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*Ab initio* investigation of electronic and magnetic properties of antiferromagnetic/ferroelectric LaMnO$_3$/BaTiO$_3$ interface

V V Kabanov$^{1,2}$, I I Piyanzina$^{1,3}$, Yu V Lysogorskiy$^4$, D A Tayurskii$^1$ and R F Mamin$^{1,3}$

$^1$ Zavoisky Physical-Technical Institute, FIC KazanSC of RAS, 420029 Kazan, Russia
$^2$ Department for Complex Matter, Jozef Stefan Institute, 1000 Ljubljana, Slovenia
$^3$ Institute of Physics, Kazan Federal University, 420008 Kazan, Russia

E-mail: viktor.kabanov@ijs.si

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**Abstract**

We investigate the structural, electronic and magnetic properties of LaMnO$_3$/BaTiO$_3$ heterostructure by means of *ab initio* calculations within the GGA+$U$ approach. We consider the heterostructure when ferroelectric polarization in the BaTiO$_3$ film is oriented perpendicular to the LaMnO$_3$ substrate. We present atom and spin-resolved density of states calculations for LaMnO$_3$/BaTiO$_3$ heterostructure with different number of BaTiO$_3$ overlayers as well as layer-resolved spectra for the conducting heterostructure. We found that the LaMnO$_3$/BaTiO$_3$ heterostructure becomes conducting with a significant spin polarization indicating that the interface becomes ferromagnetically ordered. The propose concept of a ferroelectrically controlled interface ferromagnetism that offers the possibility to design novel electronic devices.

**1. Introduction**

Multiferroic materials are compounds where at least two order parameters coexist in the same phase [1, 2]. One very important but extremely rare group is ferroelectric ferromagnets, which have recently stimulated an increasing number of research activities for their scientific uniqueness and application in the novel multifunctional devices [3]. For example, BiMnO$_3$ exhibits magnetic [4] and ferroelectric [5] properties. Another example of ferroelectromagnet is thin film of BiFeO$_3$, which display a room-temperature spontaneous polarization (50 to 60 microcoulombs per square centimeter), as well as enhanced thickness-dependent magnetism [6, 7]. Magnetoelectric materials are mainly interesting due to the possibility to control magnetic properties by an external electric field [8, 9]. Besides their unique property of reversal polarization switching ferroelectrics have a wide range of other distinctive properties, like spontaneous polarization switching, high dielectric permeability, dielectric nonlinearity, piezo- and pyro- activity, linear and quadratic electro-optical effects.

However, so far just a few ferromagnetic ferroelectric compounds have been synthesized. Among them Bi$_2$NiMnO$_6$, which was synthesized by Azuma et al [10] and investigated by means of *ab initio* calculations by Ciucivara et al [11]. It was found that magnetization equals 4.94µB/f.u. (4.99 including $U$) and polarization equals 18.41 µC cm$^{-2}$ (18.18 including $U$). Another material synthesized by Gajek et al [12] is ferroelectromagnet La$_{0.9}$Bi$_{0.1}$MnO$_3$, which retains its properties down to 2 nm thick film. Due to the extraordinary challenge of creating multiferroic compounds, it was essential to create superlattice multicomponent materials as more efficient [13, 14]. Moreover, the discovery of a quasi-two-dimensional electron gas properties in LaAlO$_3$/SrTiO$_3$ heterostructures has stimulated intense research activity in the last fifteen years and provided new functionality for electronic devices [15, 16]. Recently, following this approach ferromagnet/ferroelectric (Pr$_{0.5}$Ca$_{0.5}$MnO$_3$)$_n$/(Ba$_{0.6}$Sr$_{0.4}$TiO$_3$)$_m$ and (La$_{0.7}$Ca$_{0.3}$MnO$_3$)$_n$/(BaTiO$_3$)$_m$ superlattices have been created [17, 18].

*Ab initio* characterization studies of magnetoelectric coupling at the interface are also rare. Theoretical studies of magnetolectric coupling involve such heterostructures as Fe/BaTiO$_3$ [19], Co$_2$MnSi/BaTiO$_3$ [20],...
Fe₂O₃/BaTiO₃ [21], Fe(Ni,Co,Cr₂O₃)/BaTiO₃/normal metal [22] etc. Recent paper considered a supercell of ferromagnetic perovskite Sr-doped LaMnO₃ and ferroelectric BaTiO₃ [23]. The spontaneous electrical polarization of BaTiO₃ causes the accumulation of spin-polarized electrons in the ferromagnetic half-metallic La₁₋ₓAₓMnO₃ layer at the interface perpendicular to the direction of polarization. The same phenomenon called electrostatic screening effect is also true for metallic (Fe, Ni or Co) ferromagnetic layers. The main idea is that magnetic properties of magnetic and semi-conducting La₀.₅Sr₀.₅MnO₃ slab can be tuned by ferroelectric polarization, in other words, a switching between FM and A-AFM ordering can be achieved by external electric field.

