Theoretical investigation of polarization-compensated II-IV/I-V perovskite superlattices

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Recent work suggested that head-to-head and tail-to-tail domain walls could be induced to form in ferroelectric superlattices by introducing compensating “delta doping” layers via chemical substitution in specified atomic planes [Phys. Rev. B 73, 020103(R), 2006]. Here we investigate a variation of this approach in which superlattices are formed of alternately stacked groups of II-IV and I-V perovskite layers, and the “polar discontinuity” at the II-IV/I-V interface effectively provides the delta-doping layer. Using first-principles calculations on SrTiO$_3$/KNbO$_3$ as a model system, we show that this strategy allows for the growth of a superlattice with stable polarized regions and large polarization discontinuities at the internal interfaces. We also generalize a Wannier-based definition of layer polarizations in perovskite superlattices [Phys. Rev. Lett. 97, 107602 (2006)] to the case in which some (e.g., KO or NbO$_2$) layers are non-neutral, and apply this method to quantify the local variations in polarization in the proposed SrTiO$_3$/KNbO$_3$ superlattice system.

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Ferroelectric materials have been the subject of increasing theoretical and experimental study in recent years. In particular, multicomponent superlattices based on ABO$_3$ perovskites have been shown to possess many interesting properties (see Ref. 1 and references therein). Currently, heterointerfaces between different ABO$_3$ perovskites are also the subject of intense investigation. Given the huge number of possible superlattice arrangements, it is prudent to investigate systems of potential interest using first-principles calculations to confirm a given system possesses the desired properties before experimental work is performed.

In recent work, Wu and Vanderbilt introduced a novel concept in which 180° head-to-head (HH) and tail-to-tail (TT) domain walls are induced to form in a ferroelectric superlattice via the insertion of compensating “delta doping” layers. For example, in a II-IV ABO$_3$ perovskite, column III or V ions could replace the IV ions in one BO$_2$ layer, inducing the formation of a HH or TT domain wall respectively. Usually the formation of a HH or TT domain wall perpendicular to the polarization direction would entail an unacceptable Coulomb energy cost, or cause the domain wall to become metallic in order that free carriers could compensate the domain wall. However, it was shown that the delta-doping layers could be arranged to compensate the polarization bound charge and allow a structure in which the ferroelectric domains are polarized in opposite directions and are separated by HH and TT domain walls.

Here we examine the possibility of forming a multicomponent perovskite superlattice with similarly large discontinuities in the local electric polarization by making use of alternating II-IV and I-V perovskite constituents. In this case, the “polar discontinuity” associated with the II-IV/I-V interface plays the role of delta-doping layer and compensates the polarization bound charge at the interface. (Clearly a similar strategy could be applied to II-IV/III-III perovskite superlattices.) The resulting structure is not switchable, but is locally polarized and has strongly broken inversion symmetry. We demonstrate this concept via first-principles calculations on SrTiO$_3$/KNbO$_3$ as a prototypical system, showing successful compensation and robust formation of locally polarized regions. Superlattices of this type are shown to remain insulating to rather large layer thicknesses. Finally, we clarify how the Wannier-based definition of layer polarization in perovskite superlattices introduced in Ref. 10 can be generalized for a system having non-neutral AO or BO$_2$ constituent layers, and apply this to the SrTiO$_3$/KNbO$_3$ system to map out the local variations in polarization.

The type of superlattice structure we have in mind is illustrated in Fig. 1. Here, two unit cells of KNbO$_3$ (in the sequence NbO$_2$–KO–NbO$_2$–KO) repeatedly alternate with two unit cells of SrTiO$_3$ (in the sequence TiO$_2$–SrO–TiO$_2$–SrO) during growth. While each added KNbO$_3$ or SrTiO$_3$ unit cell is neutral, in KNbO$_3$ this neutrality results from the cancellation of charges on the KO$^-$ and NbO$_2^+$ layers, while in SrTiO$_3$ the individual layers are neutral. When the layers are assembled as in Fig. 1 the presence of the “polar discontinuity” introduces effective compositional charges of ±1/2 at the NbO$_2$/SrO and TiO$_2$/KO interfaces respectively, as shown. Similar effects have recently been extensively discussed for SrTiO$_3$/LaAlO$_3$ and related interfaces. Intuitively, we may regard each KO$^-$ layer in bulk KNbO$_3$ as being half-compensated from each of its two immediate NbO$_2^+$ neighbors, whereas at the TiO$_2$/KO interface the KO$^-$ is only half-compensated because it has only a single NbO$_2^+$ neighbor. The resulting compositional charge densities are $\sigma_{comp} = \pm e/2a^2$ at the NbO$_2$/SrO and TiO$_2$/KO interfaces respectively.

