**Ab initio** design of charge-mismatched ferroelectric superlattices

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We present a systematic approach to modeling the electrical and structural properties ofchargemismatched superlattices from first principles. Our strategy is based on bulk calculations ofthe parent compounds, which we perform as a function of in-plane strain and out-of-plane electricdisplacement field. The resulting two-dimensional phase diagrams allow us to accurately predict,without performing further calculations, the behavior of a layered heterostructure where the aforementioned building blocks are electrostatically and elastically coupled, with an arbitrary choiceof the interface charge (originated from the polar discontinuity) and volume ratio. By using the[\(\text{PbTiO}_3\)]\(_m\)/[\(\text{BiFeO}_3\)]\(_n\) system as test case, we demonstrate that interface polarity has a dramaticimpact on the ferroelectric behavior of the superlattice, leading to the stabilization of otherwiseinaccessible bulk phases.

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INTRODUCTION

When layers of perovskite oxides are epitaxially stacked to form a periodically repeated heterostructure,new intriguing functionalities can emerge in the resulting superlattice \(^1\,\,2\). These are further tunable viaapplied electric fields and thermodynamic conditions, and thus attractive for nanoelectronics and energyapplications. An excellent example is the [\(\text{PbTiO}_3\)]\(_m\)/[\(\text{SrTiO}_3\)]\(_n\) system, where the polarization, tetragonality, piezoelectric response, and ferroelectric transition temperaturestrongly change with the volume ratio of the parent compounds \(^3\,\,4\). Such a remarkable tunability is usuallyrationalized in terms of epitaxial strains \(^5\), electrostatic coupling (see Fig. 1a) \(^5\,\,8\), and local interfaceeffects \(^5\,\,10\).

While perovskite titanates with \(\text{ATiO}_3\) formula (\(\text{A}=\text{Sr, Pb, Ba or Ca}\)) have traditionally been the most popularchoice as the basic building blocks, a much wider range of materials (e.g., \(\text{BiFeO}_3\)) is currently receiving increasingattention by the community. The motivation for such an interest is clear: a superlattice configuration provides theunique opportunity of enhancing materials properties via “strain engineering”, and a multifunctional compound such as \(\text{BiFeO}_3\) appears to be a natural candidate in thiscontext. (For example, strain has been predicted to enhance the magnetoelectric response of \(\text{BiFeO}_3\) by severalorders of magnitude compared to bulk samples \(^11\,\,12\).) Also, a superlattice geometry can alleviate the leakageissues of pure \(\text{BiFeO}_3\) films \(^13\,\,14\).

Combining a III–III perovskite like \(\text{BiFeO}_3\) (or I–V, like \(\text{KNbO}_3\)) with a II–IV titanate appears, however,problematic from the conceptual point of view. In fact, the charge-family mismatch inevitably leads to polar (and hence electrostatically unstable) interfaces between layers \(^15\). This is not necessarily a drawback, though: recent research has demonstrated that polar interfaces can be, rather than a nuisance to be avoided, a rich playground to be exploited for exploring exciting new phenomena. The prototypical example is the \(\text{LaAlO}_3/\text{SrTiO}_3\) system, where a metallic two-dimensional electron gas appears at the heterojunction to avoid a “polar catastrophe” \(^16\,\,17\). Remarkably, first-principles calculations have shown that interfaces in oxide superlattices can remain insulating provided that the layers are thin enough, and produce rather dramatic effects on the respective polarization of the individual components \(^15\,\,18\). This means that, in a superlattice, polar discontinuities need not be compensated by electronic orionic reconstructions; they can, instead, be used as an additional, powerful materials-design tool to control thebehavior of the polar degrees of freedom therein. Such a control may be realized, for instance, by altering the stoichiometry at the interfaces (see Fig. 1b). To fully explore the potential that this additional degree of freedom (the interface built-in polarity) provides, and guide the experimental search for the most promising materials combinations, one clearly needs to establish a general theoretical framework where the “compositional charge” \(^15\) is adequately taken into account.

