exotic polar textures. The electrostatic depolarization, thought to be responsible for the complex polar textures in these superlattices, can be alleviated by replacing the dielectric layer with a metallic one. One would thus expect that a close to uniform polarization state be recovered in the ferroelectric layer. However, here we show, using density-functional theory calculations, that metastable antipolar motions may still appear in superlattices combining multiferroic BiFeO₃ and metallic SrRuO₃ perovskite layers. We find that a complex oxygen octahedra tilt order, a so-called nanotwin phase, exists in BiFeO₃/SrRuO₃ superlattices and competes with a more conventional phase. It leads to a doubling of the chemical period along the out-of-plane direction, owing to the presence of an oxygen octahedra tilt-wave pattern and antipolar motions caused by trilinear energy couplings. We also show that out-of-plane polar displacements in the BiFeO₃ layer may reverse the (anti)polar displacements thanks to a strong quadrilinear coupling term. The oxygen tilt-driven couplings identified here may open new ways to engineer and control polar displacements in superlattice-based polar metals and hybrid improper (anti)ferroelectrics.

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Ferroelectric superlattices (SLs) are repeated stacking of alternating ferroelectric nanolayers and dielectric or metallic layers. SL architectures allow to control both mechanical and electrical boundary conditions felt by the ferroelectric nanolayers. Intriguing new physics has resulted from exploring ferroelectric SLs and nanostructures, such as the presence of polar, topologically protected quasiparticles [1–7], often emerging as low-energy metastable states [5,8,9]. In fact, metastable phases have been wildly evidenced in ferroelectric nanostructures and manipulated, for instance with strain, electric fields [10,11] or optical excitation [12,13] to achieve new exotic properties such as negative capacitance [14–16] when reaching these hidden phases.

In most ferroelectric/dielectric SLs, a uniformly out-ofplane polarized ferroelectric nanolayer would experience a large depolarizing electric field, resulting from poor electrostatic screening of the polarization-bound charges by the dielectric layer. Electrostatic frustration was thus put forward as an explanation of the resulting structure, and thus functional properties [3,17,18] of ferroelectric SLs. It is however legitimate to ask whether other degrees of freedom, such as oxygen octahedra tilts in perovskite oxides, play an important role in the formation of complex structural phases in SLs. One way to test this hypothesis is to employ a *metallic* spacing layer rather than a dielectric one, thus limiting or canceling electrostatic depolarizing effects.

In this regard, we mostly focus on BiFeO₃/SrRuO₃ SLs. BiFeO₃ (BFO) is a prototypical multiferroic with large spontaneous polarization, antiferromagnetic order superimposed with a cycloidal spin modulation and strong $a^{-}a^{-}a^{-}$ oxygen octahedra tilt pattern in Glazer notation [19] at room temperature [20-23]. Recent works have reported emerging complex phases in BFO-based superlattices, such as antiferroelectric phases in BiFeO₃/LaFeO₃ [24] and BiFeO₃/NdFeO₃ [25] SLs. Perhaps most strikingly, BiFeO₃/TbScO₃ SLs have shown the room-temperature coexistence of a complex polar phase and an antiferroelectric Pnma phase as well as their electrical control [10]. In addition, BFO has a rich polymorphic playground, with for instance a low-energy lying Pnma phase [26,27] with $a^-a^-c^+$ tilts. It can thus be hoped that a large number of phases, and properties, can be addressed even in BFO/metal SLs if one manages to frustrate its octahedra rotation pattern, for instance by associating BFO with a perovskite metal having an $a^-a^-c^+$ tilt pattern such as SrRuO₃ (SRO) [28,29].

