

Control of Octahedral Tilts and Magnetic Properties of Perovskite Oxide Heterostructures by Substrate Symmetry

Jun He,^{1,3} Albina Borisevich,¹ Sergei V. Kalinin,² Stephen J. Pennycook,^{1,3} and Sokrates T. Pantelides^{3,1}

¹*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

²*The Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

³*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

(Received 29 June 2010; published 23 November 2010)

Perovskite transition-metal oxides are networks of corner-sharing octahedra whose tilts and distortions are known to affect their electronic and magnetic properties. We report calculations on a model interfacial structure which avoids chemical influences and show that the symmetry mismatch imposes an interfacial layer with distortion modes that do not exist in either bulk material, creating new interface properties driven by symmetry alone. Depending on the resistance of the octahedra to deformation, the interface layer can be as small as one unit cell or extend deep into the thin film.

DOI: 10.1103/PhysRevLett.105.227203

PACS numbers: 75.70.-i, 68.35.Ct, 71.15.Mb, 73.20.-r

The unique magnetic and electronic properties of perovskite transition-metal oxides with ABO_3 stoichiometry have attracted broad attention both from fundamental physical perspective and for information storage and logic devices [1,2], with epitaxial films taking center stage as the medium where strain can be explicitly controlled [3–7]. Tailoring the strain can allow stabilization of phases non-existent in the bulk [8–10], induce novel polarization states [11,12], and even enable transition to morphotropic-like states [4,13]. Similarly well recognized are the effects related to the charge at the interfaces arising from chemical or polarization discontinuity [14–16]. The key aspect of all the polarization, chemical, and strain effects is that they act uniformly along the interface, corresponding to zone-center type wave vectors.

However, we note that magnetic, electrical, and structural functionalities of perovskites are also influenced by the deformations and distortions of the octahedral network controlled by zone-boundary phonon modes [17–19]. For magnetic oxides such as ruthenates and manganites, the B - O - B tilt angle between corner-shared octahedra has been shown to affect electron hopping matrix elements and hence the transport properties [20–23]. The deformations of oxygen octahedra driven by collective Jahn-Teller distortions control both metal-insulator transitions and magnetic properties [24]. Recently, first-principles calculations found unexpected ferroelectricity in $PbTiO_3/SrTiO_3$ heterostructure, arising from octahedron rotation coupling across the interface [25]. Also, the concept of exchange bias coupling in electrically tunable magnetic devices has been proposed to change the magnetic order laterally at the interfaces between a multiferroic oxide and a ferromagnetic oxide [26]. Thus, effective control of the magnetic and orbital degrees of freedom requires the symmetry control tied to the zone-boundary modes of the material [27].

Calculations on interfaces between dissimilar materials cannot easily unravel the distinct role of symmetry mismatch at the interface from effects arising from the discontinuity in the chemical identity of constituent elements, their valences, and the materials lattice parameters. On the other hand, Fig. 1 illustrates that symmetry mismatch alone, due to the constraints of the continuity of the octahedral network, imposes a distinct transition layer in which the octahedra undergo additional distortions that are not present in either bulk material. Figure 1(a) illustrates this