In this Letter, we present a general first-principles approach to predict the behavior of charge-mismatchedperovskite oxide superlattices based exclusively on the properties of their individual bulk constituents. Our formalism combines the constrained-\(D\) strategies of Wu \textit{et al.} \(^19\), which are key to decomposing the total energy of the system into the contributions of the individual layers, with the rigorous description of the interface polarity proposed in Ref. \(^20\). As a result, we are able to exactly describe the electrostatic coupling and mechanical boundary conditions, enabling a clear separation between genuine interface and bulk effects. Crucially, the present method allows one to quantify, in a straightforward way, the impact that interface polarity has on the equilibrium (and metastable) phases of the superlattice. As a proof of concept we apply our formalism to the study...
FIG. 1: (Color online) (a) Description of the electrostatic coupling in a ferroelectric (orange)/paraelectric (blue) bilayer; $P$, $E$, and $D$ represent the component of the polarization, electric field and electric displacement vectors along the stacking direction, and $\sigma_{\text{int}}$ is the interface charge density. (b) Intermixed AO-type interfaces in a $[\text{BiFeO}_3]_m/[\text{PbTiO}_3]_n$ superlattice and the resulting interface charge densities. (c) Illustration of the 20-atom simulation cell used in our calculations; red, blue and black spheres represent O, B, and A atoms in the ABO$_3$ perovskite.

FIG. 2: (Color online) Energy of PTO/BFO superlattices with $a = 3.81$ Å expressed as a function of $D$, for selected values of $\lambda$ and $\sigma_{\text{int}}$. Equilibrium and metastable superlattice states are represented with solid and empty dots. Red (green) vertical lines indicate phase transitions occurring in bulk BFO (PTO) under different $D$ conditions. (a) and (b) represent the cases of neutral and polar interfaces, respectively.

We find that (i) our bulk model accurately matches earlier first-principles predictions obtained for ultrashort-period superlattices (i.e., $m = n = 3$) by using explicit supercell simulations [21], and (ii) by assuming interface terminations with different nominal charge, we obtain a radical change in the overall ferroelectric properties of the superlattice, which demonstrates the crucial role played by the polar mismatch.

We start by expressing the total energy of a monodomain two-color superlattice (i.e., composed of species A and B) as,

$$U_{\text{tot}}(D, \lambda, a) = \lambda \cdot U_A(D, a) + (1 - \lambda) \cdot U_B(D, a).$$

Here $U_A$ and $U_B$ are the internal energies of the individual constituents, $D$ is the electric displacement along the out-of-plane stacking direction (i.e., $D \equiv \mathcal{E} + 4\pi P$ where $\mathcal{E}$ is the electric field and $P$ is the effective polarization, relative to the centrosymmetric reference configuration), $\lambda$ is the relative volume ratio of material A (i.e., $\lambda \equiv m/(n + m)$ where $m$ and $n$ are the thicknesses of layers A and B, respectively), and $a$ is the in-plane lattice parameter (we assume heterostructures that are coherently strained to the substrate). Note that short-range interface effects have been neglected. (While it is certainly possible to incorporate the latter in the model, e.g. along the guidelines described in Ref. [19], we believe these would have been an unnecessary complication in the context of the present study.) By construction, Eq. (1) implicitly enforces the continuity of $D$ along the out-of-plane stacking direction (which we label as $z$ henceforth), which is appropriate for superlattices where the interfaces are nominally uncharged [1].

In presence of a polar mismatch, one has a net "external" interface charge, of compositional origin (see Fig. [14]), which is localized at the interlayer junctions. In such a case, Eq. (1) needs to be revised as
follows,

$$U_{\text{tot}}(D, \sigma_{\text{int}}, \lambda, a) = \lambda U_A(D, a) + (1 - \lambda) U_B(D - \sigma_{\text{int}}, a),$$

i.e. the $U_B$ curve is shifted in $D$-space to account for the jump in $D$ produced by $\sigma_{\text{int}}$. (Recall the macroscopic Maxwell equation, $\nabla \cdot \mathbf{D} = \rho_{\text{ext}}$, where $\rho_{\text{ext}}$, the “external” charge, encompasses all contributions of neither dielectric nor ferroelectric origin.) Once the functions $U_A$ and $U_B$ are computed and stored (e.g. by using the methodology of Ref. [22]), one can predict the ground-state of a hypothetical A/B superlattice by simply finding the global minimum of $U_{\text{tot}}$ with respect to $D$ at fixed values of $\sigma_{\text{int}}$, $\lambda$ and $a$. The advantage of this procedure is that, for a given choice of $A$ and $B$, the aforementioned $\sigma$ parameter space.

