Dynamical control of orbital occupations via a ferroelectric-induced polar state in metallic manganites

Hanghui Chen\textsuperscript{1,2,3,5}, Qiao Qiao\textsuperscript{6}, Matthew S. J. Marshall\textsuperscript{3,5}, Alexandru B. Georgescu\textsuperscript{4,5}, Ahmet Gulec\textsuperscript{6}, Patrick J. Phillips\textsuperscript{6}, Robert F. Klie\textsuperscript{6}, Frederick J. Walker\textsuperscript{3,5}, Charles H. Ahn\textsuperscript{3,5} and Sohrab Ismail-Beigi\textsuperscript{3,5}

\textsuperscript{1}Department of Physics, Columbia University, New York, NY 10027, USA
\textsuperscript{2}Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA
\textsuperscript{3}Department of Applied Physics, Yale University, New Haven, CT 06511, USA
\textsuperscript{4}Department of Physics, Yale University, New Haven, CT 06511, USA
\textsuperscript{5}Center for Research on Interface Structures and Phenomena (CRISP), Yale University, New Haven, CT 06511, USA
\textsuperscript{6}Department of Physics, University of Illinois at Chicago, Chicago, IL 60607, USA

(Dated: May 11, 2014)

Abstract

The breaking of orbital degeneracy on a transition metal cation and the resulting unequal electronic occupations of these orbitals provide a powerful lever over electron density and spin ordering in metal oxides. Here, we show how to dynamically modulate the orbital populations on Mn atoms at ferroelectric/manganite interfaces by switching the ferroelectric polarization. The change in orbital occupation can be as large as 10\%, greatly exceeding that of bulk manganites. This flippable orbital splitting is in large part controlled by the propagation of ferroelectric polar displacements into the interfacial region, a structural motif absent in the bulk and unique to the interface. We use \textit{ab initio} theory, epitaxial thin film growth, and scanning transmission electron microscopy to verify the predicted interfacial polar state and concomitant orbital splittings.
A key characteristic of transition metal oxides is the presence of electronically active \(d\) orbitals on the transition metal cations \([1, 2]\). These degrees of freedom create a rich variety of behaviors, and a large area in materials science and technology focuses on understanding and controlling these properties (e.g., magnetism, superconductivity, ferroelectricity, etc.) \([3]\). Perovskite complex oxides form a large subset of such oxides. For a transition metal in a cubic perovskite, crystal fields split its five \(d\) orbitals into a lower energy three-fold degenerate \(t_{2g}\) manifold (\(d_{xy}, d_{xz}, d_{yz}\)) and a higher energy two-fold degenerate \(e_g\) manifold (\(d_{3z^2-r^2}, d_{x^2-y^2}\)) \([4]\). These degeneracies can be further removed, for example, by Jahn-Teller distortions, in order to create unequal electronic occupancies within each originally degenerate manifold \([5]\). The resulting charge anisotropy can in turn affect electronic transport and magnetic ordering \([6]\). Hence, controlling the energies of the \(d\) orbitals tailors the physical properties of metal oxides in the bulk as well as at surfaces and interfaces \([7-13]\). A classic example is provided by manganites \([14]\), where the \(e_g\) orbitals are active in transport and magnetic ordering, and the energetic ordering of the \(e_g\) orbitals on each Mn site as well as neighboring Mn sites profoundly affects the ground state magnetic ordering \([15-29]\).

Although structural distortions (e.g., Jahn-Teller or GdFeO\(_3\) distortions) are common for bulk perovskite manganites, they only weakly remove orbital degeneracy. With the development of epitaxial thin film growth techniques, it is possible to remove orbital degeneracy through strain-induced Jahn-Teller-like distortions. Tensile (compressive) strain modifies the crystal field so as to favor the in-plane orbital \(d_{x^2-y^2}\) (out-of-plane orbital \(d_{3z^2-r^2}\)). However, utilizing strain is a static approach to tailoring the desired orbital \([30]\).

In this Letter, we describe a dynamic (i.e., flippable) approach to modulating the orbital occupations at La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (LSMO, \(x=0.2\) for the current study) interfaces. We use first principles theory and experimental growth and characterization to show that switching the ferroelectric polarization at a (001) ferroelectric/manganite interface can modulate the atomic-scale structure, change the electronic distribution at the interface, and split the orbital degeneracy of the interfacial Mn \(e_g\) levels. Furthermore, the sign of the splitting is opposite for the two different ferroelectric polarizations.