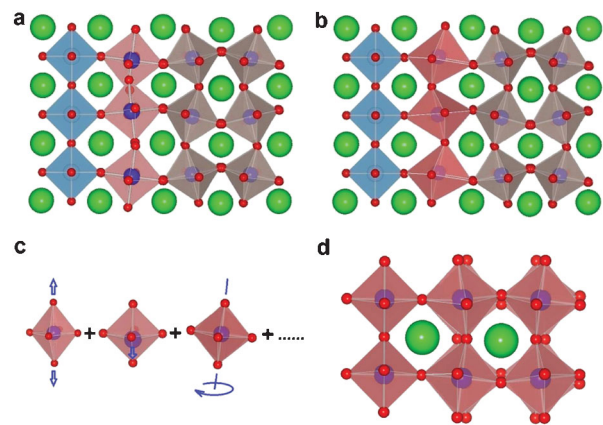


FIG. 1 (color). Schematics of the oxygen octahedral deformations at the interface between two perovskite oxides. (a) Untilted (blue octahedra) and tilted (beige octahedra) perovskites are connected via an interfacial layer (pink) of undistorted octahedra of intermediate tilt; the continuity of the corner-sharing network is disrupted (note disconnected vertices at interface). (b) The continuity can be restored by distorting the interfacial octahedra. (c) Possible components of the resulting distortion, such as Jahn-Teller elongation, polar off-centering, and additional rotational modes. (d) Slab model with tilt fixed to zero on the left side. Oxygen atoms are in red, A-site atoms are in green, and B-site atoms are in grey and blue.

point by attempting to connect two materials with different intrinsic octahedral tilts by a single sheet of *undistorted* octahedra with intermediate tilts. Figure 1(b) shows that the network continuity can be restored by modifications of the interfacial octahedra that can involve [Fig. 1(c)] any or all of the single-octahedron distortions, such as Jahn-Teller elongation and polar off-centering, as well as additional distortions of the octahedral network, such as new rotational modes. The need for such modifications persists even if one employs a wider transition layer. Clearly, the presence of such a symmetry-dictated transition layer has the potential to generate interfacial properties that are distinct from those of the bulk materials.

Another limitation of the accepted approach to the interface calculations lies in employing a superlattice, in which a distinction between the substrate and the thin film cannot be made. In modeling lattice mismatch, one can easily impose the planar lattice parameter of the substrate. Accommodation of the symmetry mismatch in a superlattice, on the other hand, becomes a battle between two thin films. In this Letter, in order to circumvent this difficulty and also to avoid interference from chemical and strain effects, we adopt a model interfacial structure that allows us to unravel the effect of symmetry mismatch at the interface between a substrate and a thin film. We employ an oxide slab of a single material and impose zero out-of-plane tilt in one of the planes. [Fig. 1(d)] The model implicitly assumes that the substrate has untilted octahedra and is infinitely rigid. In this fashion, we can explore how different perovskite materials in different strain states accommodate the symmetry mismatch and how their electronic, structural, and magnetic properties are affected. We envision several scenarios for symmetry relaxation. Depending on the energetics of deforming the individual octahedra, the transition region can be narrow (if the octahedra are easily deformed) or wide (if the octahedral deformation is unfavorable). For the case of a coherent ultrathin film, it is conceivable that the relaxation length could exceed sample thickness. This approach allows us to predict the character and a characteristic length for relaxation of the interface-related octahedral tilt disruptions, and classify different materials based on this behavior. We report results for two prototype materials that exhibit different behavior in order to illustrate the approach.

We performed density-functional theory calculations to compare the behavior of SrRuO_3 and $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (LSMO). The results show that the disruption of the tilt system in SrRuO_3 is quickly relaxed with full return of the tilts and rotations to the bulk values, while for LSMO (in the thickness range of this calculation) tilts and rotations stabilize at the values substantially different from the bulk. At the same time, local magnetic structure of LSMO remains almost unchanged in both strained and unstrained heterostructures. For SrRuO_3 , on the other hand, the local magnetic moment of Ru changes considerably as the changes in octahedral tilts are absorbed. The results suggest that the rigidity of the octahedral network is a critical

factor in designing oxide thin films and multilayers with desired properties.

