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<td><strong>Author(s)</strong></td>
<td>Chen, L. Y.; Chen, C. L.; Jin, K. X.; Wu, T.</td>
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Prediction of giant magnetoelectric effect in LaMnO3/BaTiO3/SrMnO3 superlattice: The role of n-type SrMnO3/LaMnO3 interface
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Observation of strong magnetoelectric effects in Ba0.7Sr0.3TiO3/La0.7Sr0.3MnO3 thin film heterostructures
Prediction of giant magnetoelectric effect in LaMnO$_3$/BaTiO$_3$/SrMnO$_3$ superlattice: The role of n-type SrMnO$_3$/LaMnO$_3$ interface

L. Y. Chen, C. L. Chen, K. X. Jin, and T. Wu

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We study the magnetoelectric coupling for the [001]-oriented (LaMnO$_3$)$_2$/(BaTiO$_3$)$_5$/(SrMnO$_3$)$_2$ superlattice, by means of the density functional theory. An interesting transition between ferromagnetic ordering and antiferromagnetic ordering is demonstrated by switching ferroelectric polarization in short-period superlattice structure. The predicted ferroelectrically induced magnetic reconstruction is less sensitive to the choice of Coulomb-correction $U$ within GGA+$U$ scheme. A possible explanation is given in terms of the favorable effect of n-type SrMnO$_3$/LaMnO$_3$ interface. Our results suggest that a sizable magnetoelectric effect may be achieved in the short-period LaMnO$_3$/BaTiO$_3$/SrMnO$_3$ superlattice, hence promising application in electrically controlled magnetic data storage. © 2014 AIP Publishing LLC.

I. INTRODUCTION

The magnetoelectric (ME) properties of multiferroic materials, which demand the coupling between ferroelectric (FE) and ferromagnetic (FM) order parameters, allow the possibility of controlling FE properties by magnetic fields and of controlling magnetic properties by electric fields, and open new routes to the next generation of electronic devices, such as FE and multiferroic tunnel junctions. The origin of ME multiferroic lies in a nonzero ME coupling that occurs due to several different mechanisms, and the recent reviews can be seen in Refs. 5 and 6. Apart from the intrinsic ME compounds with no time-reversal and no space-inversion symmetries (i.e., single-phase multiferroics with weak ME coupling), a mechanism of ME coupling also takes place in composites of FE and FM or ferrimagnetic compounds, e.g., artificial heterostructures or superlattices. At ferromagnet/ferroelectric interfaces, ME effect originates from the purely electronic mechanisms and can be mediated by both strain and field effects from the ferroelectric. First-principle calculations on magnetoelectric multiferroic composite systems, such as Fe/PbTiO$_3$, Fe$_2$O$_3$/BaTiO$_3$, and Co$_2$MnSi/BaTiO$_3$, have predicted that charge reconstruction at the interface could cause the ferromagnet to become sensitive to the FE polarization direction and, reciprocally, induce magnetic moments in the ferroelectric. Experimentally, composite multiferroics have also been fabricated by artificially making ferroelectrics and ferromagnets in nanoscale heterostructures. Both of theoretical and experimental results show that a change in interface magnetization could be achieved by switching ferroelectricity under the influence of applied electric field. The electronic orbital hybridization at interface (e.g., charge transfer and chemical bonding) plays a role for the ME phenomenon in these composite multiferroic systems, and another electronic mechanism for an interface ME effect originates from the spin-dependent screening. For the latter, the FE polarization can modulate carrier concentration by producing an accumulation of spin-polarized electrons (or depletion of holes) near the ferromagnet/ferroelectric interfaces, and thus alters the interface magnetization, as was predicted for the La$_{1-x}$Sr$_x$MnO$_3$/BaTiO$_3$ and SrRuO$_3$/BaTiO$_3$ interfaces. Recently, the carrier-induced ME coupling was also suggested experimentally in the BaTiO$_3$/La$_{0.5}$Ca$_{0.5}$MnO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ and PbZr$_{0.25}$Ti$_{0.75}$O$_3$/La$_{0.5}$Sr$_{0.5}$MnO$_3$ tunnel junctions.