It is useful, before going any further, to specify the physical origin of $\sigma_{\text{int}}$ in the context of this work. Consider, for example, a periodic BiFeO$_3$/PbTiO$_3$ superlattice, which we assume (i) to be stoichiometric (and therefore charge-neutral) as a whole, (ii) to have an ideal AO-BO$_2$-AO-BO$_2$ stacking along the (001) direction, and (iii) to form (say) AO-type interfaces (see Fig. 1b). (The same arguments can be equally well applied to the case of BO$_2$-type interfaces.) Depending on the growth conditions, one can have a certain degree of intermixing in the boundary AO layers, which will adopt an intermediate composition Bi$_x$ Pb$_{(1 - x)}$O. As a pure BiO layer is formally charged $+1$ and PbO is neutral, we can readily write $\sigma_{\text{int}} = \pm \left(x - \frac{1}{2}\right)$ (expressed in units of $e$/S with S being the surface of the corresponding 5-atom perovskite cell), where the choice of plus or minus depends on the arbitrary assignment of BiFeO$_3$ and PbTiO$_3$ as the A or B component in Eq. (2) [see Fig. 1c]. In the following we shall illustrate the crucial role played by $\sigma_{\text{int}}$ (and hence, by the interface stoichiometry) on the ferroelectric properties of a BFO/PTO superlattice, by combining Eq. (2) with the bulk $U_{\text{BFO}}(D, a)$ and $U_{\text{PTO}}(D, a)$ curves that we calculate from first principles.

Our calculations are performed with the “in-house” LAUTREC code within the local spin density approximation to density-functional theory. (We additionally apply a Hubbard $U = 3.8$ eV to Fe ions.) We use the 20-atom simulation cell depicted in Fig. 1d for both BFO and PTO, which allows us to describe the ferroelectric and anti-ferrodistortive (AFD) modes of interest (i.e. in-plane AFD$_{xz}$ and out-of-plane AFD$_{x0}$ and AFD$_{xy}$, see Ref. [18]). Atomic and cell relaxations are performed by constraining the out-of-plane component of $D$ and the in-plane lattice constant $a$ to a given value. Calculations are repeated many times in order to span the physically relevant two-dimensional $(D, a)$ parameter space.

We start by illustrating the results obtained at fixed strain, $a = 3.81$ Å (see Fig. 2), by assuming $\sigma_{\text{int}} = 0$, which corresponds to fully intermixed junctions ($x = 0.5$), and we vary the BFO volume ratio, $\lambda$. At the extreme values of $\lambda$, the results are consistent with the expectations: the equilibrium configuration of BFO (i.e., the minimum of $U_{\text{tot}}$ with $\lambda = 1$) at this value of $a$ is the well-known R-type $Cc$-I phase [23], derived from the bulk ground state via the application of epitaxial compression; PTO ($\lambda = 0$), on the other hand, is in a tetragonal $P4mm$ phase with the polarization vector oriented out of plane. Intermediate values of $\lambda$ yield a linear combination of the two single-component $U(D)$ curves, where the spontaneous $P_s$ at equilibrium gradually moves from the pure PTO to the pure BFO value.

Unfortunately, the possible equilibrium states that can be attained by solely varying $\lambda$ (at this value of $a$ and $\sigma_{\text{int}}$) lie far from any physically “interesting” region of the phase diagram. For example, note the kink at $|D| \sim 0.3$ C/m$^2$ in the pure BFO case, which corresponds to a first-order transition to an orthorhombic $Pn\overline{2}a_1$ phase (a close relative of the higher-symmetry $Pnma$ phase, occurring at $D = 0$). A huge piezoelectric and dielectric response is expected in BFO in a vicinity of the transition [20], raising the question of whether one could approach this region by playing with $\sigma_{\text{int}}$, in addition to $\lambda$.

The answer is yes: when oxide superlattices with $\sigma_{\text{int}} = 0.5$ are considered [corresponding to “ideal” (BiO)$^+$/TiO$_2$ and (FeO$_2$)$^-$/PbO interfaces], the stable minimum of the system favors a smaller spontaneous polarization in the BFO layers, approaching the aforementioned ($Cc$–I $\rightarrow$ $Pn\overline{2}a_1$) phase boundary in the limit of small $\lambda$. Interestingly, the $U_{\text{tot}}(D)$ curve becomes asymmetric (the interfacial charge breaks inversion symmetry), and a secondary, metastable minimum appears. Overall, the resulting phase diagram turns out to be much richer, with new combinations of phases emerging (e.g. in region II$, where BFO exists in the orthorhombic $Pn\overline{2}a_1$ phase and PTO in the tetragonal $P4mm$ phase), and highly non-trivial changes in the electrical properties occurring as a function of $\lambda$.