SrRuO_3 and $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ are chosen as model materials as both are metallic ferromagnetic oxides, often used as bottom electrodes for ferroelectric thin films grown on SrTiO_3 . These materials have similar tilt systems ($a^-a^-c^+$ for SrRuO_3 and $a^-a^-c^-$ for LSMO in Glazer notation) in the bulk [28], albeit very a different electronic structure and magnetic properties (SrRuO_3 is a narrow band itinerant ferromagnet and LSMO is a double-exchange ferromagnet) [29], making them ideal candidates for comparative studies. Density-functional theory calculations were performed using a plane-wave basis set and the projector-augmented-wave method as implemented in the Vienna *ab initio* simulation package (VASP) code [30,31]. Calculations for the bulk material (20 atom cells) using a $8 \times 8 \times 8$ Monkhorst-Pack k -point mesh and a 500 eV plane-wave cutoff produced structural parameters in good agreement with experimental data. For the 80-atom supercells, a $4 \times 4 \times 1$ k -point mesh and a 400 eV cutoff were used. The heterostructures are built to contain 16 atomic layers (8 A-O layers and 8 B-O layers) along the z axis. The orthorhombic structure (space group $Pnma$) was adopted for SrRuO_3 and the rhombohedral structure (space group $R\bar{3}c$) was adopted for LSMO. The structures were relaxed using the spin-polarized generalized-gradient approximation for exchange-correlation [32]. The substitution of Sr at La sites in LSMO is simulated using regular arrangements of 3:1 ratio of La to Sr atoms in the appropriate sublattice. To explore the epitaxial strain effects on the tilt and rotation behavior, we have considered the strained heterostructure by implicitly constraining the in-plane lattice constant to the bulk lattice parameter of SrTiO_3 . In this case, SrRuO_3 undergoes a compressive strain and LSMO undergoes a tensile strain. Following the Ref. [23], the octahedron tilt angle along the z axis is defined as $(180^\circ - \Theta)/2$, where Θ is the bond angle of $B\text{-O-B}$ along the z axis. The rotation angle in the x - y plane is defined as $(90^\circ - \Omega)/2$, where Ω is the angle among three oxygen ions between two corner-shared oxygen octahedra in the x - y plane. For unstrained SrRuO_3 and LSMO, the calculated tilt angles are 10.2° and 7.8° , in good agreement with neutron diffraction measurement [22,33]. To explore the evolution of octahedral tilts across the interface, the tilt angle is fixed to zero in one plane (virtual interface plane), and the rest of the heterostructure is allowed to relax.

We first focus on the tilt angles of MnO_6 octahedra along the z axis in unstrained LSMO. Figure 2(a) illustrates the increase of the tilt angle from zero at the virtual interface to the nearly bulk value at the center of the heterostructure. In comparison, the rotation angle becomes larger than the bulk value at the virtual interface and decreases gradually towards the bulk value at the center. These results indicate that, when the tilts are disabled or suppressed by external perturbations, the out-of-plane rotation becomes the dominant octahedral network distortion in the unstrained

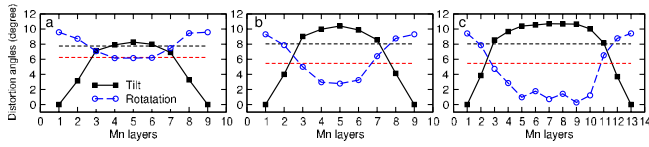


FIG. 2 (color online). Octahedral tilt and rotation angles for $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ as a function of Mn layers along the z axis. The tilt angle is set to zero at the virtual interface plane. The dashed lines indicate the values of corresponding bulk tilt angles (black) and rotation angles (red). (a) Unstrained in-plane lattice. (b) Strained in-plane lattice. (c) Strained in-plane lattice for a larger supercell.

LSMO. At the same time, the magnetic moments of Mn ions are found almost unchanged along the z axis from the virtual interface to the center, which is consistent with the unchanging geometry of the individual octahedra.

In the case of strained LSMO [Fig. 2(b)], a similar trend is observed for tilt and rotation angles at the virtual interface plane. However, the tilt and rotation angles at the center deviate strongly from the bulk values. To exclude the finite size effect, we have also performed the calculations on a larger LSMO strained heterostructure containing 24 atomic layers. In this structure [Fig. 2(c)], we found the tilt angles at the center still deviate from its bulk value (8.0°), reaching saturation at 10.7° . More interestingly, the rotations at the center are effectively suppressed by the tensile strain. Similar to the unstrained case, the magnetic moment remains almost constant.