Among the many artificial magnetic heterostructures, superlattices are of current interest because of the diverse magnetic and electronic phases they exhibit. For example, recent experiments and theoretical calculations indicate that (LaMnO$_3$)$_{2n}$/(SrMnO$_3$)$_n$ superlattices are ferromagnetism for the short-period structures ($n \leq 2$), while the long-period superlattices exhibit the ferromagnetic ordering only at interfaces. Particularly, multiferroic superlattices, as one of the most promising candidates for strengthening ME coupling, have recently received attention. The issue of how to construct the multiferroic superlattices with robust and stable ME coupling, however, is still being explored. Very recently, a transition between antiferromagnetic (AFM) and FM orders through strain effect from the ferroelectric substrate is reported in FeRh layered structure. Implementing electronic structure calculations based on the DFT, in this paper, we report a magnetic reconstruction for the short-period [001]-oriented (LaMnO$_3$)$_2$/(SrMnO$_3$)$_2$ (LMO)$_2$/BTO$_3$(SMO)$_2$ artificial tri-component superlattices, which is mostly driven by field effect related to the FE polarization. Our work suggests a potential approach to design the multiferroic superlattices with excellent properties, and may be interesting for technological applications such as electrically controlled magnetism.

II. COMPUTATIONAL DETAILS

All calculations are performed within the framework of DFT using the projected augmented wave method and a
plane-wave basis set, as implemented within Vienna ab initio simulation package. To electron exchange and correlation, we chose the Perdew-Burke-Ernzerhof formulation of the generalized gradient approximation plus on-site Coulomb correction (GGA + U), which is essential for the correct description of structural and AFM ground states of LaMnO$_3$ (LMO) and SrMnO$_3$ (SMO). The Coulomb (U) and exchange parameter (J) are taken as 8 and 1 eV, respectively, to treat the localized Mn-3d states. In our case, these values can properly describe LMO and SMO as AFM semiconductors rather than metals, giving reasonable band gaps for them: $E_g$ = 0.98 and 0.25 eV for LMO and SMO, respectively. Simultaneously, U is set to be 8 eV for Ti 3d states, while the fairly large $U$ (12 eV) is introduced to La 4f states. In addition, the cutoff energy of plane-waves is set to be 520 eV that is large enough to deal with all the elements considered here within the PAW method.

LMO, BaTiO$_3$ (BTO), and SMO (001) layers are stacked in a supercell to simulate the [001]-oriented (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattices. Because most of the experimental results are based on the LMO/SMO superlattices grown on the SrTiO$_3$ (STO) substrate, the in-plane ($x$ and $y$) lattice parameters for the (LMO)$_n$(BTO)$_5$(SMO)$_2$ superlattices, $a$ and $b$, are chosen to be in accordance with those of bulk STO, i.e., $a = b = a_{STO} = \sqrt[4]{2} a_{STO}$ (see Fig. 1), where $a_{STO}$ is the bulk STO lattice parameter obtained from experiments (3.905 Å). Meanwhile, the out-of-plane (c) lattice parameter of superlattice, c, is optimized for eliminating the influence of strain effect from STO substrate. Atomic relaxations are performed using a 8 x 8 x 2 Monkhorst-Pack grid for k-point sampling, and all atomic coordinates within a supercell are fully relaxed until the forces acting on each atom are smaller than 20 meV/Å for both paraelectric and FE relaxations. Additionally, the initial oxygen-octahedron rotation and Jahn-Teller distortion ($Q_3$) are taken about $10^\circ$ and 0.63 Å combining with experimental data, respectively, in LMO site.