The present work uses density-functional theory (DFT) calculations to explore the impact of oxygen octahedra tilt rotation on the emergence of complex phases in BFO-based SLs. We show that, despite the metallic nature of SRO, which limits depolarizing effects, unexpected in-plane antipolar motions may be retained in the SL in a competing superordered phase. We attribute this result to the strong trilinear coupling between Bi cations motion and oxygen octahedra tilts. Concurrently, polar displacements in the out-of-plane direction are retained in the BFO layer due to screening of the polarization charges by the metallic SRO layer. We show that this

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FIG. 1. Phonon instabilities in high-symmetry superlattices $[BiFeO_3]_1/[SrRuO_3]_1$ superlattices. (a) Sketch of the $2 \times 2 \times 2$ supercell with atoms in their cubiclike, high-symmetry positions. (b) Phonon dispersion in the cubiclike phase (high-symmetry points in the first Brillouin zone are defined in the Supplemental Material [43]).

out-of-plane polar displacement may help control the direction of (anti)polar in-plane atomic motions thanks to quadrilinear coupling involving oxygen octahedra tilts.

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [30-33] with the projector augmented waves method [33,34]. Our pseudopotentials include valence electrons from Bi 5d, 6s, and 6p, Fe 3s, 3p, 3d, and 4s, Sr 4s, 4p, 5s, Ru 4s, 4p, 4d, 5s, and O 2s, 2p states. We employ the PBESol exchange-correlation functional [35]. Following the literature, we apply a Hubbard correction [36] of 4 eV and 0.6 eV on the d orbitals of Fe [26] and Ru [37,38] atoms. Collinear magnetism is assumed. The plane-wave cutoff is 500 eV, meanwhile a $5 \times 5 \times 5$ Monkhorst-Pack mesh [39] is employed. Total energy is converged below 10^{-7} eV in self-consistent cycles. Structural convergence is achieved when the forces are smaller than 2 meV/Å. To mimic the effect of epitaxial strain imposed by a cubic SrTiO₃ substrate, we fix the in-plane lattice constants of the SLs to 3.895 Å, as calculated from DFT. At the SrTiO₃ in-plane lattice constant (and in general reasonable strains in the range -2%to +2%), we do not expect strained BiFeO₃ and SrRuO₃ to exhibit markedly different structural properties from the bulk according to the literature [40,41]. Phonon band structures for high-symmetry (cubiclike) BFO/SRO SLs were obtained using density-functional perturbation theory as implemented in VASP and the PHONOPY package [42].

We start by calculating the phonon dispersion of $[BiFeO_3]_1/[SrRuO_3]_1$ SL (subsequently noted BFO₁/SRO₁), with all ions fixed in the high-symmetry positions of the cubic perovskite structure [see Fig. 1(a)]. The high-symmetry structure has *P4mm* space group due to the chemical arrangement. The phonon dispersion, shown in Fig. 1(b), shows strong imaginary frequencies (depicted as negative), a hallmark of major structural instabilities. The most prominent instabilities exist at the *M* (1/2, 1/2, 0) and *A* (1/2, 1/2, 1/2) points in the Brillouin zone. The lowest-frequency unstable *M* mode corresponds to antiphase oxygen octahedra tilts along the



FIG. 2. Atomic patterns in conventional and superordered phases. (a) Ground-state relaxed structure and (b) its projection on phonon modes of the high-symmetry structure; (c) superordered relaxed structure and (d) its projection on phonon modes of the high-symmetry structure. Arrows on the left of each structure depict *A*-site cation displacements, while rotating arrows on the structure depict M_5 -related oxygen tilts. Right side rotating arrows depict clockwise (blue) or anticlockwise oxygen octahedra rotation associated with M_2 (a) and A_2 (c) modes.