Two possibilities for cancelling these compositional charges in a I-V/II-IV superlattice are shown in Fig. 2. In Fig. 2a we assume that both I-V and II-IV materials are ferroelectrics, and to take an extreme case we assume
their spontaneous polarizations are equal \((P_s^{(1)} = P_s^{(2)})\) at the specified in-plane lattice constant. Arranging the polarizations so that they alternate up and down as shown, the ideal compensation \(\sigma_{\text{bound}} + \sigma_{\text{comp}} = 0\) between polarization bound charge and compositional interface charge is realized when \(P_s^{(1)} = P_s^{(2)} = e/4a^2\). A second scenario, shown in Fig. 2(b), would result from the alternation of I-V and II-IV materials, only one of which is ferroelectric, while the other is paraelectric. In this case, ideal compensation requires \(P_s = e/2a^2\) for the ferroelectric component. Intermediate cases, with the alternation of a strong and a weak ferroelectric, are also possible.

In the remainder of this paper, we focus on the scenario sketched in Fig. 2(b) as realized in the SrTiO\(_3\)/KNbO\(_3\) superlattice system, using density-functional calculations to demonstrate the compensation mechanism proposed above. The choice of SrTiO\(_3\) as the II-IV paraelectric component is motivated by the fact that it is a well-studied material\(^{11,12}\) and by the common use of SrTiO\(_3\) as a substrate for growth of thin perovskite films. With this in mind, we assume coherent epitaxy of our superlattices on SrTiO\(_3\), so that the in-plane lattice constants are constrained to the experimental value \(a_0 = 3.905\) Å of bulk SrTiO\(_3\). As explained above, ideal compensation would require that the ferroelectric I-V component should have a spontaneous polarization of \(P_s = e/2a_0^2 = 0.525\) C/m\(^2\). We have chosen KNbO\(_3\) for the I-V component because it provides a reasonable match to this value. While bulk KNbO\(_3\) is a rhombohedral ferroelectric with polarization along (111) at low temperature, its lattice constant is nearly 3% larger than that of SrTiO\(_3\). The calculations of Diéguez \emph{et al.}\(^{13}\) have shown that SrTiO\(_3\) should become a tetragonal ferroelectric with polarization along (001) when compressed in-plane to fit to the SrTiO\(_3\) lattice constant. Moreover, those same calculations indicated that the polarization of KNbO\(_3\) would be \(\sim 0.45\) C/m\(^2\) under these conditions, which is fairly close to the target value. KNbO\(_3\) also has the advantage of being a commonly used and very well-studied I-V perovskite\(^{11,12}\).

The open-source plane-wave density-functional code \textsc{pwscf}\(^{14}\) was used for the calculations, with the local-density approximation to exchange and correlation\(^{15}\) and use of ultrasoft pseudopotentials\(^{16}\). Because we have no reason to expect the appearance of in-plane polarization components in this system (see above), we have assumed tetragonal \(P4mm\) symmetry throughout.

We first calculate the theoretically optimized value of the lattice constant \(a_0\) for bulk SrTiO\(_3\) using an \(8 \times 8 \times 8\) k-point grid and a plane-wave energy cutoff of 30 Rydberg, obtaining a value of value of 3.849 Å. This leads to a theoretical ideal matching condition of \(P_s = 0.54\) C/m\(^2\). Using the same k-point grid and cutoff to study bulk KNbO\(_3\) in \(P4mm\) symmetry with its in-plane lattice constant constrained to this \(a_0\), we calculate its spontaneous polarization to be 0.42 C/m\(^2\). These results are in good agreement with previous work\(^{13}\).

Of primary importance is whether the compensation of the bound charge is sufficient to maintain the insulating nature of the system as the supercell size is increased. We consider superlattices consisting of \(n\) unit cells of SrTiO\(_3\) alternating with \(n\) unit cells of KNbO\(_3\), so that the supercell contains \(10n\) atoms. Figure 1 illustrates the case of \(n = 2\). Relaxations of the multilayered supercells are performed for values of \(n\) ranging from 1 to 5. The plane-wave energy cutoff is 30 Rydberg in all cases, and the k-point grid is \(8 \times 8 \times M\) with \(M = 4\) for \(n = 1\) and \(M = 2\) for \(n \geq 2\).

We find that the system remains insulating in all these cases. The density of states for \(n = 2\) is shown in Fig. 3 showing a clear gap between valence and conduction band states. There is, however, a gradual closing of the band

![FIG. 1: (Color online) Sketch of a possible II-IV (SrTiO\(_3\)) / I-V (KNbO\(_3\)) superlattice grown along [001].](image1)

![FIG. 2: (Color online) Two possible II-IV/I-V superlattice arrangements yielding compensating heterointerfaces and stabilized ferroelectric discontinuities. (a) Both materials are ferroelectric, with antiparallel polarizations along the growth direction. (b) One material is paraelectric and the other ferroelectric. Green and red interface charges denote polarization-induced charges, respectively.](image2)
Due to the imperfections in these multilayered systems, it is useful to start from a simple model and test whether its predictions are borne out by a more detailed analysis. The calculated band gap as a function of the supercell size is shown in the inset of Fig. 3. The results for \( n \geq 2 \) suggest a nearly linear decrease in band gap with increasing \( n \). This reduction is rather modest; a simple linear extrapolation suggests that the system would not become metallic until \( n \approx 32 \).

