Coupling between octahedral rotations and local polar displacements in WO₃/ReO₃ superlattices

Joseph T. Schick
Department of Physics, Villanova University, Villanova, PA 19085

Lai Jiang, Diomedes Saldana-Greco, and Andrew M. Rappe
The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

We model short-period superlattices of WO₃ and ReO₃ with first-principles calculations. In fully-Relax superlattices, we observe that octahedral tilts about an axis in the planes of the superlattices do not propagate from one material, despite the presence of the corner-shared oxygen atoms. However, we find that octahedral rotation is enhanced within WO₃ layers in cases in which strain couples with native antiferroelectric displacements of tungsten within their octahedral cages. Resulting structures remain antiferroelectric with low net global polarization. Thermodynamic analysis reveals that superlattices with sufficiently thick ReO₃ layers, the absolute number being three or more layers and the Re fraction ≥ 50%, tend to be more stable than the separated material phases and also show enhanced octahedral rotations in the WO₃ layers.

I. INTRODUCTION

Perovskites and related materials offer a wide variety of electronic, magnetic, and structural properties, along with couplings between these properties that can form the basis for numerous technological applications. In most cases, the structures of real perovskites deviate from the ideal case, most commonly in the form of coherent rotations of the octahedra in the crystal.¹ These rotations break cubic symmetry and typically require changes in the primitive lattice vectors, as well. Further symmetry reductions result from other changes in the structure, including Jahn-Teller and breathing mode distortions of the octahedra, and displacements of the A or B site cations.

Concomitant with the structural deviations are changes in the electronic, magnetic, and optical properties of the materials. The size of the semiconducting gap can be correlated with the degree of octahedral tilt in families of perovskites. For example, the metal-insulator transition temperature is correlated with the degree of octahedral tilt in rare-earth nickelates.² There is a growing literature on the relationships between octahedral tilting and properties of interest including Jahn-Teller distortions and cation ordering,³ ferroelectricity,⁴ and multiferroicity in perovskite layered phases and superlattices. The emergence of spontaneous polarization in short period perovskite superlattices due to the combination of two non-polar rotation patterns, hybrid improper ferroelectricity, has been recently discussed as a route to creating novel multifunctional materials.⁵,⁶

Because these useful material properties couple to octahedral tilting, there has been an effort to study the ways in which tilting can be adjusted, by creating interfaces or layered structures or by applying strain or electric or magnetic fields. Octahedral tilting is the primary way perovskites respond to applied strains because the octahedra are relatively rigid, due to the covalent B-O bonding.⁷,⁸ However, the exact structure of any perovskite is a result of the interplay between the ionic and covalent nature of the bonding between the A- and B-cations and the O anions.

In a layered heterostructure, the tilts and rotations vary with distance from the interface, converging to bulk values. In addition, tilts and rotations will be affected by strains. The effect of epitaxial strain, in particular, has been previously investigated in theoretical studies,⁹,¹⁰ including determination of phase diagrams for numerous perovskites.¹⁰ Strain-induced changes in bond lengths and angles were investigated experimentally in LaNiO₃ on SrTiO₃ and LaAlO₃, with a first principles analysis demonstrating the ability to access structural phase changes in the response to tensile strain.¹¹

The dependence of tilt and rotation with respect to distance from a perturbation in La₀.₇₅Ca₀.₂₅MnO₃ and SrRuO₃ was recently investigated by distorting a single layer of the bulk material, while relaxing the remaining atoms but fixing the in-plane lattice parameters to mimic the effect of a substrate.¹² These calculations show that La₀.₇₅Ca₀.₂₅MnO₃ sustains out-of-plane tilts for a few layers, and that if the material is biaxially compressively strained, the imposed tilt results in a larger deep-layer tilt and a smaller in-plane rotation than found in the same biaxially, compressively strained material without an imposed tilt layer.¹² However, in SrRuO₃ the authors show that imposed tilts have no long-range propagation into the material, whether or not it is biaxially strained.¹² In both cases, the distance to attain the deep-layer behavior is very short, of the order of one or two layers.