Theoretically, we use first principles density functional theory with a plane wave basis set and ultrasoft pseudopotentials as implemented in the quantum-espresso package \([31]\). We generally choose the prototypical ferroelectric PbTiO\(_3\) for most of the interfacial calculations below within the local density approximation (LSDA+\(U\) approach as detailed in \([32, 33]\), but
for the theoretical interfacial electron energy loss (EEL) spectra we use GGA-PBE and BaTiO$_3$ as the ferroelectric for direct comparison to experiment. *Ab initio* EEL spectra are simulated using the $Z+1$ approximation. As we describe below, our results are in fact independent of the magnitude of the ferroelectric polarization or choice of ferroelectric. Our calculations describe PbO/MnO$_2$ or BaO/MnO$_2$ ferroelectric/manganite (001) interfaces because our experimental systems are grown by starting with TiO$_2$-terminated SrTiO$_3$ substrates followed by depositing an integer number of unit cells of LSMO before depositing the ferroelectric film. In the present experiments, LSMO/BaTiO$_3$/LSMO samples are grown and characterized via aberration-corrected scanning transmission electron microscopy (STEM) to identify the atomic-scale and electronic structure of the interfaces. All high-angle annular dark-field (HAADF) and annular bright field (ABF) STEM images and electron energy loss (EEL) spectra are acquired on a probe-corrected JEOL JEM-ARM200CF operated at 200 kV with a 22 mrad convergence angle.

First principles calculations show that at a ferroelectric/LSMO interface, the termination of the ferroelectric polarization and presence of surface bound charge pulls screening charges to the interface. Two interfacial states are possible: accumulation or depletion of holes, as illustrated in the left panels of Fig. 1. For accumulation, the interfacial PbO layer is polarized with its O anion pushed towards the interfacial Mn; due to the epitaxial constraint on the in-plane lattice constant $a$, this means that the out-of-plane lattice constant $c$ becomes smaller than $a$ so $c/a < 1$ for the octahedral oxygen cage surrounding the interfacial Mn, lending to stabilization of the in-plane $d_{x^2-y^2}$ (as per standard crystal field theory). For depletion, the PbO layer’s oxygen is pushed away from the Mn, leading to $c > a$ and favoring $d_{3z^2-r^2}$. In addition, we compute an artificial “paraelectric” reference state where the PbTiO$_3$ is fixed to be non-polarized and where we expect $c \approx a$. The actual fully relaxed atomic structures from first principles calculations are shown in Fig. 1.

To quantify the difference in orbital populations, we use a standard definition of orbital polarization $\pi$ from Ref. 2

\[
\pi^i = \frac{n^i_{d_{x^2-y^2}} - n^i_{d_{3z^2-r^2}}}{n^i_{d_{x^2-y^2}} + n^i_{d_{3z^2-r^2}}}
\]

(1)

where $n^i_{\alpha}$ is the occupancy of atomic orbital $\alpha$ in the $i$th unit cell of the LSMO. Fig. 2A shows the computed $\pi^i$ of each layer moving away from the interface. The positive interfacial orbital polarization for accumulation means that $d_{x^2-y^2}$ is stabilized while in depletion the
FIG. 1: Panels A-C: Schematic of a PbTiO$_3$/LSMO interface. Yellow parts represent LSMO and green parts are PbTiO$_3$. The interface is PbO/MnO$_2$. The oxygen octahedron enclosing the interfacial Mn atom has different $c/a$ ratio as the ferroelectric polarization flips. A) Accumulation state; B) paraelectric state; C) depletion state. Panels D-F: Relaxed structure of LSMO/PbTiO$_3$ interfaces from first-principles calculations. The orange dashed line in F highlights the PbO/MnO$_2$ interface. The whole structure is strained to a SrTiO$_3$ substrate (substrate not shown in the figure). $\delta$ is the Mn-O displacement. D) Accumulation state; E) paraelectric state; F) depletion state.