out-of-plane direction (see Supplemental Material [43]). We adopt a Glazer-like notation $a^{-/+}b^{-/+}c^{-/+}$ for each pseudocubic perovskite cell, where -/+ indicates anticlockwise and clockwise rotation of the oxygen octahedron. We can then describe the lowest unstable M mode by the sequence $00c^+/00c'^+$ for the BFO₁/SRO₁ SL. The unstable mode at the A point, which has A_2 symmetry [43], corresponds to a complex wavelike arrangement of oxygen octahedra tilts, leading to doubling of the SL period [see Fig. 2(c) and Fig. 3]. In our Glazer-like notation, this mode corresponds to a tilt pattern $00c^{-}/00c^{+}/00c^{+}$. Concurrently, less unstable modes at Γ [see Fig. 1(b)] show polar displacements carried by off-centering of the Bi ions in plane (Γ_5 symmetry) and out of plane (Γ_1 symmetry), respectively. Interestingly, the Γ -Z lowest unstable branch is flat, indicating that polar motions of the Bi ions between two BFO layers separated by a SRO layer do not carry an additional electrostatic cost compared to their antipolar displacement. The metallic nature of the SRO, therefore, likely screens the electrostatic dipolar energy cost associated with in-plane polar motions, and thus effectively decouples the in-plane polar motions of successive BFO layers. Note that the Γ -Z branch flatness also suggests the possibility to access polar states which combine



FIG. 3. Complex tilt patterns in BFO/SRO superlattices. (a) BFO₁/SRO₁ in-plane tilt angle (yellow diamonds) associated with the M_5 mode and out-of-plane tilts (circles) associated with the M_2 (yellow) and A_2 (orange) modes. The conventional and superordered phase are depicted by dashed and plain lines, respectively. (b) Oxygen octahedra tilt angles in the conventional (dashed lines) and superordered (plain lines) phase of BFO₂/SRO₂, with the same color code as (a).

multiple k points, as can be the case for polar skyrmions or vortices [1,2].

Next, we relax the full BFO_1/SRO_1 superlattice in a $2 \times 2 \times 4$ pseudocubic supercell (effectively simulating a BFO₁/SRO₁/BFO₁/SRO₁ arrangement in the out-of-plane direction), thus allowing the significant A and Z instabilities to develop and double the chemical wavelength. After exploring various atomic distortions starting points, we eventually find two structures with minimal energy. The first one, the ground state, is depicted in Fig. 2(a). It is characterized by (i) an $a^{-}a^{-}c^{+}$ general tilt system in Glazer notation and (ii) outof-plane and in-plane polar motions in the BFO layer along the $[00\overline{1}]$ and [110] directions, respectively. Out-of-plane polar motions show displacements of the Bi ions towards FeO₂ planes, and have Γ_1 symmetry. They represent $\approx 40\%$ of the distortions [Fig. 2(b)]. In-plane polar motions, of Γ_5 symmetry, consist mostly of opposite motions of Bi and O along the [110] direction and represent 40% of the distortions. Small Sr and O motions, opposite to the BiO plane motions, are also present, a feature reminiscent of hybrid improper ferroelectrics [44,45], and whose origin can be traced back to known atomistic couplings between dipolar displacements and oxygen octahedra tilts in perovskite oxides [46]. Of course, the present SLs are metallic in the RuO₂ planes (see Supplemental Material [43]). Thus the ground state (which we coin conventional phase) is not ferroelectric but exhibits polar features. Octahedra tilts account for the remaining 20% of the structural distortions, with M_5 [a^-a^-0 tilts of amplitude 6–8°, see Fig. 3(a)] and M_2 (00 c^+ tilts with typical amplitude of 11.5° in the BFO layer and 4° in the SRO layer) modes each contributing to about 10% of the distortion. In comparison, our calculated value for bulk octahedra rotation in BFO and SRO are respectively 12.6° and 7° .