Certain binary transition-metal oxides form in a perovskite-like structure, forming BO₆ octahedra with empty A-sites. ReO₃ and WO₃ possess this structure and allow us to focus on the BO₆ octahedra exclusively. WO₃ is a monoclinic insulator at room temperature. WO₃ undergoes numerous structural phase transitions both above and below room temperature, with the tri-
clinic phase stable below 290 K, for example. The tungsten atoms in WO₃ are displaced from their octahedral centers, in an antiferroelectric pattern. ReO₃ is a conductor with cubic symmetry at room temperature and below. Numerous ab initio studies of ReO₃ and WO₃ have been carried out, and the link between the WO₃ band gap and the polar distortion of the W atoms has been investigated; the reduction in energy of the occupied states is cited as the driver of the polar displacement.

In a recent theoretical investigation of the surfaces of WO₃, ReO₃, and surface layers of WO₃ on ReO₃ and ReO₃ on WO₃, it was found that layering is the preferred ordering for Re and W in bulk WReO₆.

In this paper, we demonstrate that WO₃ and ReO₃ both possess longer characteristic decay lengths for out-of-plane tilts than the reference material CaZrO₃, but their in-plane rotation characteristic decay lengths are comparable. We also present results for superlattices and compare their tilt and rotation behaviors to the pure materials. We determine that the antiferroelectric displacements of tungsten and the superlattice strain combine to influence the tilt and rotation angles.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed with the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA). Norm-conserving non-local pseudopotentials were generated with the OPIUM code. Calculations were performed with QUANTUM ESPRESSO. The energy cutoff for plane waves was 680 eV. A 2×2×2 Monkhorst-Pack k-point mesh was used for relaxing bulk materials; a 6×6×6 grid was tested to ensure convergence. In four-layer supercells a 2×2×2 k-point grid was used. In six- and eight-layer supercells, a 2×2×1 k-point sampling was employed. Ionic forces were converged to 0.0004 Ry/a₀ and pressures in full-cell relaxations were below 0.2 kbar. Electronic energy was converged to 10⁻⁸ Ry. Full structural convergence was tested in the four-layer superlattices with a 4×4×4 k-point grid. The bulk ReO₃ valence band is composed of strongly delocalized Re d and O p states. It has been previously found in LaNiO₃, which is also metallic, that similarly delocalized states strongly screen the electron-electron interactions. From this screening it was concluded that Hubbard U and hybrid functionals cannot accurately represent the screening effects of these delocalized electrons. For this reason we do not include these methods in this calculation.

III. RESULTS AND DISCUSSION

Imposing tilt on a single layer in CaZrO₃ (Fig. 1 panel (a)) has little effect on the material. In a CaZrO₃ 2×2×6 unit supercell, we held one layer fixed at the bulk tilt and rotation values, and tilted or rotated the oxygen cages on the opposite end. The rest of the atoms in the supercell were relaxed. The length of decay is characterized with an exponential fit. In Fig. 1-(a) we imposed only a tilt on layer zero and fit the resulting tilt distribution with the expression

\[ \theta(x) = \theta_\infty + (\theta_0 - \theta_\infty) e^{-x/\lambda}, \]  

where \( \theta \) is the tilt angle, \( x \) is the layer index, \( \theta_\infty \) is the bulk tilt angle, \( \theta_0 \) is the imposed tilt at the first layer, and \( \lambda \) is a characteristic length, in units of layers, for the decay of the tilts and rotations into the bulk. In Fig. 1-(b) the same analysis is displayed for imposed rotation angle. Surprisingly, we find that although tilts involve displacement of the apical oxygen atoms, which are shared by neighboring layers, the characteristic length \( \lambda_{\text{tilt}} \) in CaZrO₃ is very short. Perhaps equally surprising is the fact that \( \lambda_{\text{rotate}} > \lambda_{\text{tilt}} \) in CaZrO₃; rotations decay more gradually than tilts, though both are quite rapidly decaying.

There is apparently only a limited relationship between the tilt or rotation in one layer and the next. However, we observe Fig. 1-(c) through -(f) that the characteristic decay lengths for tilt (but not rotation) angles in WO₃ and ReO₃ are significantly longer than for CaZrO₃ and that \( \lambda_{\text{rotate}} < \lambda_{\text{tilt}} \) in the BO₃ materials.