$\pi^i < 0$ means that $d_{3z^2-r^2}$ is more populated. Qualitatively, these results are consistent with our preceding schematics-based expectations. However, the interfacial $\pi^i$ values shown in Fig. 2A are hard to rationalize using the actual $c/a$ ratios in Fig. 2B because for accumulation $c/a \approx 1$ but we find significant positive $\pi^i$. The key neglected degree of freedom turns out to be the polar distortion (ferroelectric rumpling) of the interfacial MnO$_2$ layer. Fig. 2C shows the rumpling amplitude $\delta$ in each MnO$_2$ layer. While $\delta$ is small for depletion, it is quite large for accumulation. There are at least two mechanisms that create the large rumpling for accumulation. First, the rumpling is the continuation of the ferroelectric distortion from the PbTiO$_3$ into the interfacial layers, much like in PbTiO$_3$/SrTiO$_3$ superlattices. Second, the paraelectric reference shows that the interfacial chemistry in the absence of ferroelectricity prefers an interfacial structure with significant rumpling (see Figs. 1E and 2C), which is also observed elsewhere. In accumulation, both effects are in the same
FIG. 2: A) Layer-resolved orbital polarization $\pi$ on successive Mn cations. Layer 1 is at the interface. The letters “a”, “p” and “d” refer to accumulation, paraelectric and depletion states, respectively. B) $c/a$ ratio of each oxygen octahedron that encloses Mn atoms. C) Mn-O displacement $\delta$ of the interfacial MnO$_2$ layer.

direction and lead to a large rumpling (Fig. [D]). In depletion, they oppose and we have a much smaller rumpling (Fig. [F]).

Before using theory to explain the origin of this flippable orbital polarization, we present experimental characterization of the atomic-scale geometry and electronic structure of such ferroelectric/manganite interfaces to ensure that the theoretical predictions based on the interfacial structure are on a firm footing.

We grow LSMO/BaTiO$_3$/LSMO samples and then characterize them by scanning transmission electron microscope (STEM) to identify the atomic-scale and electronic structure of the interfaces. Fig. [A] shows a pair of HAADF and ABF images of the entire LSMO/BaTiO$_3$/LSMO thin film in the [100] orientation, along with pertinent EEL spectra. The HAADF image shows a largely defect-free, atomically abrupt LSMO/BaTiO$_3$ interface. Within the BaTiO$_3$, the Ba atoms appear as the brighter spots in HAADF forming a rectangular lattice with the Ti located at the center of these rectangles. O atomic columns are
observed in the ABF image \[42\]. Fig. 3B is an inverted and averaged ABF image – previously interpolated (2×) and filtered – of the accumulation interface, which reveals Mn-O z-displacement δ in the first few MnO₂ layers. The magnitude of the Ti-O displacement in the BaTiO₃ is measured to be \(\approx 0.13 \text{ Å}\) based on the inverted ABF image. Fig. 3C shows the Mn-O and La-O atomic column profiles (more precisely, the La here refers to La\(_{1-x}\)Sr\(_x\)), which are fit with a Gaussian. The peak positions of Mn and La (from the Mn-O and La-O line profiles) are determined from the Gaussian fit: we find δ of 0.18 Å, 0.16 Å and 0.03 Å in the first three layers of MnO₂ from the right interface (highlighted by the yellow box in Fig. 3A). In subsequent MnO₂ layers, δ is below the measurement limit.

The theoretically predicted rumplings at the interface are clearly evidenced in the atomic column profile images with correct sign albeit reduced value, which may result from imaging artifacts due to the convolution of the Mn and O peaks in the mixed Mn-O column. Our BaTiO₃/LSMO interface calculation shows a rumpling of 0.22 Å in the interfacial MnO₂ layer, which compares more favorably to the experiment than the rumpling of 0.28 Å from the PbTiO₃/LSMO interface calculation (Fig. 1D). The Mn-O rumplings observed in experiment are further quantitatively confirmed by calculating the ion displacements from the multi-slice simulated STEM images of the optimized atomic structures in Fig. 1 which also yields interfacial rumplings of a smaller magnitude than \textit{ab initio} values (see Fig. 6 in the Supplementary Materials).

One- and two-dimensional atomically-resolved EEL spectra data are acquired from the LSMO/BaTiO₃ interfaces and the bulk-like regions of the LSMO \[43\]. Fig. 3D shows the Mn L₃/L₂ ratio as a function of distance from the right interface (highlighted by the yellow box in Fig. 3A) for both accumulation and depletion. We clearly observe an excess of screening holes (electrons) for accumulation (depletion) that decays back to bulk LSMO level over about two unit cells.