Surprisingly, our relaxation evidenced a second structure with very close energy to the ground state (9 meV/perovskite cell), depicted in Fig. 2(c). We observe that the structural period is doubled out of plane with respect to the superlattice chemical period. We refer to this structure as superordered. The superordered structure has similar M_5 -symmetry a^-a^-0 tilt pattern and amplitude as the ground-state structure [see Fig. 3(a)]. It possesses, as well, similar out-of-plane polar motions of the Bi ions, albeit with smaller amplitude than the conventional phase. The main differences between the conventional and superordered structure arise from the condensation of a tilt-wavelike pattern of A_2 symmetry [see Fig. 2(c) and Fig. 3] and in-plane antipolar displacements of Z_5 symmetry. The Z_5 displacements resemble the Γ_5 displacements of the conventional phase, but reverse sign every SL chemical period [see Fig. 2(c)]. They account for 60% of the superordered structure distortions. The A_2 mode, a tilt-wavelike pattern where rotations around the out-of-plane axis alternate between clockwise and anticlockwise every period [see Figs. 2(c) and 3(a)], represents about 14% of the total distortions [Fig. 2(d)]. It is an instance of the nanotwin phases predicted to occur in BFO at high temperature [47] or in BiFeO₃/NdFeO₃ solid solutions [48], and generates the antipolar displacement pattern Z_5 arising from trilinear couplings in the free-energy landscape of the form $M_5A_2Z_5$ (see below, and Ref. [46]).

Whether combining perovskites with competing tilt systems in superlattices universally leads to the existence of (meta)stable superordered phases likely relies on the relative strength of the tilt instabilities in the high-symmetry phase of the perovskites composing each nanolayer. Yet, our work shows that BFO-based SLs are an interesting playground to engineer such superordered phases, as recent experimental reports have found some evidence of their existence via high-resolution transmission electron microscopy [49] or xray diffraction [50,51]. In addition, we predict that (i) larger SLs, such as BFO₂/SRO₂, also exhibit metastable superorder tilt-wavelike patterns associated with antipolar features (see Fig. 3(b) and Supplemental Material [43]); (ii) BFO/dielectric SLs, such as BiFeO₃/LaFeO₃ (BFO/LFO), also harbor such metastable superordered phases (see Supplemental Material [43]), consistent with recent observations [49] indicating competing conventional and superordered phases in BFO_n/LFO_n up to n = 5.

Since the conventional [Fig. 2(a)] and superordered [Fig. 2(c)] phases are so close in energy (9 meV/p.u.), it is possible that they coexist at room temperature $(\frac{k_BT}{2} \approx 12.5 \text{ meV} \text{ at room temperature})$, as coexisting metastable phases have already been observed in some BFO-based superlattices [10,49]. It is also known that external stimuli such as THz or visible excitation [52], thermal quenching [53], or electric field application [10] (for dielectric superlattices such as BFO/LFO) may be employed to access close in energy metastable states. We now set out to understand the atomistic energy landscape explaining the emergence of this superordered phase in BFO₁/SRO₁ using symmetry-relevant modes and a Taylor expansion of the energy around the high-symmetry structure of Fig. 1(a). Such approach has been



FIG. 4. Energetics and potential for polar displacement switching. (a) Energy with respect to the high-symmetry phase, when modes are condensed. (b) Energy with respect to the high-symmetry phase when u_{Z_5} (red) is condensed while ϕ_{M_5} , $\phi_{A_2} = 1$ and when Γ_5 (blue) is condensed while ϕ_{M_2} , $\phi_{M_5} = 1$. Dashed lines indicate no out-of-plane polar displacement ($u_{\Gamma_1} = 0$), while plain lines indicate $u_{\Gamma_1} = 1$; (c) and (d) are (ϕ_{M_2} , ϕ_{Γ_5}) and (ϕ_{A_2} , ϕ_{Z_5}) energy maps when $u_{\Gamma_1} = 1$ and $\phi_{M_5} = 1$.