III. RESULT AND DISCUSSION

Generally speaking, there are two types for the atomic layer stacking in unit cell of (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattices, depending on the interface termination. The ultrathin BTO layer is sandwiched between the hole-doped $p$-type LaO/MnO$_2$/BaO/TiO$_2$ and the un-doped BaO/TiO$_2$/SrO/MnO$_2$ interfaces in type-1 structure, while that is sandwiched between the electron-doped $n$-type MnO$_2$/LaO/TiO$_2$/BaO and the un-doped TiO$_2$/BaO/MnO$_2$/SrO interfaces in type-2 structure. Implementing calculations for the two superlattices in the paraelectric state, we find that total free energy per unit cell for the type-1 superlattice is about 268 meV lower than that for the type-2 superlattice. This means that more stable interface configuration may occur in type-1 superlattice structure. Inspecting the polarization displacements (FE polarization along [001] orientation is assumed in this paper), we notice that an overall net polarization along $z$ orientation (P(z)) or $-z$ orientation (P(-z)) could be retained for the tetragonal phase BTO layer in optimized type-1 (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattice. Given the stable polarization states in (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattices, we can estimate the energy profile associated with polarization reversal by linearly scaling the atomic displacement, keeping track of the total energy of each tested structure. And, the detailed analysis indicates that two energy minima correspond to P(z) and P(-z) states. In consideration of these results, in the remainder of this paper, we focus our attention only to the type-1 (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattices unless stated otherwise. In order to determine the ground-state magnetic ordering, we calculated the neighboring Mn-Mn exchange interaction, J, by performing a number of total-energy calculations for various magnetic configurations for each superlattice and fitting the energies with the nearest-neighbor Heisenberg model. $E = - \sum_{i,j} J_{ij} m_i m_j$, the symbol $\langle i,j \rangle$ denotes a sum over nearest neighbours only and $m_i$ is the magnetization in each MnO$_2$ layer of manganites.) Note that positive (negative) J denotes the FM (AFM) alignment of two neighboring Mn spins within the nearest-neighbor Heisenberg model. Fig. 2 presents the various exchange interactions for the considered (LMO)$_2$(BTO)$_5$(SMO)$_2$ superlattice.
The calculated magnetic exchange interactions are listed in Table I for (LMO)2/(BTO)5/(SMO)2 superlattice we consider. The case of (La0.5Sr0.5MnO3)4/(BaTiO3)5 [(LSMO)4/(BTO)5] superlattice is also examined for comparison. All the in-plane exchange interactions are independent of the polarization direction of BTO and strongly positive, hence stable FM alignment in the \(xy\) planes. At the MnO2 layer sandwiched by two SrO layers, we point out, the favorable in-plane FM ordering that obviously deviate from the bulk SMO may originate from epitaxial strain.\(^{29}\) Intriguingly, with the presence of P(\(z\)) state, the out-of-plane exchange interactions \(J_{12}, J_{23}, \) and \(J_{34}\) for (LMO)2/(BTO)5/(SMO)2 superlattice are negative so as to stabilize the AFM alignment between neighboring MnO2 layers (see Fig. 2). When the polarization reverses from P(\(z\)) state to P(\(-z\)) state, however, they become positive. These findings suggest that a spin-flip could be ferroelectrically induced in the (LMO)2/(BTO)5/(SMO)2 superlattice, hence a favorable ME coupling. By contrast, A-type AFM ordering, which is also observed in bulk La0.5Sr0.5MnO3 (LSMO) compound,\(^{32}\) is stabilized in (LSMO)4/(BTO)5 superlattice, and it is independent of the FE polarization in BTO layer.

Let us now shift our attention to the related physical mechanisms. The different ground-state magnetic structure can be qualitatively understood in terms of the FM double exchange (FMDE) mediated by itinerant e\(_g\) electrons and the AFM superexchange (AFMSE) between the core spins. They often coexist in strongly correlated manganite and compete against each other. For the (LMO)2/(BTO)5/(SMO)2 superlattices, the itinerant character of Mn-e\(_g\) electrons can be modulated electrostatically by the FE polarization, thereby altering the dominant interaction mechanism. P(\(z\)) state