Finally, we consider O K-edge EEL spectra for the Mn-O atomic columns directly adjacent to the interface for accumulation and depletion as well as for bulk-like LSMO. The energy scales for all spectra shown in Fig. 3 are calibrated with respect to the Mn L₃ peak. We observe significant changes in the O K-edge fine structure at the interfaces for both accumulation and depletion compared to the bulk. The main experimental observation is that the interfacial O K-edge spectra do \textit{not} simply behave as hole- or electron-doped bulk LSMO: one would expect the accumulation (depletion) of holes to lead to a higher (lower)
FIG. 3: A) HAADF/ABF images of the LSMO/BaTiO$_3$/LSMO film with the interfaces marked and O columns clearly visible in ABF; B) interpolated, filtered, inverted, and averaged ABF image of the bottom interface which reveals the Mn-O polarization. The apparent triangular shape of the atomic columns is an artifact of the cross-correlation and averaging process; C) intensity line profiles of the Mn-O and La-O atomic column revealing the Mn-O polarization as shown theoretically in Fig. 1D, highlighted with green lines are the displaced Mn and O planes. The higher peaks in the two curves correspond to the positions of La and Mn atoms and the lower peaks to the positions of O atoms; D) the calculated Mn $L_3/L_2$-ratio for each polarization (accumulation and depletion) as a function of distance from the right interface (highlighted in the yellow box in A). More details on the Mn valence are found in [33]. E) O K-edge EEL spectra (solid dots for experimental data and solid line for $Z+1$ simulations) of the right interface for each polarization (accumulation and depletion), as well as bulk LSMO;
FIG. 4: Orbital polarization $\pi$ of bulk LSMO. A) tetragonal LSMO. B) cubic LSMO with the Mn atom shifted along $z$ direction. $x$ is the hole doping of LSMO.

pre-peak to main peak ratio [33], whereas the opposite is observed here. While the theoretical $Z + 1$ spectra match some (but not all) of the experimental observations, they do provide hints regarding this unusual behavior of pre-peak to main peak ratio. For example, the $d$ orbitals of the Ba adjacent to the interface turn out to play an important and unexpected role in modifying the EEL spectra away from bulk behavior [33]. A detailed study of the O $K$-edge is ongoing and will be the subject of future work. In brief, the O $K$-edge spectra contain relevant information about the local electronic structure, but the presence of the interface leads to non-bulk behavior and complexities in their interpretation. To summarize the experiments, STEM images and EEL spectra separately corroborate the intended polarization and the presence of an accumulation or depletion region at the interface. The theoretically predicted interfacial Mn-O displacements for the accumulation state (Fig. 1D) are indeed observed in the experimental HAADF/ABF images for BaTiO$_3$/LSMO.

Armed with confidence in the predicted interfacial structure, we return to the mechanisms that control the interfacial orbital polarization. We have argued that the MnO$_2$ rumpling is just as effective as the canonical Jahn-Teller-like $c/a$ effect in creating orbital polarization. Theoretically, this is demonstrated explicitly by modifying bulk LSMO. Figs. 4A and B show how the orbital polarization $\pi$ of LSMO is modulated separately as a function of $c/a$ and rumpling $\delta$, and we see that for accumulation it is $\delta$ that creates $\pi > 0$ while for depletion...
FIG. 5: Dependence of interfacial Mn orbital polarization $\pi$ as a function of ferroelectric polarization $P$. The green dashed lines correspond to the calculated polarization of SrTiO$_3$-strained bulk PbTiO$_3$.

c/a is mainly responsible for $\pi < 0$. In terms of microscopic mechanisms, the c/a dependence of $\pi$ is consistent with basic ideas of crystal field theory. The cation-ion rumpling $\delta$ always stabilizes $d_{x^2-y^2}$ and leads to $\pi > 0$. The $\delta$ dependence is, however, more intricate. Briefly, $\delta \neq 0$ breaks inversion symmetry of the MnO$_6$ octahedron and permits mixing of $d_{3z^2-r^2}$ and apical O $p_z$ orbitals for the conduction band edge states, a mixing that is symmetry-forbidden when inversion symmetry is present. This makes for a more anti-bonding $d_{3z^2-r^2}$ orbital that is pushed to higher energy and consequently has fewer electrons. A detailed explanation with diagrams is found in the supplement [33].