In contrast to LSMO, the local octahedral distortions and magnetic properties of SrRuO_3 behave differently when the local symmetry is broken. For unstrained SrRuO_3 in Fig. 3(a), both tilt and rotation angles reach the bulk values in a distance of three Ru layers. For strained SrRuO_3 in Fig. 3(b), we applied two distortion approaches: only setting the tilt angle to zero at the virtual interface plane (first approach) and setting both the tilt and rotation angles to zero at the virtual interface (second approach). We found in both approaches both tilt and rotation angles reach the bulk values in same distance as in the unstrained case. The local

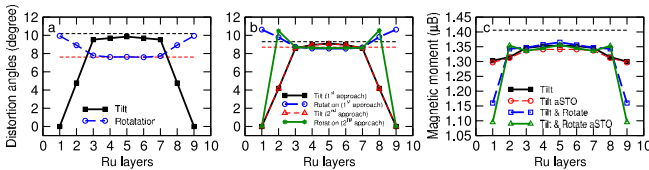


FIG. 3 (color online). Octahedral tilt and rotation angles, and magnetic moment profile of Ru atoms as a function of Ru layers along z -axis in SrRuO_3 . The dashed lines in (a) unstrained and (b) strained lattices indicate the corresponding bulk tilt angles (black) and rotation angles (red). In (b), two approaches are applied (see text). (c) Magnetic moments in SrRuO_3 . The tilt angle is set to zero at the virtual interface for unstrained (black solid square) and strained (red circle) SrRuO_3 . Both tilt and rotation angles are set to zero at the virtual interface for unstrained (blue square) and strained (green triangle) SrRuO_3 . The dashed line indicates bulk magnetic moment of Ru in unstrained SrRuO_3 .

magnetic properties in SrRuO_3 are affected by the strain effect. Compared in Fig. 3(c) are the local magnetic moments of Ru ions in both unstrained and strained SrRuO_3 in two distortion approaches. In both approaches, we found a reduction in the magnetic moment across the SrRuO_3 heterostructure. Especially, when both the tilt and rotation are disabled simultaneously, the magnetism is degraded by 20% at the virtual interface plane [Fig. 3(c)]. Such degradation shows that the local magnetism of SrRuO_3 can be significantly affected by abrupt changes in octahedral tilts.

The possible origins of the difference between the LSMO and SrRuO_3 behavior include (a) magnetic anisotropy, (b) Jahn-Teller activity, and (c) a degree of hybridization between the metal d and oxygen p orbitals. The orthorhombic SrRuO_3 thin film under compressive strain has a magnetic easy axis along the pseudocubic [001] direction while rhombohedral LSMO thin film under tensile strain has an easy axis along the pseudocubic in-plane [110] direction [34,35]. Correspondingly, structural distortion applied in the [001] direction could easily affect SrRuO_3 , rather than LSMO. Secondly, when local symmetry is broken in a strained SrRuO_3 heterostructure, we observed a decreased Ru-O bond length (about $0.02 \text{ \AA}$) along the z axis in RuO_6 octahedra at the virtual interface plane. This change is sufficient to trigger additional Jahn-Teller distortions and increase the magnitude of the t_{2g} splitting, which correspondingly alters the Ru spin configuration [23].