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<th>Polarization</th>
<th>(J_1)</th>
<th>(J_2)</th>
<th>(J_3)</th>
<th>(J_4)</th>
<th>(J_{12})</th>
<th>(J_{23})</th>
<th>(J_{34})</th>
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<tr>
<td>(LMO)2/(BTO)5/(SMO)2</td>
<td>P((z))</td>
<td>14.09</td>
<td>12.06</td>
<td>11.74</td>
<td>11.09</td>
<td>-1.23</td>
<td>-1.36</td>
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<tr>
<td></td>
<td>P((-z))</td>
<td>9.71</td>
<td>7.24</td>
<td>5.97</td>
<td>11.80</td>
<td>0.72</td>
<td>1.96</td>
</tr>
<tr>
<td>(LSMO)4/(BTO)5</td>
<td>P((z))</td>
<td>14.24</td>
<td>13.94</td>
<td>13.92</td>
<td>12.32</td>
<td>-0.36</td>
<td>-5.77</td>
</tr>
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**FIG. 3**. Layer-projected orbital-resolved DOS [(a): P(\(z\)) state; (b): P(\(-z\)) state] and estimated potential profile (c) for (LMO)2/(BTO)5/(SMO)2 superlattice. Here, Mn-d\(_x^2\)\(-\)\(y^2\) state (shade), Mn-d\(_x^2\)\(-\)\(z^2\) state (blue line), and p\(_z\) state of the oxygen atom located at A-O plane (A = La or Sr) are shown in (a) and (b). Note that arrows indicate the occupied e\(_g\) state at Mn-2 and -3 atoms. In (c), dashed and solid lines correspond to P(\(z\)) and P(\(-z\)) states, respectively.

**TABLE I.** The calculated exchange interaction between neighboring Mn atoms for (LMO)2/(BTO)5/(SMO)2 and (LSMO)4/(BTO)5 superlattices. A negative \(J\) corresponds to an AFM interaction (anti-parallel) and a positive \(J\) corresponds to a FM interaction (parallel).
induces a strong depletion of \( e_g \) electrons in the vicinity of the BaO interface\(^{33,34} \) by enhancing hole injection into the LMO side, and then \( e_g \) electron is transferred from \( p \)-type MnO\(_2\)/BaO interface to \( n \)-type MnO\(_2\)/LaO interface and strongly occupies the \( d_{z^2-r^2} \) state of Mn-2 atom. To gain further insight into the \( e_g \) orbital reconstruction, Fig. 3 shows the layer-projected orbital-resolved density of states (DOS) for the \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice. Here, Mn \( e_g \) states and \( p_x \) state of the oxygen atom located at A-O plane (\( A = \mathrm{La} \) or \( \mathrm{Sr} \)), which are involved with FMDE interaction, are considered. It is readily identified that the \( e_g \) orbitals are dramatically reconstructed as FE polarization reverses. In particular, when \( \text{P}(z) \) state occurs, the \( e_g \) states of Mn-2 atom are Jahn-Teller split into two bands, with the lower one (\( d_{z^2-r^2} \) state) occupied. Similar situation is also accomplished for the Mn-3 atom. Besides, there is nearly no contribution of \( p_z \) state of oxygen atoms at Fermi level. As a consequence, the out-of-plane itinerant character of Mn-\( e_g \) electrons significantly weakens, with very few \( e_g \) electrons leaked into the SMO layer. So, the out-of-plane magnetic coupling becomes dominated by the AFMSE interaction and, the most likely ground state for \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice is AFM state as \( \text{P}(z) \) state becomes stable. When it comes to \( \text{P}(-z) \) state, the \( e_g \) states fail to split into two bands for the LMO part and interface Mn-2 atom and, electron transfer is expected between \( d_{z^2-r^2} \) and conductive \( d_{z^2-r^2} \) bands. Moreover, relatively modest potential barrier at MnO\(_2\)/LaO interface, which could be inferred from the potential lineups within the SMO/LMO layers (illustrated in Fig. 3(c)), allows the \( d_{z^2-r^2} \)-orbital electrons to cross the interface and leak into SMO layer. In this case, some Mn-\( e_g \) electrons are spread throughout LMO and SMO layers as seen from layer-projected orbital-resolved DOS (Fig. 3(b)). These serve as the itinerant carriers to mediate the FMDE interaction stabilizing the FM ordering. For short-period (LSMO\(_x\)/(BTO)\(_y\)) superlattice, epitaxial strain effect may continue the intrinsic A-type AFM ordering in LSMO layer as the FE polarization reverses. Tensile strain from STO substrate yields the contraction in the \( \hat{c} \) direction for LSMO (i.e., \( c_{\text{LSMO}} < a_{\text{STO}} \)), which favors the \( d_{z^2-r^2} \) orbital occupation and lowers the \( d_{z^2-r^2} \) orbital occupation.\(^{35} \) Therefore, the hopping between Mn atoms more readily becomes two dimensional (\( \chi y \) plane), suppressing out-of-plane FM alignment. As a result, the A-type AFM ordering is dominant in both FE states.

