Strain effects on multiferroic heterointerface La$_{0.5}$Sr$_{0.5}$MnO$_3$/BaTiO$_3$ by DFT calculations

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Abstract

La$_{1-x}$Sr$_x$MnO$_3$/Ba TiO$_3$ based multi-ferroic tunnelling junction structures promise practical on/off resistance ratio for low-field switching 4-state non-volatile memory. This work aims at investigating the nature of magnetoelectric coupling on La$_{1-x}$Sr$_x$MnO$_3$/BaTiO$_3$ interface in the framework of density functional theory. Our results suggest that owing to electrostatic screening effect, electric polarization of BaTiO$_3$ layer can act as the intermediary to electrically modulate not only the magnitude but also the order of local magnetic moment in La$_{1-x}$Sr$_x$MnO$_3$ layer. Moreover, it is demonstrated that both lateral and perpendicular strains are of particular importance to modify this kind of magnetoelectric coupling. The magnetic ordering is electrically tunable only with the application of suitable strain.

Keywords: multiferroic, interface, magnetoelectric coupling

Classification numbers: 2.01, 2.07, 4.11, 4.14

Introduction

In response to the growing demand for faster, higher density and lower power consuming non-volatile memory devices, several alternatives to the traditional silicon technology have been developed [1–7]. Recently, multi-ferroic tunnelling junction (MFTJ) has emerged as the most attractive technology because of its feasibility into 4-state non-volatile memories [6, 7]. A typical MFTJ includes a multi-ferroic interface between ferroelectric barrier and ferromagnetic electrodes which leads to key properties of MFTJ [8–10]. Among various materials of choice for multi-ferroic interface in MFTJ, BaTiO$_3$ (BTO) and La$_{1-x}$Sr$_x$MnO$_3$ (LSMO-x with x denoting dopant concentration) are of special interest. Noticeable TMR and TER effects were experimentally observed in LSMO-0.3/BTO/Fe (Co, permalloy Ni$_{0.8}$Fe$_{0.2}$) MFTJs with coefficients, respectively, up to 97% and 93% at 40 K [7, 11]. LSMO/BTO based MFTJs were improved with structure LCMO-0.3/BSTO-0.5/LCMO-0.3/Au (C = Ca, S = Sr dopants) with TMR and TER coefficients respectively 300% and 90% at 40 K [6]. However, a critical drawback of this structure is low working temperature because of low Curie temperatures of LCMO-0.3 and BSTO-0.5. The substitution of LCMO-0.3/BSTO-0.5 with LSMO-0.3/BSTO-0.05 can help to increase working temperature up to room temperature but significantly reduces TMR and TER coefficients.

Another way to improve MFT behaviour of this kind of MFTJ was based on the theoretical predictions of Burton and Tsymbal [12]. Firstly, it should be reminded that LAMO-x (A can be Ba, Sr or Ca) is well-known for the competition between the ferromagnetic (FM) double exchange and antiferromagnetic (AFM) super exchange. The dominating magnetic interaction can be determined by the $e_g$ electron concentration which, in turn, can be modulated by dopant concentration x. The FM-AFM phase transitions occur at $e_g$ electron concentrations around 0.5 (corresponding to x = 0.5). Burton and Tsymbal’s ab initio calculations suggest that electrostatic screening effect at LBMO-0.5/BTO (B is Ba) interfaces provides an additional mechanism for the spatial modulation of $e_g$ electron concentration [12]. Hence, this electrostatic screening effect can induce an ME coupling which implies not only the change in the magnitude of the magnetic moments but also the FM-AFM switch when the ferroelectric polarization is flipped. They proposed that this effect can be also achieved for A = Ca or Sr. Their prediction was latter experimentally evidenced with an amazing...
increase of TER coefficient in LSMO-0.3/BTO/LCMO-0.5/LSMO-0.5 up to 5000% at 40 K [6]. Removing LCMO-0.5 layer strongly reduces TER coefficient down to 30%. It is believed that the ME-coupling induced FM-AFM switch at LCMO-0.5/BTO interface suggested before acts as a spin valve effect similar to TMR effect and, hence, strongly increased TER coefficient. Such effect might be absent in LSMO-0.3/BTO/LSMO-0.5 structure so that TER effect wasn’t enhanced in this case. However, again, because of low Curie temperature of La0.5Sr0.5MnO3 the working temperature of LSMO-0.3/BTO/LCMO-0.5/LSMO-0.5 MFTJ is below room temperature.