The dynamic nature of the interfacial orbital polarization is generic in that it does not depend on a specific choice of ferroelectric material. We have verified the robustness of our results over a wide range of magnitudes (from 0.44 to 1.04 C/m$^2$) for the ferroelectric polarization (bulk PbTiO$_3$ has a theoretical polarization of 0.7 C/m$^2$). Fig. 5 shows that the orbital polarization remains significant with a difference of 7%-10% between the two polarization states. This difference should be detectable by x-ray linear dichroism [9,10] or orbital reflectometry [2]. Having a flippable orbital polarization makes for easier detection, since by measuring the change in the signal, any potential difficulties due to a bulk-like background are automatically eliminated.
In conclusion, we have used \textit{ab initio} calculations combined with experimental growth and characterization to describe the atomic-scale geometry and electronic structure of ferroelectric/manganite interfaces. The orbital degeneracy of the Mn \(e_g\) states at such an interface is removed in a flippable manner: by changing the ferroelectric polarization, one can change the sign and magnitude of the orbital degeneracy breaking. Microscopically, a new structural distortion, absent in bulk manganites, is shown to be critical in determining the orbital polarization: the polar rumpling of the interfacial cation-anion layer. Moreover, this mechanism is generic and should be present in other interfacial materials systems.

\textbf{Acknowledgments}

This work at Yale was supported by NSF MRSEC DMR 1119826, NSF CNS 08-21132, FAME, ONR, and by the facilities and staff of the Yale University Faculty of Arts and Sciences High Performance Computing Center. Additional computations used the NSF XSEDE resources via grant TG-MCA08X007. At UIC, the work was supported by a grant from the National Science Foundation [DMR-0846748]. The acquisition of the UIC JEOL JEM-ARM200CF is supported by a MRI-R\(^2\) grant from the National Science Foundation [DMR-0959470]. Support from the UIC Research Resources Center is also acknowledged.

[1] E. Dagotto, \textit{Nanoscale Phase Separation and Colossal Magnetoresistance: The Physics of Manganites and Related Compounds} (Springer, 2002).

[2] E. Benckiser, M. W. Haverkort, S. Brck, E. Goering, S. Macke, A. Fra, X. Yang, O. K. Andersen, G. Cristiani, H.-U. Habermeier, et al., Nat. Mater. \textbf{10}, 189 (2011).

[3] Y. Tokura and H. Hwang, Nat. Mat. \textbf{7}, 694 (2008).

[4] Y. Tokura and N. Nagaosa, Science \textbf{288}, 462 (2000).

[5] J. B. Goodenough, Annu. Rev. Mater. Sci. \textbf{28}, 1 (1998).

[6] Z. Fang, I. V. Solovyev, and K. Terakura, Phys. Rev. Lett. \textbf{84}, 3169 (2000).

[7] J. Chakhalian, J. W. Freeland, H.-U. Habermeier, G. Cristiani, G. Khaliullin, M. van Veenendaal, and B. Keimer, Science \textbf{318}, 1115 (2007).

[8] A. D. Rata, A. Herklotz, K. Nenkov, L. Schultz, and K. Dörre, Phys. Rev. Lett. \textbf{100}, 076401
(2008).

[9] A. Tebano, C. Aruta, S. Sanna, P. G. Medaglia, G. Balestrino, A. A. Sidorenko, R. De Renzi, G. Ghiringhelli, L. Braicovich, V. Bisogni, et al., Phys. Rev. Lett. 100, 137401 (2008).

[10] M. Huijben, L. W. Martin, Y.-H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, and R. Ramesh, Phys. Rev. B 78, 094413 (2008).

[11] M. Salluzzo, J. C. Cezar, N. B. Brookes, V. Bisogni, G. M. D. Luca, C. Richter, S. Thiel, J. Mannhart, M. Huijben, A. Brinkman, et al., Phys. Rev. Lett. 102, 166804 (2009).

[12] P. Yu, J.-S. Lee, S. Okamoto, M. D. Rossell, M. Huijben, C.-H. Yang, Q. He, J. X. Zhang, S. Y. Yang, M. J. Lee, et al., Phys. Rev. Lett. 105, 027201 (2010).

[13] J. M. Chen, Z. Hu, H. T. Jeng, Y. Y. Chin, J. M. Lee, S. W. Huang, K. T. Lu, C. K. Chen, S. C. Haw, T. L. Chou, et al., Phys. Rev. B 81, 201102 (2010).