Having established that tilt and rotation disturbances result in layer-to-layer correlations in these binary materials, we investigate superlattices that are more readily synthesized. Our superlattices are constructed from 2×2×N pseudocubic unit cells. Each of the \( N \) layers is composed of either four WO₆ or four Re₆ octahedra. The lattice and all the atomic coordinates are fully relaxed in these calculations. Calculated lattice parameters of the bulk materials are listed in Table I.

The rotation and tilt profiles of the six-layer superlattices are displayed in Fig. 2. For systems with half or more ReO₃ (Fig. 2-(a,b,c)), the ReO₃ exerts compressive strain on the WO₃ (discussed below), leading to enhanced rotation angles \( \approx 8° \) in the WO₃ layers. For the two cases with more W than Re, the rotations are near

| Parameter | ReO₃ | WO₃ |
|-----------|------|------|
| \( a \)   | 7.55 (7.50) Å | 7.46 (7.31) Å |
| \( b \)   | —    | 7.56 (7.53) Å |
| \( c \)   | —    | 7.75 (7.69) Å |
| \( \alpha \) | 90° (90°) \( ^\circ \) | 90° (88.9°) \( ^\circ \) |
| \( \beta \) | 90° (90°) \( ^\circ \) | 90.02° (90.9°) \( ^\circ \) |
| \( \gamma \) | 90° (90°) \( ^\circ \) | 90° (90.9°) \( ^\circ \) |

Mean oct. tilt | 0° | 2° |
Mean oct. rotation | 0° | 5° |

\( ^a \) From Ref. 26.
\( ^b \) From Ref. 27.
FIG. 1. (Color online) Octahedral tilt and rotation angles in each plane along the long axis of 2 × 2 × 6 supercells of CaZrO$_3$, WO$_3$, and ReO$_3$. The layer zero equatorial oxygen atoms were held fixed to maintain an excess octahedral tilt (panels (a), (c), and (e)) or octahedral rotation (panels (b), (d), and (f)) alone. The equatorial oxygen atoms in layer five were held fixed to maintain calculated bulk tilt and rotation angles. All other O atoms and all A and B cation locations were relaxed. The characteristic decay lengths, $\lambda$, are computed by fitting to Eq. 1 and given in units of the layer index. (g) Tilt angles are the angles between the supercell $c$-axis and the polar axis of the octahedra. (h) Rotation angles evaluated by averaging the angles between the supercell $a$- and $b$-axes and $ab$-projected line of the nearest octahedral O-O axis. The differences between the lattice directions and the Cartesian axes in this work are small and are ignored.

the bulk value $\approx 5^\circ$. In all cases, rotations are zero in the ReO$_3$ layers, with an abrupt change in the octahedral rotation angle across the boundary. The single-layer change in the rotation angle across the superlattice boundaries is consistent with the short characteristic length for the decay of rotations (small values of $\lambda_{\text{rot}}$) observed previously.

Octahedral tilt angles (Fig. 2-(f - j)) are anticorrelated with rotation angles in WO$_3$; the systems with larger rotations have lower tilts. However, unlike the results for rotations, the ReO$_3$ layers also exhibit non-zero tilts for the majority WO$_3$ superlattices. The penetration of tilt angles through these superlattices is consistent with the longer characteristic length for tilts within both materials (larger values of $\lambda_{\text{tilt}}$).

The increase of rotation angles in superlattices with more ReO$_3$ arise largely from superlattice strain, with some contribution due to WO$_3$ polar displacements. As seen in Table I, two of the WO$_3$ lattice parameters differ from ReO$_3$ by 1% or 2% with the $b$ lattice parameter nearly identical. The in-plane lattice parameters of the superlattices discussed here remain close to that of bulk ReO$_3$. Because ReO$_3$ has a much larger bulk modulus ($\approx 200$ GPa)$^{28,29}$ than WO$_3$ ($\approx 41$ GPa)$^{30}$, the domination of the superlattice in-plane lattice parameters by ReO$_3$ is not surprising. The long dimension in bulk WO$_3$ is a result of minimal tilt $\approx 2^\circ$ and the slight elongation of the octahedral axis closest to the direction of the polar (antiferroelectric) displacement of the W ions.