In this work, on the base of ab initio calculations, we propose a way to overcome the low working temperature. We first note that according to Burton and Tsymbal’s calculations [12], ME-coupling induced FM-AFM switch can also occur at LSMO-0.5/BTO interface. Hence, similar spin valve effect is possible in LSMO-0.3/BTO/LSMO-0.5 structure. On the other hand, LSMO-0.5 and BTO have Curie temperatures 360 K and 400 K respectively [13]. Consequently, high TER coefficient and higher working temperature can be expected for LSMO-0.3/BTO/LSMO-0.5 structure with some suitable modification. Such modification is suggested from our results which demonstrate that ME-coupling induced FM-AFM switch can occur under suitable strains.

1. Calculation details

Our ab initio calculations were introduced within generalized gradient approximation (GGA) of density functional theory (DFT). The explicit form for exchange-correlation functional in use was the one formulated by Perdew et al., i.e. PBE functional [14]. The wave functions were expanded in plane wave basis set which was cut-off at kinetic energy of 400 eV (29.4 Ry). Another approximation arises from the fact that an efficient formula which can reproduce the scattering effect of strong Coulomb potential of nuclei and core electrons on valence electrons is needed for feasible computations. In our calculations, projector augmented wave (PAW) formula with frozen core approximation was used. This considers the core electrons together with the nuclei to form non-polarizable ion cores. The valence electron wave functions are divided into two parts, i.e. localized functions for rapidly-varying part in core region and plane wave functions for smooth part outside the core region [15]. All of the above algorithms were implemented with Quantum Espresso Package [16].

(001) LSMO-x/BTO interface was simulated using super-lattice model. A fourfold rotation symmetry P4mm super-cell was built up by stacking 4 tetragonal unit cells of BTO onto 5 tetragonal LSMO unit cells along (001) direction (figure 1(a)). Because when incorporated into hetero-structures, the critical thickness of BTO can be reduced down to 3 unit cell, 4 BTO unit cells should be enough to stabilizing ferroelectricity in BTO layer [17]. To avoid artificial polarization, the same contacts were made at all interfaces of the super-lattice, i.e. Ba (Sr) O/TiO2. Consequently, both of the BTO and LSMO-x layers are non-stoichiometric with an extra layer of Ba (Sr) O and MnO2 layer respectively. Then the formula of (001) LSMO-0.5/BTO super-lattice can be written as (BaTiO3)1/2BaO/(La0.5Sr0.5MnO3)1/2-MnO2. In spite of that, the spontaneous ferroelectric polarization P of BTO gives rise to discriminated interfaces in the super-lattice, i.e. interface 1 (IF1) where P points towards and interface 2 (IF2) where P points away. Atomic layers between these interfaces are named according to figure 1(a). The lateral size of the supercell is a\(\sqrt{2}\times a\sqrt{2}\) where a is the lateral lattice constant so that there are two metal sites in each atomic layer. The Sr dopant was introduced into one of the two La sites in each LaO layer to get dopant concentration x = 0.5 (figure 1(b)). It should be noted that because of the non-stoichiometry, the number of e\(_{f}\) electrons per one Mn sites is not 0.5 but 0.58. With the above super-cell, the total energy, density of states, electron density and other electronic structure integrals were calculated using an 8 x 8 x 8 Monkhorst-Pack grid for k-point sampling.