In contrast to the aforementioned La₀.₅Sr₀.₅MnO₃/BaTiO₃ interface, heterostructure investigated in the present study is composed of two insulating components LaMnO₃ and BaTiO₃. This system was also investigated previously by Giucvara et al [24], where (LaMnO₃)ₓ/(BaTiO₃)ₙ superlattice was considered. They reported that starting with A-AFM LaMnO₃ the optimization of the superlattice converged to a ferromagnetic order. It was concluded that interfaces increase the magnetization and may favor ferromagnetic ordering [24]. We should also mention another recent ab initio study involving heterostructure based on two insulators SrTiO₃ and BaTiO₃, where it was shown that the band gap of the studied system depends on the termination of the BaTiO₃ overlayer [25]. The essential issue of the present study is to understand an impact of polarization inside the BaTiO₃ slab on the electronic states as well as magnetic moments distribution inside the LaMnO₃ slab. In order to shed the light on this subject we performed ab initio calculation for the BaTiO₃/LaMnO₃/BaTiO₃ superlattice having different types of interfaces with LaMnO₃ central slab.

2. Computational method

The ab initio calculations were based on density functional theory (DFT) [26, 27]. Exchange and correlation effects were accounted for by the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE) [28]. The Kohn–Sham equations were solved with projector-augmented-wave (PAW) potentials and wave functions [29] as implemented in the Vienna Ab-Initio Simulation Package (VASP) [30–32], which is part of the MedeA® software of Materials Design [33]. Specifically, we used a plane-wave cutoff of 400eV. The force tolerance was 0.05 eV/Å and the energy tolerance for the self-consistency loop was 10⁻⁵ eV. The Brillouin zones were sampled using Monkhorst–Pack grids [34] including 5 × 5 × 1 k-points. Finally, the electronic densities of states were calculated using the linear tetrahedron method [35] on 4 × 4 × 1 k-point grids. It is well known that the hybrid exchange correlation functionals like B3LYP or B3PW allow to achieve good results in computer modeling of the electronic structure of ABO₃ perovskites. In particular, the band structure of ABO₃ perovskites calculated with the hybrid exchange-correlation functional B3LYP provides the values of the band gaps which are in excellent agreement with experiments [36, 37]. On the other hand, the GGA functional often underestimate the band gaps of ABO₃ perovskite materials. In our case, the exact value of the band gap was not so important. We were more interested in qualitative behaviour of the heterostructure. Since the heterostructure is quite large it requires substantial amount of computations. Therefore, we decided to use the GGA functional in our calculations to save time and computer resources. This, along with the fact that there are strong correlations between d and f-electrons in the studied system, led us to add the GGA + U correction using the approach proposed by Dudarev et al [38] to our computational scheme. This simplified approach takes into account only the difference U − J into account. Therefore, the U − J parameters were added to La 4f, Ti 3d and Mn 4d (U = 8 eV, 2 eV and 4 eV, respectively). This choice was based on our previous detailed investigation of the effect of local electronic correlations as captured by the GGA + U method [39], as well as [40]. In our previous study of U effect on the LaAlO₃/SrTiO₃ system we have concluded that U parameter is important and it affects quantitatively the band gap. However, qualitatively all conclusions are correct for any U tested in our calculations. The same conclusions are valid for the case of LaMnO₃/BaTiO₃ heterostructure. Finally, all calculations were performed taking into account magnetic nature of the material except of bulk BaTiO₃.

3. Results

3.1. Bulk BaTiO₃ and LaMnO₃

As a first step bulk components were optimized separately. For BaTiO₃ cell we started with tetragonal structure and imposed tiny displacement of Ti atom out of oxygen plane in the c-axis direction. The tetragonal BaTiO₃ lattice parameters were found to be equal to a = b = 4.003 Å, c = 4.019 Å (experimental values are a = b = 3.992 Å, c = 4.036 Å [41]). The displacement of Ti atom out of O-plane was 0.0650 Å. The corresponding density of states (DOS) spectra are shown in figure 1.

In order to get antiferromagnetic order in the bulk LaMnO₃ we considered A-type AFM cell shown in figure 2, where arrows indicate magnetic moments directions at each Mn atom in the unit cell. The LaMnO₃
magnetization was calculated to be 3.833 \( \mu_B \) per Mn atom, what is in a good agreement with experimental value of 3.7 \( \pm \) 0.1 \( \mu_B \) [42]. Calculated lattice parameters are: \( a = 5.650 \, \text{Å}, b = 5.616 \, \text{Å}, c = 7.935 \, \text{Å} \) (experimental values are: \( a = 5.537 \, \text{Å}, b = 5.747 \, \text{Å}, c = 7.693 \, \text{Å} \) obtained by neutron diffraction at room temperature [43]).