[14] M. B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001).

[15] C. Zener, Phys. Rev. 82, 403 (1951).

[16] P. W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955).

[17] Y. Tokura, Rep. Prog. Phys. 69, 797 (2006).

[18] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. Lett. 76, 4825 (1996).

[19] H. J. A. Molegraaf, J. Hoffman, J. Hoffman, S. Gariglio, D. van der Marel, C. H. Ahn, and J.-M. Triscone, Advanced Materials 21, 3470 (2009).

[20] H. Lu, T. A. George, Y. Wang, I. Ketsman, J. D. Burton, C.-W. Bark, S. Ryu, D. J. Kim, J. Wang, C. Binek, et al., Applied Physics Letters 100, 232904 (2012).

[21] V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, X. Crassous, A. Moya, S. Enouz-Vedrenne, A. Gloter, D. Imhoff, C. Deranlot, et al., Science 327, 1106 (2010).

[22] J. D. Burton and E. Y. Tsymbal, Phys. Rev. B 80, 174406 (2009).

[23] J. D. Burton and E. Y. Tsymbal, Phys. Rev. Lett. 106, 157203 (2011).

[24] C. A. F. Vaz, J. Hoffman, Y. Segal, J. W. Reiner, R. D. Grober, Z. Zhang, C. H. Ahn, and F. J. Walker, Phys. Rev. Lett. 104, 127202 (2010).

[25] D. A. Muller, L. Fitting Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby, and O. L. Krivanek, Science 22, 1073 (2008).

[26] L. Fitting Kourkoutis, J. H. Song, H. Y. Hwang, and D. A. Muller, PNAS 107, 11682 (2010).

[27] M. J. Calderón, S. Liang, R. Yu, J. Salafranca, S. Dong, S. Yunoki, L. Brey, A. Moreo, and E. Dagotto, Phys. Rev. B 84, 024422 (2011).
[28] C. T. Nelson, P. Gao, J. R. Jokisaari, C. Heikes, C. Adamo, A. Melville, S. H. Baek, C. M. Folkman, B. Winchester, Y. J. Gu, et al., Science 334, 968 (2011).
[29] C. Jooss, L. Wu, T. Beetz, R. F. Klie, M. Beleggia, M. A. Schofield, S. Schramm, J. Hoffmann, and Y. Zhu, PNAS 104, 13597 (2007).
[30] A. Sadoc, B. Mercey, C. Simon, D. Grebille, W. Prellier, and M.-B. Lepetit, Phys. Rev. Lett. 104, 046804 (2010).
[31] http://www.quantum-espresso.org/.
[32] H. Chen and S. Ismail-Beigi, Phys. Rev. B 86, 024433 (2012).
[33] See the supplementary materials.
[34] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[35] W. Luo, M. Varela, J. Tao, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. B 79, 052405 (2009).
[36] S. J. Pennycook and L. A. L. A. Boatner, Nature 336, 565 (1988).
[37] S. D. Findlay, N. Shibata, H. Sawada, E. Okunishi, Y. Kondo, T. Yamamoto, and Y. Ikuhara, Applied Physics Letters 95, 191913 (2009).
[38] R.F. Klie, A. Gulec, Z. Guo, T. Paulauskas, Q. Qiao, R. Tao, C. Wang, K.B. Low, A.W. Nicholls, P.J. Philips, “The new JEOL JEM-ARM200CF at the University of Illinois at Chicago” to be published in Crystal Research, 2013.
[39] C.-G. Duan, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. Lett. 97, 047201 (2006).
[40] J. M. Rondinelli, M. Stengel, and N. A. Spaldin, Nat. Nanotech. 3, 46 (2008).
[41] M. Dawber, C. Lichtensteiger, M. Cantoni, M. Veithen, P. Ghosez, K. Johnston, K. M. Rabe, and J.-M. Triscone, Phys. Rev. Lett. 95, 177601 (2005).
[42] Y. J. Kim, R. Z. Tao, R. F. Klie, and D. N. Seidman, ACS Nano 7, 732 (2013).
[43] The EEL spectra were treated with the multivariate statistical analysis (MSA) package for Gatan Digital Micrograph (Watanabe Microsc Anal 2009) [44].
[44] M. Watanabe, E. Okunishi, and K. Ishizuka, Microscopy and Analysis 23, 5 (2009).