In order to further illustrate the power of our approach, we shall now fix the volume ratio to $\lambda = 0.5$ (corresponding to alternating BFO and PTO layers of equal thickness) and vary the in-plane lattice parameter in the range $3.6 \leq a \leq 4.2$ Å. We shall first consider the case of charged interfaces with $\sigma_{\text{int}} = 0.5$, as this choice allows for a direct comparison with the results of Yang et al. (obtained via standard supercell simulations) [21]. In Fig. 3 we show the energy and spontaneous electric displacement of the equilibrium and metastable states as a function of $\lambda$. Four regions can be identified in the diagrams depending on the phases adopted by BFO and PTO at each value of the in-plane strain. (Their crystal space groups, AFD pattern and in-plane / out-of-plane ferroelectric polarization, respectively $P_{xy}$ and $P_z$, are specified in compact form in the figure.) In region I’
related to the orthorhombic $I$ state. In region III, BFO remains $P$ zero characterized by large in-phase AFD $z$. Such a monoclinic $P$ phase is closely related to the orthorhombic $Pmc_{2}$ structure which has been recently predicted in PTO and BFO at large tensile strains [24].

In region II' PTO adopts an orthorhombic $Ima_{2}$ phase, characterized by vanishing AFD distortions and a large in-plane $P$ (we neglect the small out-of-plane $P_{z}$), while BFO is in its well-known $Cc$-I state. In region III, BFO remains $Cc$-I, while PTO adopts a $P4mm$ phase, both with opposite out-of-plane polarization with respect to region II'. These structures switch back to a positively oriented $P_{z}$ in region IV', respectively transforming into a monoclinic $Cc$-II and a tetragonal $I4cm$ phase. The $I4cm$ phase is characterized by anti-phase AFD distortions and an out-of-plane $P$, while the $Cc$-II corresponds to the “supertetragonal” $T$-type phase of BFO [27]. Note that, as observed already while discussing Fig. 2, the net interface charge leads to an asymmetric double-well potential, and consequently to an energy difference (typically of $\sim 20$ meV/f.u. or less, see Fig. 3b) between the two oppositely polarized states. (Only one minimum survives at large tensile strains, where the superlattice is no longer ferroelectric.)

At the phase boundaries such energy difference vanishes; the obvious kinks in the $U_{tot}$ curve shown in Fig. 3(a) indicate that the transitions (at $a = 3.71, 3.87$, and $4.05$ Å) are all of first-order type.

The above results are in remarkable agreement with those of Yang et al. [21]. The only apparent discrepancy concerns the ordering of the stable/metastable states in region III, which anyway involves a very subtle energy difference (and is therefore sensitive to short-range interface effects, not considered here). Obtaining such an accurate description of superlattices where the individual layers are as thin as three perovskite units [21] provides a stringent benchmark for our method, and validates it as a reliable modeling tool. From the physical point of view this comparison suggest that, even in the ultrathin limit, PTO/BFO superlattices can be well understood in terms of macroscopic bulk effects, i.e., short-range interface-specific phenomena appear to play a relatively minor role.

Having gained confidence in our method, we can use it to predict the behavior of a hypothetical superlattice with $\sigma_{int} = 0$, corresponding to a centrosymmetric reference structure with fully intermixed $Pb_{0.5}Bi_{0.5}O$ interface layers (see Fig. 4). Note the symmetry of the two opposite polarization states, and the common value of the spontaneous electric displacement adopted by BFO and PTO. The resulting phase diagram consists, again, in four regions, with a first-order and two second-order phase transitions occurring at $a = 4.07, 3.88$ and $3.73$ Å, respectively (see Fig. 4b). In three of these regions, the individual layers display structures which are different from those obtained in the $\sigma_{int} = 0.5$ case: in region I both PTO and BFO stabilize in an orthorhombic $Pmc_{2}$ phase [24], characterized by a vanishing $P_{z}$; in region II PTO adopts a monoclinic $Cm$ phase with the polarization roughly oriented along (111) ($P_{z} \neq P_{xy}$) and no AFD, while BFO stabilizes in the already discussed $Cc$-I phase; finally, in region IV, PTO is tetragonal $P4mm$ and BFO is monoclinic $Cc$-II. These findings quantitatively demonstrates that the interface charge mismatch can have a tremendous impact on the physical properties of oxide superlattices. Our simple and general method allows one to model and quantify accurately these effects, and most importantly to rationalize them in terms of intuitive physical concepts.

In summary, we have discussed a general theoretical framework to predict the behavior of charge-mismatched superlattices. We have showed that the effect of the interface stoichiometry, which we describe via the “com-
positional” interface charge $\sigma_{\text{int}}$, is quite dramatic, and needs to be properly accounted for in the models. More generally, we argue that $\sigma_{\text{int}}$ can be regarded, in addition to $\lambda$ and $a$, as a further degree of freedom in designing oxide heterostructures with tailored functionalities, opening exciting new avenues for future research.

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