In order to understand the resulting local polarizations in these multilayered systems, it is useful to start from a simple model and test whether its predictions are borne out by a more detailed analysis. Due to the imperfect compensation in the system, if one starts by assembling regions of spontaneously polarized K\( \text{NbO}_3 \) alternating with regions of unpolarized Sr\( \text{TiO}_3 \), one finds planar charge densities \( \pm \sigma \) at the interfaces, with \( \sigma = P_s - e/2a^2 = -0.12 \text{C/m}^2 \). Assuming that the screening of this charge can be treated using a linear dielectric analysis and that the thicknesses of the two constituents are approximately the same, one finds a screened charge density of \( \sigma_{\text{scr}} = 2\sigma/(\epsilon_1 + \epsilon_2) \), where \( \epsilon_{1,2} \) are the dielectric constants of K\( \text{NbO}_3 \) and Sr\( \text{TiO}_3 \) respectively. The screened polarizations then become \( P_{\text{K\text{NbO}_3}} = P_s - \sigma(\epsilon_1 - 1)/(\epsilon_1 + \epsilon_2) \) and \( P_{\text{SrTiO}_3} = \sigma(\epsilon_2 - 1)/(\epsilon_1 + \epsilon_2) \). Since \( \sigma < 0 \), we expect \( P_{\text{K\text{NbO}_3}} \) to be enhanced slightly beyond its spontaneous value, and \( P_{\text{SrTiO}_3} \) to have a small value of the opposite sign.

To investigate the correctness of this picture, we perform more precise calculations of the local polarization profile. An accurate method for obtaining layer polarizations was introduced in Ref. 16, where a one-dimensional Wannier analysis was employed. To do this, the overlap matrices \( M^{(k)}_{mn} = \langle \psi_{mk} | \psi_{n,k+h} \rangle \) between neighboring k-points along strings in the \( \vec{z} \) direction are computed, where \( \psi_{mk} \) is the periodic part of the Bloch function. The singular value decomposition \( M = V \Sigma W^\dagger \) is used to obtain \( \tilde{M} = UW^\dagger \), which is exactly unitary. The eigenvalues \( \lambda_m \) of the product \( \Lambda = \prod_M^{(k)} \) of these matrices along the k-point string yield the Wannier centers as \( z_m = (-c/2\pi) \text{Im} \ln \lambda_m \). These Wannier centers form into “sheets” of charge that are localized in the growth direction but delocalized in the plane. For each layer \( j \), we define the layer center \( z_{0,j} \) to be the average position of the ions associated with that layer. The “intralayer polarization” is then given by

\[
p_{ij} = \frac{1}{S} \sum_{\tau \in j} Q_{\tau} R_{\tau z} - \frac{2e}{S} \sum_{m \in j} \bar{z}_m,  
\]

where \( S = a^2 \) is the basal cell area, \( Q_{\tau} \) is the core charge of ion \( \tau \) belonging to layer \( j \), \( R_{\tau z} \) is the position of the ion measured relative to \( z_{0,j} \), and \( \bar{z}_m \) is the position of the Wannier center \( \bar{z}_m \) relative to \( z_{0,j} \) after a \( k_x \) and \( k_y \) average over wavevector strings.

As long as each layer is neutral, the total polarization of the supercell can be obtained just as \( \langle \sum_j p_{ij}^l \rangle / c \) where \( c \) is the supercell lattice constant, because the dipole moment of a neutral layer is independent of origin. For a supercell containing charged layers like those associated with an I-V material, this sum needs to be modified to \( \langle \sum_j (p_{ij}^l + \sigma_j z_{0,j}) \rangle / c \) in order to remain meaningful as a total polarization. Here \( \sigma_j = \pm e/4 \) for a NbO\(_2\) or KO layer respectively, or 0 for a TiO\(_2\) or SrO layer. However, the second term does not take the form of a sum over layer contributions. To cast the sum into this form, we define a layer-offcentering polarization \( p_{ij}^l \) that reflects the displacement of the layer charge \( \sigma_j \) from the average position of its neighbors according to

\[
p_{ij}^l = \sigma_j \left( \frac{1}{2} z_{0,j} - \frac{1}{4} z_{0,j-1} - \frac{1}{4} z_{0,j+1} \right).  
\]