To explore the electronic effects associated with the octahedral tilt control, we studied the electronic structure of both oxides by plotting the projected partial density of states of B -site cation and oxygen in Fig. 4. It is well known that both oxides are half-metallic and the strong hybridization between the B -site cation and oxygen is very important to their magnetic properties. In our study, the calculated spin magnetization is $1.40 \mu_B$ per Ru in SrRuO_3 , and $3.37 \mu_B$ per Mn in LSMO. As seen from

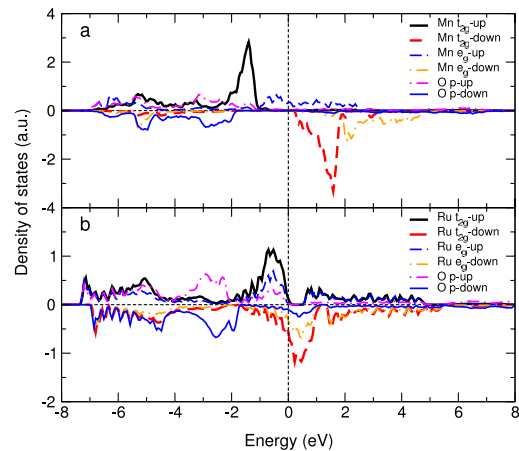


FIG. 4 (color online). Partial density of states of Mn and O ions in unstrained bulk $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (a); and Ru and O ions in unstrained SrRuO_3 (b). The majority spin is plotted as up spin and the minority spin is plotted as down spin.

Fig. 4(a), the LSMO is purely half-metallic, with only majority spin densities existing at the Fermi level. In contrast, SrRuO₃ is a nearly half-metallic oxide with both minority spin densities at Fermi level and majority spin densities just below Fermi level. Thus, the spin configuration could be easily affected by manipulating the hybridization between Ru *d* orbitals and oxygen *p* orbitals through adjusting Ru-O-Ru tilting angles. However, for the LSMO, the Mn minority spin density is effectively insulating, meaning that it is away from the Fermi level [Fig. 4(a)]. Thus, the octahedral tilt and rotation distortion in LSMO is insufficient to bring the majority spin band edge closer to Fermi level and the spin magnetization remains unchanged.

Another important aspect of the partial density of states is related to the hybridization between *B*-site cation and oxygen. As seen in Fig. 4, there is strong hybridization in SrRuO₃ between Ru *d* orbitals and oxygen *p* orbitals, indicated by the consistent overlap between Ru *t_{2g}*, Ru *e_g*, and O 2*p* states. As a result, when local symmetry is broken in SrRuO₃, these states can feel each other and response accordingly. This is the reason why the local magnetism of SrRuO₃ is very susceptible to symmetry changes. Opposingly, the hybridization in LSMO between the Mn *t_{2g}*, Mn *e_g*, and O 2*p* states is less pronounced. The Mn *t_{2g}* and *e_g* states are essentially completely polarized with a large exchange splitting. Thus, magnetic properties are relatively insensitive to local structural symmetry.

To summarize, we demonstrate the pathway towards control of the electronic and magnetic properties of correlated oxides though the symmetry of the octahedral network of the substrate. The octahedral deformation is an essential element of the interface between materials with dissimilar tilt systems, and, depending on the mode of deformation, can give rise to novel structural, electronic, and magnetic behaviors. The results suggest that rigidity of the octahedra should be taken into account when designing thin films and multilayers with desired properties.

Finally, we address the feasibility of experimental implementation of these systems. The static component of interface charge and strain are determined by the lattice parameters and composition mismatch of the material and substrate, and can be manipulated by the field effect in transistor-like structures, chemical adsorption, and remnant polarization. Recently, strain control by piezoelectric substrates has been demonstrated [36]. The direct control of the oxygen tilt network can be achieved through the electric field control of nonequivalent ferroelastic variants (e.g., for [110]-oriented rhombohedral perovskites [37]). An even simpler model system is offered by the antiferroelectric materials, where the octahedral tilts and polar order are strongly coupled. We believe that further theoretical understanding of the symmetry-mismatched interfaces between functional oxides will enable control of orbital degrees of freedom for magnetoelectric and other correlated-electron-based memory and logic devices [38].

This research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, by DOE Grant No. DE-FG02-09ER46554, and by the McMinn Endowment at Vanderbilt University. Computations were performed at the National Energy Research Scientific Computing Center.