We calculated electronic structure of the super-lattice at different configurations of ferro-electricity and magnetism. These configurations are named FM, A1-FE1, A1-FE2 and AAFFM and represented in figure 2(a). Here, FM means ferromagnetic ordering all over the LSMO-0.5 layer. A1-FE1(FE2) means that the magnetic moment of Mn ions at MnO2-IF1 (IF2) layer is switched to be anti-parallel to the others. AAFFM means that the magnetic moments of Mn ions in neighbouring MnO2 layers are anti-parallel all over LSMO-0.5 layer.

Finally, lateral strain induced by substrates was taken into account by fixing the lateral lattice constant a at the lattice constant of substrate material. Here, we considered two substrate materials, BTO with optimized cubic lattice constant a = 4.099 Å and SrTiO3 (STO) with optimized cubic lattice constant a = 3.937 Å. The optimized lattice constant of LSMO-0.5 is 3.887 Å. Hence, lateral strain bear by LSMO-0.5

\begin{enumerate}
\item \textbf{Figure 1.} (a) P4mm super-cell of (001) LSMO-x/BTO super-lattice. (b) La0.5Sr0.5O layer viewed along (001) direction. Crystal directions are denoted by thin black arrows. Spontaneous electric polarization of BTO layers are denoted by thick green arrows.
\end{enumerate}
magnetic moments in –’ and ‘+’ signs denote ‘+’ and electrostatic screening effect in LSMO/BTO super-lattice. Black arrows denote BTO ferroelectric polarization.

Figure 2. (a) Configurations of ferro-electricity and magnetism considered in our calculations. Green horizontal arrows denote Mn magnetic moments in LSMO-0.5 layer. Blue vertical arrows denote BTO ferroelectric polarization. (b) A schematic representation of electrostatic screening effect in LSMO/BTO super-lattice. Black arrows denote BTO ferroelectric polarization.

Table 1. Comparison between total energies (meV) of considered configurations and FM configuration.

|                      | FM  | A1-FE1 | A1-FE2 | AAFM |
|----------------------|-----|--------|--------|------|
| BTO substrate        | 0   | -38    | -55    | -287 |
| STO substrate        | 0   | 34     | 21     |      |
| BTO substrate with stretched c | 0   | 11     | -43    |      |

layer is tensile strain of ~5% and 3% respectively. The lateral strain bear by BTO layer is 0% and compressive strain ~1.8% respectively.

2. Results and discussions

2.1. Magnetoelectric coupling behavior

We summarize in table 1 the comparison in total energy between considered configurations and FM configuration of LSMO-0.5/BTO super-cell. According to this, under STO strain, the IF1 region of LSMO-0.5 layer where the BTO polarization points towards prefers FM ordering while the other prefers AFM ordering. Hence, we arrived at a ME coupling similar to that one predicted by Burton and Tsymbal in LBMO-0.5/BTO super-lattice under STO strain [12]. Namely, the flip of BTO polarization leads to FM-AFM switch in LSMO-0.5 layer.

In contrast, under BTO strain, the favourite magnetic ordering all over the LSMO-0.5 layer is AAFM, i.e. the Mn magnetic moments of neighbouring MnO$_2$ layers are anti-parallel all over LSMO-0.5 layers. Therefore, the switching of BTO polarization should give no change in magnetic ordering of LSMO-0.5 layer and there should be no ME coupling as predicted in case of STO strain. Nevertheless, this observation can explain quite well previous experimental work. It was observed that the strong enhancement of TER effect by ME-coupling in LSMO-0.3/BTO/LCMO-0.5/LSMO-0.5 MFTJ was absent in LSMO-0.3/BTO/LSMO-0.5 MFTJ [6].

Our predictions on different ME coupling behaviours of LSMO-0.5/BTO interface under STO and BTO strains affirm the importance of strain in designing LSMO-x/BTO based MFTJ. A question arises here: how to choose an appropriate strain for a strong ME coupling? In order to answer this question, we first clarify the electronic mechanism of the predicted ME coupling and then discuss the role of strain.