The superlattices were initially set up with the $ab$-planes of bulk WO$_3$ forming surfaces of contact. The lattice parameters (Table I) lead us to expect a tensile strain on the WO$_3$ layers, which would reduce the rotation angle, the opposite of the observed results. In bulk WO$_3$, calculated W displacements from the geometric centers of their octahedral cages are generally toward octahedral edges and make angles $\approx 31^\circ$ with respect to

FIG. 2. (Color online) The rotation (panels a - e) and tilt (panels f - j) angles of six-layer WO$_3$/ReO$_3$ fully-relaxed superlattices are presented as a function of layer index. The vertical dashed line indicates the boundary between WO$_3$ (to the left) and ReO$_3$ (to the right). ReO$_3$ layers all have nearly zero rotation. The superlattices with three or fewer WO$_3$ layers have rotation angles $\approx 8^\circ$. The rotation in majority WO$_3$ superlattices are near the bulk values $\approx 5^\circ$. All WO$_3$ tilt angles are small, nearly zero in majority ReO$_3$ superlattices.
the $c$-axis. However, in the cases with increased rotation (those with more ReO$_3$), the directions of the antiferroelectric polar displacements of the W cations make angles from $\approx 60^\circ$ to $90^\circ$ with respect to the $c$-axis, increasing with the fraction of ReO$_3$. (See Table II.) This results in the long axis of the WO$_3$ octahedra also lying in the superlattice planes, requiring the WO$_3$ octahedra to rotate more strongly to fit within the lattice.

The average magnitude of local polar (antiferroelectric) displacement in the ReO$_3$ layers increases as the Re fraction decreases and as the superlattice thickness decreases. Superlattices with a single ReO$_3$ layer have the largest Re displacements. The directions of Re displacements are close to the long axis of the superlattice. The average magnitude of local polar displacements of W atoms are $\approx 0.2$ Å, decreasing to $\approx 0.15$ Å for the highest Re fractions. The W polar displacement angle to the superlattice axis varies with Re polar displacement at the interface plane (Fig. 3), lying completely in the plane for the highest Re fraction (Table II). The polar displacement angles throughout the WO$_3$ layers differ by $< 1^\circ$ from the surface value.

To test the effect of the initial conditions on the fully-relaxed final structures and formation energies of the superlattices, we also created four- and six-layer superlattices with the bc-planes of bulk WO$_3$ forming the initial contact surfaces. All possible $m/n$ superlattices were formed. After full relaxation, the energies of the test superlattices were higher than the $ab$-oriented superlattices, $\approx 0.03$ eV for the four-layer and $\approx 0.07$ eV for six-layer superlattices. The lattice parameters are controlled by the ReO$_3$ material, as discussed above. In these tests, rotations do not penetrate into the ReO$_3$ layers and the tilt and rotation profiles are consistent with the superlattices explored above. In these test configurations, when there are odd numbers of WO$_3$ layers, the initial condition has a net polar shift of W cations along the $b$ direction, transverse to the axis of the superlattice. (The initial polar displacement vectors’ largest components remain along the $c$-direction.) These net displacements vanish in the fully-relaxed (WO$_3$)$_3$/[ReO$_3$]$_1$ and (WO$_3$)$_5$/[ReO$_3$]$_1$ superlattices but persist in the Re-dominated superlattices. The W-rich superlattices also have polar displacements closer to the superlattice direction, consistent with the lower energy superlattices.

Above we observed that tilts penetrate across the interfaces (Fig. 2), consistent with the larger $\lambda_{ik}$ in these materials. As a result, when ReO$_3$ makes up the majority of the superlattice, tilts are suppressed within the WO$_3$ layers. Furthermore, when ReO$_3$ is the majority material, the induced polar displacements in ReO$_3$ layers are smallest and the polar displacements in WO$_3$ lie in superlattice layers. We tested the response of the polar displacements in bulk WO$_3$ to biaxial strain, of the same amount as in the (WO$_3$)$_3$/[ReO$_3$]$_7$ superlattice, and found that the angle of the polarization increases only to $\approx 40^\circ$ (in comparison to the bulk $\approx 31^\circ$ and the superlattice $\approx 89^\circ$). Strain alone is not enough to cause the large in-plane polar displacement in WO$_3$.