In an extended region of I-V layers, the sum \( \sum_j p_{ij}^l \) counts each charged layer once and only once, but this counting is violated at the interfaces with the II-IV layers. For example, at a NbO\(_2\)/SrO interface, we have not accounted for a charge density of \( e/4S \) in the last NbO\(_2\) layer, and we have incorrectly assigned a charge of \(-e/4S\) to the first SrO layer. The missing charge is equivalent to a charge density of \( e/2S \) located midway between the \( z_{0,j} \) values of these two layers. Similarly, a TiO\(_2\)/KO interface is assigned a charge \(-e/2S\) located halfway between these layers. Thus, the total polarization of the supercell can finally be written as \( \langle \sum_j (p_{ij}^l + p_{ij}^l) + \sum_{\mu} z_{\mu}^l \sigma_{\mu}^l \rangle / c \), where \( z_{\mu}^l \) and \( \sigma_{\mu}^l \) are the positions and charges of the extra interface charges.

The charges \( \sigma_{\mu}^l \) are, of course, nothing other than the compositional polar discontinuity charges \( \sigma_{\text{comp}} \) discussed earlier. Having accounted for these, we are left with total layer polarizations \( p_j = p_j^l + p_j^l \) associated with each layer, which thus provide a layer-by-layer picture of the polarization in this type of system. To convert these into localizations \( P_j \) having units of charge per unit area, we let \( P_j = p_j / c_j \) where \( c_j = (z_{0,j+1} - z_{0,j-1})/2 \).

The results for \( n = 4 \) are shown in Fig. 4. These are very indicative of the results obtained for the supercell.
The saw-tooth behavior is broken. However, there is a noticeable modification of the TiO$_2$ layer that is adjacent to KO at the TiO$_2$/KO heterointerface; the polarization of this layer is enhanced, so that the region it is about 0.45 C/m$^2$. Recalling that $P_3$ of bulk KNbO$_3$ should be enhanced relative to its bulk $P_2$ while $P_{SrTiO_3}$ should be small and of opposite sign, are clearly confirmed.

In summary, our calculations on perovskite superlattices composed of II-IV and I-V components have shown that sharp local polarization discontinuities can be stabilized at the charged heterointerfaces that are intrinsic to such superlattices. Focusing on the SrTiO$_3$/KNbO$_3$ system, our calculations show that while the charge compensation is not perfect, the superlattice period can be increased to rather large dimensions before the remaining uncompensated bound charges drive the system metallic. The same principles should apply to II-IV/III-III perovskite superlattices. By suitable choice of materials, and/or by tuning the polarization via the application of epitaxial strain, which can have a strong effect on the spontaneous polarization, it should be possible to obtain even better compensation. The resulting superlattices have strongly broken inversion symmetry, and may be of interest for piezoelectric, pyroelectric, non-linear optical, and other applications. Finally, we have also demonstrated how a layer-by-layer Wannier analysis may be applied to a perovskite system in which non-neutral layers are present, as an important step towards a more complete understanding of the local behavior of multilayered superlattices.

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1. P. Gherose and J. Junquera, in Handbook of Theoretical and Computational Nanotechnology, edited by M. Rieth and W. Schommers (American Scientific Publisher, Stevenson Ranch, CA, 2006).
2. A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004).
3. N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nat. Mater. 5, 204 (2006).
4. C. Cen, S. Thiel, G. Hammerl, C. W. Schneider, K. E. Andersen, and C. S. Hellberg, Nature Materials 7, 298 (2008).
5. G. Rijnders and D. H. A. Blank, Nature Materials 7, 270 (2008).
6. A. Kalabukhov, R. Gunnarsson, T. Claeson, and D. Winkler, arXiv:0704.1050v1.
7. A. M. George, J. Íñiguez, and L. Belloaie, Nature 433, 395 (2005).
8. G. Rijnders and D. H. A. Blank, Nature 433, 369 (2005).
9. X. Wu and D. Vanderbilt, Phys. Rev. B 73, 020103(R) (2006).
10. X. Wu, O. Diéguez, K. M. Rabe, and D. Vanderbilt, Physical Review Letters 97, 107602 (2006).
11. D. Vanderbilt, Current Opinion In Solid State and Materials Science 2, 701 (1997).
12. K. Rabe and P. Gheose, in Physics of Ferroelectrics: A Modern Perspective, edited by K. Rabe, C. Ahn, and J.-M. Triscone (Springer, Berlin, 2007).
13. O. Diéguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B 72, 144101 (2005).
14. S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Gallibio, S. Scandolo, G. Chiarotti, P. Facher, A. Pasquarello, et al., http://www.pwscf.org.
15. J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
16. D. Vanderbilt, Phys. Rev. B 41, 7892(R) (1990).
17. N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).