2.2. Electronic mechanism of magnetoelectric coupling

It is necessary to mention the ME coupling mechanism proposed by Burton and Tsymbal first [12]. On the base of their calculated local density of states (LDOS), they evidenced an accumulation of electrons, and hence the increase of $e_g$ electron concentration, at the interface where BTO polarization point towards (IF1 in our notations) to screen the BTO bound charges and the depletion in the other region. We represent this electrostatic screening effect in figure 2(b). On the other hand, by calculating the evolution of the magnetic ground state of La$_{1-x}$Ba$_x$MnO$_3$ with $e_g$ electron concentration, they emphasized that in mixed valence manganites, high $e_g$ electron concentration ($>0.4$ $e_g$ electrons per Mn site, $x < 0.6$ in case of La$_{1-x}$Ba$_x$MnO$_3$) prefers FM order while low $e_g$ electron concentration prefer AAFM order. Accordingly, the electrostatic-induced modulation of $e_g$ electron density causes FM order in the accumulation interface region (IF1) and AAFM order in the depletion interface region (IF2).

We achieved similar charge accumulations at the two asymmetry interfaces in both BTO and STO strains. Figure 3 shows the LDOS at Mn site in each MnO$_2$ layer. According to this, there is a modulation of $e_g$ electron density in which the $e_g$ electron density (the corresponding LDOS below Fermi level) is reduced along LSMO-0.5 layer from IF1 to IF2. A consequent modulation of local magnetic moment is also obvious in both cases (figure 4(a)). Despite that, ME-coupling induced FM-AFM switch only occurs in the case of STO strain. A possible explanation is suggested from the fact that lattice distortions and $e_g$ orbital ordering are crucial for stabilizing magnetic ordering in mixed valence manganites [18]. Hence, the degeneracy lifting of $e_g$ states under strain-induced lattice
2.3. Influences of strain on magnetoelectric coupling

Lattice distortions in perovskite materials are usually divided into three categories, i.e. Jahn-Teller (JT) distortion, ferroelectric (FE) distortion and tilting of octahedron. During the optimization procedures, the 4-fold symmetry of the supercell was kept unchanged. Thus, only JT and FE distortions were expected.

Figure 4(b) represents the evolution of the difference between perpendicular lattice constant and lateral lattice constant along $\text{LSMO-0.5}/\text{BTO}$ super-lattice. Here, we are interested in lattice distortions in $\text{LSMO-0.5}$ layer which decide the distribution of $e_g$ electrons. The negative differences demonstrate that $\text{MnO}_6$ octahedra are stretched in-plane and compressed along perpendicular direction (figure 5(a)). The more negative values in case of BTO strain indicate that $\text{MnO}_6$ octahedra are stretched in-plane more strongly than in case of STO. These observations are in accordance with the fact that both BTO and STO substrates induce tensile strains on $\text{LSMO-0.5}$ and the strain induced by BTO is larger than that one by STO. Another important thing is that the JT distortion is enhanced from IF1 to IF2-1 layer and then slightly weakened in IF2 layer.

Figure 4(c) represents the evolution of the FE distortion, which is characterized by the displacement of metal cation from octahedron center (figure 5(c)), along $\text{LSMO-0.5}/\text{BTO}$ super-lattice. According to this, the ferroelectric state of 4-unit cell BTO layer is obtained in both case with all Ti cations shifted toward IF1. STO strain leads to larger BTO polarization. The positive displacement in $\text{LSMO-0.5}$ side denotes that Mn cations move in the same direction as Ti due to the lattice coupling between BTO and $\text{LSMO-0.5}$ layers. The weakening of the lattice coupling into the center of $\text{LSMO-0.5}$ layer should lead to the symmetry reduction of FE distortion from the two interfaces to center. However, an asymmetry evolution was obtained, exhibiting the contribution of the interface rumpling due to the broken crystal symmetry. It is the interface rumpling that weakens the FE distortion at IF1 but enhances the FE distortion at IF2.