In order to further understand whether the strong electro-magnetic coupling changes with electron-electron correlation effect, in Fig. 4, we plot the change in exchange interaction as a function of \( U \) for \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice. As the amount of correlation is altered in the calculation through the \( U \) term, the out-of-plane exchange interactions \( J_{12}, J_{13}, \) and \( J_{34} \) are always negative for the \( \text{P}(z) \) state, implying an intrinsic AFM ground-state. When it comes to the \( \text{P}(-z) \) state, the ground-state magnetic structure is correlated with \( U \). In the LMO part FM ordering continues, while spin ordering undergoes a transition from AFM alignment to FM alignment as \( U \) increases in the SMO part. Since any prediction of the magnetic properties depends greatly on the choice of \( U \), we examine the magnetic and electronic structures of ground-state for bulk LMO and SMO with different Coulomb-correction, and the calculations show that the reasonable \( U \) is in the range of 5 to 8 eV. The results shown in Fig. 4 are in favor of the prediction that a robust and stable coupling between FE polarization and magnetization could be present in \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice. It is worth mentioning that the ferroelectrically induced magnetic reconfigurations predicted in previous \( \mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3/\mathrm{BaTiO}_3 \) nano-scale heterojunctions may be absent for more reliable GGA + \( U \) scheme.\(^{35} \) Besides, the notorious “dead-layer” problem in ultrathin \( \mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3 \) layer\(^{36-39} \) is also likely to hinder the ferroelectric control of magnetization in short-period superlattices composed of FM \( \mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3 \) and ferroelectric. In view of these results, the superlattice structure we present probably have some advantages over other multiferroic composites\(^{35,33,39-41} \) for the use of ferroelectrics in the electric modulation of magnetization.

### FIG. 4. The out-of-plane exchange interaction dependence of Coulomb-correction \( U \) for the \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice. Solid and open symbols correspond to \( \text{P}(z) \) and \( \text{P}(-z) \) states, respectively.

### IV. CONCLUSION

In summary, we have studied the ME properties of [001]-oriented \((\mathrm{LMO})_2/(\mathrm{BTO})_5/(\mathrm{SMO})_2\) superlattice, using the first-principle method based on DFT. Intriguingly, superlattice experiences a transition between FM ordering and AFM ordering by switching the FE polarization, indicating a substantial ME coupling effect. Furthermore, such a strong electro-magnetic coupling appears to be less sensitive to the value of \( U \) chosen in GGA + \( U \) computation. The different ground-state magnetic configurations between two opposite polarization states are qualitatively explained via the competition between FMDE and AFMSE mechanisms. With the polarization reversal, one of main theoretical findings is that the out-of-plane itinerant character of \( e_g \) electrons could be modulated through a change in \( d_{z^2-r^2} \)-orbital occupancy occurring at \( n \)-type SMO/LMO interface. The results obtained herein provide a potential design for pursuing the ferroelectric field effect control of magnetism. We hope that the theoretical predictions will stimulate experimental studies of such superlattices to search for a robust ME coupling.

### ACKNOWLEDGMENTS

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