successfully applied over the years to derive effective Hamiltonians in complex perovskite oxides such as BiFeO₃ [54] and related superlattices [55] providing excellent agreement with experimental observations [56,57]. Based on the projection of the atomic displacements onto the phonon calculated in Fig. 1, we were able to construct a set of six symmetryadapted characteristic displacement patterns: u_{Γ_1} represents polar displacements of the Bi sublattice in the [001] direction; u_{Γ_5} represent antipolar motions of Bi and Sr ions along the [110] direction and it is akin to polar displacements found in hybrid improper ferroelectrics [44]. Meanwhile u_{Z_5} indicates that these latter displacements change sign every chemical period along the out-of-plane direction; ϕ_{M_2} and ϕ_{A_2} represent the oxygen tilting pattern around [001] summarized in Fig. 3; ϕ_{M_5} represents an a^-a^-0 pattern of oxygen octahedra rotations. Both the conventional and superordered phases show the M_5 tilts with similar magnitude (see Fig. 3), as well as the Γ_1 polar out-of-plane polar motion of the Bi ions towards the FeO₂ plane.

To further elucidate the origin of the structural features of BFO/SRO SLs, we condense individually the displacement patterns of different symmetry to understand the energy couplings at play. Clearly, the Γ_1 out-of-plane polar mode and M_5 in-plane tilt modes are the strongest instabilities, leading each to a lowering of the energy from the high-symmetry structure by about 250 meV/p.u. each [see Fig. 4(a)].

Subsequently, once the Γ_1 and M_5 modes are condensed, only the oxygen octahedra rotation along the out-of-plane direction lower the energy, with the M_2 and A_2 modes slightly lowering the energy further. Only then, once the modes Γ_1 , M_5 , and either M_2 or A_2 are condensed, can the energy be further lowered by condensing the in-plane polar Γ_5 mode (when M_2 is condensed) or the in-plane antipolar mode Z_5 (when A_2 is condensed) as plotted in Fig. 4(b). Interestingly, Figs. 4(b)-4(d) show that the energy curve is asymmetric; symmetry analysis of possible energy couplings (see Supplemental Material [43]) reveals that it is the result of trilinear coupling terms of the form $\phi_{M_2}\phi_{M_5}u_{\Gamma_5}$ and $\phi_{A_2}\phi_{M_5}u_{Z_5}$. Quite surprisingly, the out-of-plane polar mode Γ_1 significantly alters these trilinear couplings: without it $[u_{\Gamma_1} = 0$, see dashed lines in Fig. 4(b)] the minimum of energy for the Z_5 or Γ_5 mode is reversed compared to the case $u_{\Gamma_1} = 1$. This quadrilinear coupling with out-of-plane polar displacements creates new opportunities to use BFO-based SLs to engineer switchable hybrid-improper polar displacements. Polarization is notoriously difficult to switch in hybrid-improper ferroelectrics. Since we have indications that the features exposed in this work apply to other BFO-based SLs [49], one may envision new pathways to switch polarization in hybrid-improper ferroelectrics. In particular, in BFO/dielectric superlattices, one could imagine to manipulate u_{Γ_1} via electric fields or optical excitation, and leverage the mechanisms demonstrated in Fig. 4(b) to eventually switch the in-plane polarization. In fact, we show in the Supplemental Material [43] that u_{Γ_1} can indeed control the direction of in-plane polar moments in $[BiFeO_3]_1/[LaFeO_3]_1$ SLs.

The present work, by means of *ab initio* calculations, reveals that tilt-induced nanotwin superorders can be engineered in multiferroic BiFeO₃-based SLs. We also show that, even in BFO/metal SLs, one may generate antipolar displacements due to trilinear couplings acting in the nanotwin phase. Furthermore, the coupling between the out-of-plane polar displacements, in-plane (anti)polar, and tilts may be a step towards control of the polarization in hybrid-improper ferroelectrics of hybrid-improper polar metals, for instance via electrical or optical means, or THz manipulation using the squeezing effect to reduce the out-of-plane polarization [58]. Future works will investigate how to further stabilize these superordered phases and manipulate the polar order in various BFO-based superlattices. A promising prospect is the use of tensile biaxial strain, as shown in the Supplemental Material [43].

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