Table II shows that the largest antiferroelectric Re displacements at the surface occur when there are one or two ReO$_3$ layers. The superlattices with three or more ReO$_3$ layers have very small surface Re displacements and also have W displacements lying closer to the superlattice planes, as noted above. Furthermore, the W

| No. of superlattice layers | No. of ReO$_3$ layers | $\bar{\theta}_{Re}$ (Å) | $\bar{\theta}_{P_\perp W}$ (deg.) |
|----------------------------|-----------------------|-------------------------|----------------------------------|
| 2                          | 1                     | 0.118                   | 41                               |
| 4                          | 1                     | 0.128                   | 40                               |
| 4                          | 2                     | 0.071                   | 60                               |
| 4                          | 3                     | 0.022                   | 90                               |
| 6                          | 1                     | 0.137                   | 37                               |
| 6                          | 2                     | 0.104                   | 44                               |
| 6                          | 3                     | 0.034                   | 75                               |
| 6                          | 4                     | 0.039                   | 73                               |
| 6                          | 5                     | 0.019                   | 90                               |
| 8                          | 1                     | 0.140                   | 35                               |
| 8                          | 2                     | 0.102                   | 44                               |
| 8                          | 3                     | 0.054                   | 62                               |
| 8                          | 4                     | 0.061                   | 60                               |
| 8                          | 5                     | 0.034                   | 74                               |
| 8                          | 6                     | 0.019                   | 88                               |
| -                          | -                     | -                       | -                                |

FIG. 3. The average angle to the $c$-axis of polar displacements in WO$_3$ interface planes vary with the average magnitude of antiferroelectric polar displacements induced in the ReO$_3$ interface planes. The horizontal dashed line indicates the average polar displacement angle in bulk WO$_3$ ($\approx 31^\circ$). See Table II for detailed comparison of the data.
displacement angles in all layers in any given superlattice remain close to the same value found at the surface. Evidently, the energy cost for displacing the Re cations is large in comparison to the energy cost to reorient the W displacements into the superlattice planes. To estimate this energy, the computed energy required for a 0.14 Å antiferroelectric displacement in bulk ReO$_3$, corresponding to the maximum displacement found in the present calculations, is $\approx 0.08$ eV per four formula units. As will be observed below, this is small in comparison to interface and strain energies.

Hybrid improper ferroelectrics have recently been highlighted as a possible means to create new multifunctional materials. The mechanism induces a spontaneous polarization through coupling to two non-polar rotational modes enabled by creation of $AA'BO_3$ double-perovskites or Ruddleston-Popper phases. The induced polarization in hybrid improper ferroelectrics is perpendicular to the layering. We note that the local polarization of the WO$_6$ octahedra lies in or close to the layers of Re-majority superlattices (Table II), which we have concluded is a result of strain and a microscopic interaction at interfaces, a mechanism perhaps related to that discussed for hybrid improper ferroelectrics.

Because there is coupling between the superlattice layers and the orientation of the W polar displacements, we computed total polar displacements by summing all the displacement vectors for each type of B-cation in each superlattice. Total displacements are all of the order $10^{-3}$ Å and less in the low energy superlattices. These displacements are negligible relative to the typical polar displacements of the W and Re atoms. The lack of overall polarization in our calculations is perhaps related to the fact that all the superlattices are conductors. In Fig. 4 the densities of states (DOS) demonstrate the superlattices are metallic, with an apparently strong contribution from ReO$_3$-like states at the Fermi level. The DOS projected onto metal-d and O-p states for the (WO$_3$)$_3$/ReO$_3$ superlattice (Fig. 5) shows that hybridized Re-d and O-p states are the strongest contributions to the DOS at the Fermi energy. Fig. 5 shows the strong hybridization between O-p states and Re d-states. Such hybridization has previously been shown to result in screening of the electron-electron interaction that cannot be properly captured with Hubbard $U$ nor with hybrid density functionals, justifying our avoidance of applying such methods in this calculation.

Projecting the densities of states into individual layers of the superlattice (Fig. 6) shows that the states at the Fermi energy are due primarily to the ReO$_3$ layer of the superlattice, with the density of states at the Fermi level decreasing rapidly with distance from the rhenium layer. We expect reduced conductivity in superlattices with respect to bulk ReO$_3$ because the total density of states at the Fermi energy is lower than in bulk ReO$_3$.