### 3.2. BaTiO\(_3\)/LaMnO\(_3\)/BaTiO\(_3\) heterostructure

BaTiO\(_3\)/LaMnO\(_3\) interface can have LaO/BaO, LaO/TiO\(_2\), MnO\(_2\)/BaO or MnO\(_2\)/TiO\(_2\) matching layers on both sides of the heterostructure. Due to a high mismatch between BaTiO\(_3\) and LaMnO\(_3\) (\( \approx 29\% \)) the BaTiO\(_3\) unit cell was rotated by 45° in the interface plane before merging with LaMnO\(_3\) substrate, since the \( a_{\text{BaTiO}_3} \times \sqrt{2} = 5.661 \, \text{Å} \) (results in \( \approx 1\% \) mismatch with LaMnO\(_3\) substrate). For modeling that heterostructure the BaTiO\(_3\) central slab was enlarged and bounded by a varying number of BaTiO\(_3\) layers with interfacial BaO or TiO\(_2\) layers on both sides. Such a unit cell guarantee an absence of the artificial dipole moment and additional polarity which may be caused by non-symmetric structure. Finally, in order to avoid interaction of the surfaces and slabs with their periodic images a 20 Å vacuum region was added. In plane \( a \) and \( b \) cell parameters were fixed, whereas atom positions were allowed to relax during the optimization procedure. The in-plane lattice parameters were fixed to the optimized values of bulk LaMnO\(_3\) and kept for all subsequent

![Figure 1. The unit cell and corresponding density of states of the bulk BaTiO\(_3\) in the tetragonal phase.](image1.png)

![Figure 2. The unit cell of the bulk A-AFM LaMnO\(_3\) in the orthorhombic structure (a). Arrows indicate magnetic moments directions. And corresponding atom- and spin-resolved density of states (b).](image2.png)
calculations reflecting the stability of the substrate. Atomic positions of all atoms were fully relaxed. All spectra have been calculated taking into account magnetic features of LaMnO$_3$. In figure 3 (a) half of the unit cell of the studied 2 BaTiO$_3$/LaMnO$_3$/2 BaTiO$_3$ heterostructure with LaO/TiO$_2$ interface is presented; the second unshown part is a mirror copy with respect to the central LaO layer.

Originally all interface types were tested for convergence. As a result, we were unable to converge heterostructures which involve LaO/BaO and MnO$_2$/BaO interfaces. The authors of [24] faced a similar problem. They claimed that possible reason for bad convergence is dissimilar interfaces, in particular, that the TiO$_2$ interface with a ferromagnet is much more stable than the BaO interface with the ferromagnet. That is why all further reasoning will be presented for the heterostructure with LaO/TiO$_2$ interface where self-consistent results were obtained. Note that we did not find significant differences in terms of electronic properties between LaO/TiO$_2$ and MnO$_2$/TiO$_2$ interfaces.

For the heterostructure with two BaTiO$_3$ overlayers (figure 3(a)) we found that at the TiO$_2$ layers Ti atoms move out of oxygen planes by $\approx 0.15$ Å. That leads to a dipole moment induction towards the interface. This feature is dissimilar to La and Al atoms displacements in the LaAlO$_3$/SrTiO$_3$ heterostructure (figure 1 in [39]). In the ideal LaAlO$_3$/SrTiO$_3$ system without any structure optimization there are not buckling inside the layers and at any number of LaAlO$_3$ overlayers conductivity occurs due to differently charged layers sequence. Resulted dipole moments have a direction towards the interface. The structural optimization of LaAlO$_3$/SrTiO$_3$ leads to the buckling inside the LaO and AlO$_2$ layers and appearing of dipole moments with an opposite direction towards the surface. As a result, conductivity in this system occurs only when the number of LaAlO$_3$ overlayers is sufficiently large to overcome the field that appears due to the buckling. Therefore, the dipoles toward the interface promote the conductivity and dipoles towards the surface prevent it. That is true for both LaAlO$_3$/SrTiO$_3$ and LaMnO$_3$/TiO$_2$ heterostructures.

Let’s go back to the LaMnO$_3$/BaTiO$_3$ system. Figure 3(b) presents the atom-resolved density of states (DOS) for Mn, La and Ti atoms for the heterostructure with two BaTiO$_3$ overlayers. It is seen that in comparison with DOSes of bulk components (figures 1 and 2) there are an overall energy shift and narrowing of the band gap. Besides, magnetic moment induction takes place mainly on Mn atoms. We do not show Ba atoms at DOS spectra since Ba levels located deep in the valence band and are non-intense.