-
- [1] M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
 - [2] R. Waser, *Nanoelectronics and Information Technology* (Wiley-VCH, Berlin, 2005).
 - [3] R. Ramesh and D. G. Schlom, *MRS Bull.* **33**, 1006 (2008).
 - [4] J. Wang *et al.*, *Science* **299**, 1719 (2003).
 - [5] R. J. Zeches *et al.*, *Science* **326**, 977 (2009).
 - [6] A. J. Hatt, N. A. Spaldin, and C. Ederer, *Phys. Rev. B* **81**, 054109 (2010).
 - [7] W. Luo, S. J. Pennycook, and S. T. Pantelides, *Phys. Rev. Lett.* **101**, 247204 (2008).
 - [8] N. A. Babushkina *et al.*, *Nature (London)* **391**, 159 (1998).
 - [9] I. E. Graboy *et al.*, *Chem. Mater.* **15**, 2632 (2003).
 - [10] J. H. Haeni *et al.*, *Nature (London)* **430**, 758 (2004).
 - [11] J. S. Speck and W. Pompe, *J. Appl. Phys.* **76**, 466 (1994).
 - [12] J. S. Speck *et al.*, *J. Appl. Phys.* **76**, 477 (1994).
 - [13] X. Du *et al.*, *Appl. Phys. Lett.* **72**, 2421 (1998).
 - [14] A. Ohtomo and H. Y. Hwang, *Nature (London)* **427**, 423 (2004); N. Nakagawa, H. Y. Hwang, and D. A. Muller, *Nature Mater.* **5**, 204 (2006).
 - [15] H. Chen, A. M. Kolpak, and S. Ismail-Beigi, *Adv. Mater.* **22**, 2881 (2010).
 - [16] G. Gerra *et al.*, *Phys. Rev. Lett.* **96**, 107603 (2006).
 - [17] A. M. Glazer, *Acta Crystallogr. Sect. B* **28**, 3384 (1972).
 - [18] P. M. Woodward, *Acta Crystallogr. Sect. B* **53**, 32 (1997).
 - [19] R. G. Mitchell, *Perovskites—Modern and Ancient* (Almaz Press, Ontario, 2002).
 - [20] I. I. Mazin and D. J. Singh, *Phys. Rev. Lett.* **79**, 733 (1997).
 - [21] A. J. Millis, *Nature (London)* **392**, 147 (1998).
 - [22] J. F. Mitchell *et al.*, *Phys. Rev. B* **54**, 6172 (1996).
 - [23] A. T. Zayak *et al.*, *Phys. Rev. B* **77**, 214410 (2008).
 - [24] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance* (Springer, New York, 2003).
 - [25] E. Bousquet *et al.*, *Nature (London)* **452**, 732 (2008).
 - [26] R. Ramesh and N. A. Spaldin, *Nature Mater.* **6**, 21 (2007).
 - [27] Y. Tokura and N. Nagaosa, *Science* **288**, 462 (2000).
 - [28] P. M. Woodward, *Acta Crystallogr. Sect. B* **53**, 44 (1997).
 - [29] M. Ziese *et al.*, *Phys. Rev. Lett.* **104**, 167203 (2010).
 - [30] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
 - [31] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
 - [32] See supplementary material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.105.227203> for relaxed structural parameters and atomic positions.
 - [33] B. Dabrowski *et al.*, *Phys. Rev. B* **71**, 104411 (2005).
 - [34] K. Terai *et al.*, *Jpn. J. Appl. Phys., Part 2* **43**, L227 (2004).
 - [35] F. Tsui *et al.*, *Appl. Phys. Lett.* **76**, 2421 (2000).
 - [36] O. Bilani-Zeneli *et al.*, *J. Appl. Phys.* **104**, 054108 (2008).
 - [37] N. Balke *et al.*, *Nature Nanotech.* **4**, 868 (2009).
 - [38] E. Dagotto and Y. Tokura, *MRS Bull.* **33**, 1037 (2008).