The formation energies of the (WO$_3$)$_m$/ReO$_3$$_n$ superlattices with respect to equivalent amounts of the bulk...
FIG. 6. Projected densities of states for the (WO$_3$)$_7$/(ReO$_3$)$_1$ superlattice are displayed for three layers within the superlattice. In panel (a) is the projection on the ReO$_6$ octahedra, in panel (b) is the projection on the WO$_6$ octahedra of the second layer after rhenium layer, and in panel (c) is the projection on the WO$_6$ octahedra on the layer farthest from the material segregation.

FIG. 7. (Color online) The formation energies $E_f$ relative to separated WO$_3$ and ReO$_3$ phases (calculated from Eq. 2) for all superlattice calculations are plotted as a function of Re concentration. Generally superlattices consisting of larger numbers of layers of ReO$_3$ are more stable than those with fewer layers. The straight lines are energies calculated from the model (Eq. 3) using the values in Table III.

TABLE III. The parameters obtained by fitting Eq. 3 with the energies obtained from DFT results.

| Parameter | Value (per 4 formula units) |
|-----------|-----------------------------|
| $\Delta E_{\text{int}}$ | 1.363 eV |
| $\Delta E_{\text{str}}^{\text{WO}_3}$ | 0.059 eV/layer |
| $\Delta E_{\text{str}}^{\text{Re}_3\text{O}_3}$ | −0.515 eV/layer |

than lower, with a preference for three rhenium layers as a minimum. The possible sources of these energy deviations are the energy associated with strains of the materials in the superlattices and the energy to create the interfaces. We parameterize the superlattice formation energy in terms of the energy costs to strain bulk layers of both WO$_3$ and ReO$_3$ ($\Delta E_{\text{str}}^{\text{WO}_3}$ and $\Delta E_{\text{str}}^{\text{Re}_3\text{O}_3}$) and to create the interfaces $\Delta E_{\text{int}}$ with the model

$$E_f(m, n) = \Delta E_{\text{int}} + m\Delta E_{\text{str}}^{\text{WO}_3} + n\Delta E_{\text{str}}^{\text{Re}_3\text{O}_3},$$

where $m$ and $n$ are the numbers of layers of WO$_3$ and ReO$_3$, respectively. The results fitting this model are displayed as straight lines in Fig. 7. The fitting parameters in Table III show that reducing the number of layers of WO$_3$ and increasing the number of layers of ReO$_3$ are both more energetically favorable. The majority of the energy change is due to distortion of the ReO$_3$ layers, as indicated by the magnitude of $\Delta E_{\text{str}}^{\text{Re}_3\text{O}_3}$ in comparison to $\Delta E_{\text{str}}^{\text{WO}_3}$. The energy reduction in increasing the Re fraction by changing a layer of WO$_3$ to ReO$_3$ (0.574 eV) is also large in comparison to the interface energy providing a reason for ReO$_3$ to form thick layers, which is consistent with the previous calculation finding that layering is the preferred order in WReO$_6$.

As noted in the discussion for Table II, increasing ReO$_3$ fraction also decreases the local polarization of ReO$_3$ and increases the angle to the superlattice long axis of the local polarization of WO$_3$. We also tried including polar displacement in the energy model but found that the fit quality was reduced, suggesting that the strain effects are dominant and that changes in polarization are a response to the constraints imposed by the superlattice.

The energy reduction from increasing ReO$_3$ fraction is apparently assisted by the ability of the tungsten layers to more readily accommodate strain through octahedral rotations, which also relates to the lower bulk modulus of WO$_3$. For the superlattices in which ReO$_3$ is the majority material, the energies are lower than the bulk phases, suggesting that these superlattices may be experimentally feasible, either through film deposition or bulk material segregation.

IV. CONCLUSION

In summary, we have found that there is a stronger layer-to-layer correlation between tilt angles in the binary transition-metal oxides WO$_3$ and ReO$_3$, than is
found in most studies of ternary transition-metal oxides. Rotation angles are enhanced in some superlattices because antiferroelectric polar distortions of the WO₆ octahedra cause them to couple with the layering of the material, reminiscent of the hybrid improper ferroelectricity concept. However, net global polarization is low. We find that short-period superlattices are stable relative to bulk XO₃ compounds when the ReO₃ layer thickness is large enough and when ReO₃ is the majority species. This stability suggests that creation of these short-period superlattices will be experimentally realizable.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge their support. JTS was supported by a sabbatical granted by Villanova University. LJ was supported by the Air Force Office of Scientific Research under Grant No. FA9550-10-1-0248. DSG was supported by the Department of Energy Office of Basic Energy Sciences, under grant DE-FG02-07ER15920. AMR was supported by the Office of Naval Research, under grant N00014-12-1-1033. Computational support was provided by the High Performance Computing Modernization Office of the Department of Defense, and the National Energy Research Scientific Computing Center of the Department of Energy.