The crystal field splitting of $3d$ orbitals under JT distortion and ferroelectric distortion in $\text{LSMO-0.5}$ layer are represented in figure 5. According to this, the degeneracy lifting of $e_g$ states due to these distortions occurs in the same trend, i.e. $d_{z^2-r^2}$ states are lifted up and $d_{x^2+y^2}$ states are pushed down. The stronger the distortions are, the stronger the degeneracy lifting is. On the other hand, in the $d_{z^2-r^2}$ and $d_{x^2+y^2}$ partial density of states (PDOS) from our calculations (figures 6(a) and (b)), the weight of $d_{z^2-r^2}$ states in occupied region within 3 eV below Fermi level in case of STO strain is larger than in case of BTO strain, denoting that these states are weaker lifted under STO strain. This observation is in good agreement with the trend predicted from JT effect because JT distortions in BTO case is stronger than in STO case. Whereas, the FE distortion in BTO case is weaker than in STO case, suggesting the opposite trends of $d_{z^2-r^2}$ and $d_{x^2+y^2}$ shifting when the strain is changed. In order to negotiate this contrary, the energy scales of the degeneracy lifting induced
by these two distortions should be noticed. JT splitting in manganite has a typical magnitude of 0.6 eV which is much larger than FE splitting (~0.1 eV in typical FE material BTO) [19, 20]. Thus, JT distortion can be considered to dominate FE distortion.

Regarding the role of $d_{2z^2-r^2} - d_{dx^2+y^2}$ splitting in determining the magnetic ordering in LSMO-0.5 layer, LDOS of Mn site on each MnO$_2$ layer are taken into account (figures 6(c) and (d)). It is noticed from figure 4(b) that JT distortion in IF1 layer in case of STO strain occurs in opposite trend.
with the other layers and with BTO strain case as denoted by the positive difference between perpendicular lattice constant and lateral lattice constant. As a result, \(d_{z^2-r^2}\) states are pushed down instead of lifted up (figure 5(b)). This JT effect is in good agreement with our calculations which produce a strong increase of the IF1 \(d_{z^2-r^2}\) weight in the region 3 eV below Fermi level in case of STO strain. This deformation of the IF1 \(d_{z^2-r^2}\) PDOS, in turn, is responsible for an out-of-plane orbital ordering which stabilized FM interaction between IF1 MnO\(_2\) layers and the next nearest neighbour layer, IF1-1 MnO\(_2\) layer. Consequently, the AAFM ordering here is switch to FM ordering. The weight of IF1 \(d_{z^2-r^2}\) states, on the other hand, is not large enough for such a AAFM-FM switch.

3. Conclusions

Influence of strain on LSMO-0.5/BTO multi-ferroic interface was studied on the base of \textit{ab initio} electronic structure calculations. Our results agree quite well with experiment work on LSMO-0.3/BTO/LSMO-0.5 MFTJ [6]. This work suggested that ferroelectric-induced AFM-FM switch doesn’t occur at LSMO-0.5/BTO interface despite the previous theoretical prediction by Burton and Tsymbal [12]. Whereas, our results suggest that such ME coupling will not occur if LSMO layer bears a strong tensile strain such as the strain induced by BTO substrate. It is also suggested from the case of STO strain that ME coupling behaviour of LSMO-0.5/BTO interface can be

Figure 6. The Mn \(d_{z^2-r^2}\) (solid lines) and \(d_{x^2+y^2}\) (dot lines) partial density of states (PDOS) diagrams in cases of STO (a) and BTO (b) strain and the local density of states of Mn site on each MnO\(_2\) layer from IF1 (top panel) to IF2 (bottom panel). The solid lines (solid shaded lines) denotes \(d_{z^2-r^2}\) \(d_{x^2+y^2}\) LDOS.
modulated via strain effect on orbital ordering. This is very helpful for designing future MFTJ with both high on/off ratio and optimal working temperature.

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