---

1. A. M. Glazer, Acta Cryst. B28, 3384 (1972).
2. M. L. Medarde, J. Phys. Cond. Mater. 9, 1679 (1997).
3. M. Lufaso and P. Woodward, Acta Cryst. B60, 10 (2004).
4. N. A. Benedek and C. J. Fennie, The Journal of Physical Chemistry C 117, 13339 (2013).
5. N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011).
6. N. A. Benedek, A. T. Mulder, and C. J. Fennie, Journal of Solid State Chemistry 195, 11 (2012), polar Inorganic Materials: Design Strategies and Functional Properties.
7. J. B. Goodenough, Phys. Rev. 100, 564 (1955).
8. P. Garcia-Fernandez, J. Aramburu, M. Barriuso, and M. Moreno, The Journal of Physical Chemistry Letters 1, 647 (2010).
9. A. T. Zayak, X. Huang, J. B. Neaton, and K. M. Rabe, Phys. Rev. B 74, 094104 (2006).
10. O. Díegez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B 72, 144101 (2005).
11. S. J. May, J.-W. Kim, J. M. Rondinelli, E. Karapetrova, N. A. Spaldin, A. Bhattacharya, and P. J. Ryan, Phys. Rev. B 82, 014110 (2010).
12. J. He, A. Borisevich, S. V. Kalinin, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. 105, 227203 (2010).
13. E. Salje, Acta Crystallographica Section B 33, 574 (1977).
14. K. M. Rabe, “Antiferroelectricity in oxides: a reexamination,” in Functional Metal Oxides (Wiley-VCH Verlag GmbH & Co. KGaA, 2013) pp. 221–244.
15. W. Biltz, G. A. Lehrer, and K. Meisel, Zeitschrift für anorganische und allgemeine Chemie 207, 113 (1932).
16. F. Corà, M. G. Stachiotti, C. R. A. Catlow, and C. O. Rodriguez, The Journal of Physical Chemistry B 101, 3945 (1997).
17. G. A. de Wijs, P. K. de Boer, R. A. de Groot, and G. Kresse, Phys. Rev. B 59, 2684 (1999).
18. A. D. Walkingshaw, N. A. Spaldin, and E. Artacho, Phys. Rev. B 70, 165110 (2004).
19. F. Wang, C. Di Valentim, and G. Pacchioni, The Journal of Physical Chemistry C 115, 8345 (2011).
20. Y. Ping, D. Rocca, and G. Galli, Phys. Rev. B 87, 165203 (2013).
21. S. Ling, D. Mei, and M. Gutowski, Catalysis Today 165, 41 (2011).
22. Opium pseudopotential generating package, http://opium.sourceforge.net/.
23. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, Journal of Physics: Condensed Matter 21, 395502 (19pp) (2009).
24. H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
25. G. Gou, I. Grinberg, A. M. Rappe, and J. M. Rondinelli, Phys. Rev. B 84, 144101 (2011).
26. J.-E. Jorgensen, J. D. Jorgensen, B. Batlogg, J. P. Reimeika, and J. D. Axe, Phys. Rev. B 33, 4793 (1986).
27. P. Woodward, A. Sleight, and T. Vogt, Journal of Physics and Chemistry of Solids 56, 1305 (1995).
28. T. P. Pearsall and L. A. Coldren, Solid State Commun. 18, 1093 (1976).
29. R. E. Benner, E. M. Brody, and H. R. Shanks, J. Solid State Chem. 22, 361 (1977).
30. W. A. Crichton, P. Bouvier, and A. Grzeghnik, Materials Research Bulletin 38, 289 (2003).
31. J. M. Rondinelli and C. J. Fennie, Advanced Materials 24, 1918 (2012).
32. V. Dvořák, Ferroelectrics 7, 1 (1974).