At the next step we increased the number of BaTiO$_3$ overlayers to three. Figure 4(a) shows the heterostructure with LaO/TiO$_2$ interface and three BaTiO$_3$ overlayers. The similar Ti atoms displacements take place as in the case of two overlayers. Figure 4 (b) presents the atom-resolved density of states (DOS) for Mn, La and Ti atoms for the heterostructure with three BaTiO$_3$ overlayers.

Adding of one BaTiO$_3$ overlayer to the heterostructure leads to the narrowing of the band gap (figure 4(b)), Ti states cross the Fermi level and the system becomes conductive. The DOS intensity at the Fermi level has increased substantially approximately to 10 eV$^{-1}$. Besides, the Fermi level is shifted even higher in energy and the band gap is closed for the spin up component. The layer-resolved DOS spectrum shown in figure 5 indicates that Ti atoms from all three TiO$_2$ atomic layers from BaTiO$_3$ overlayer contribute to the conductivity. Moreover,
Figure 4. Half of the unit cell of the 3 BaTiO$_3$/LaMnO$_3$/3 BaTiO$_3$ heterostructure with a LaO/TiO$_2$ interface (a). Spin-polarized density of states of the 3 BaTiO$_3$/LaMnO$_3$/3 BaTiO$_3$ heterostructure with LaO/TiO$_2$ interface (b).

Figure 5. Layer- and spin-resolved density of states of the 3 BaTiO$_3$/LaMnO$_3$/3 BaTiO$_3$ heterostructure with a LaO/TiO$_2$ interface.
there is a contribution from Mn atoms located in the LaMnO₃ slab. Note, that BaO and LaO layers do not contribute to the conductivity. In contrast to the LaAlO₃/SrTiO₃ system here the main part of the conducting electrons is from the overlayers. We can suggest a possible explanation for this. First of all, Ti levels in the bulk BaTiO₃ and Mn levels in the bulk LaMnO₃ are located in the high energy region. The slab geometry shifts the Fermi level to higher energies and it crosses Ti states. This Fermi energy shifting is similar to that in the LaAlO₃/SrTiO₃ system, when conducting electrons correspond to Ti atoms located in the central slab, however, in the LaMnO₃/BaTiO₃ heterostructure conductivity occurs in the overlayers. A possible reason for that could be the thickness of BaTiO₃ slab. In particular, a shielding charge normally occurs at the surface of ferroelectric, or, as in our case, at the surface and at the interface of the LaMnO₃/BaTiO₃ heterostructure. If the ferroelectric slab is not thick enough, the charge is distributed overall the BaTiO₃ overlayer as we observe. Thus, we assume that increasing of the thickness of ferroelectric slab will result in conducting interface and surface with insulating inner layers. Recently, by means of DFT calculations we observed similar mechanism of conducting state emergence at the interface of La₂CuO₄ with ferroelectric BaTiO₃ [44], which was lately confirmed experimentally at the Ba₀.₈Sr₀.₂TiO₃/La₂CuO₄ heterostructure [45]. However, the conducting state was localized mainly at the interfacial CuO₂ layer.

4. Discussion

It follows that the band gap vanishes for the heterostructure with relatively small number of BaTiO₃ layers. And we expect the interface area to absorb the light having the energy less than the band gap of LaMnO₃, in other words the photon energies considerably less than 1.8 eV. Besides, there is a metallic state at the interface, which might lead to the absorption in the terahertz spectrum area. Thus, light absorption experiments at the terahertz spectrum area may be useful in order to analyze the conductive properties. It is utterly important during such experiments to distinguish two contributions: the first one is related to the absorption by charge carries in the conductive area, and the second one related to the soft mode of the ferroelectric order parameter in the BaTiO₃ film, since such a contribution might take place quite far from the phase transition temperature Tₘ.

The initial magnetic ordering of the LaMnO₃ crystal is A-AFM, whereas in the slab geometry it becomes anyway ferromagnetic due to the odd number of atomic layers in the central LaMnO₃ slab. A distinctive feature of discussed two states is the fact that in the first case of two BaTiO₃ overlayers the total magnetic state of the heterointerface is considerably smaller than in the second case of three BaTiO₃ overlayers. Possibly, that is related to the number of free charge carriers at the interface area. In the first case concentration is smaller, since the DOS at the Fermi-level is small in figure 4(b). As a result, indirect ferromagnetic exchange through charge carriers is not efficient enough and ferromagnetic order doesn’t appear. In contrast, in the case of three BaTiO₃ overlayers the DOS at the Fermi level as well as charge carriers concentration are higher. Consequently, indirect ferromagnetic exchange through charge carries becomes efficient enough for the ferromagnetic ordering. That can be well observed from figure 4(c), where density of states for Mn atoms with spin up and down differs considerably.

Therefore, the BTO/LMO system attracts the interest because it contains an antiferromagnetic insulator LaMnO₃, which becomes conducting and ferromagnetic when concentration of the free carriers increases. We may further expect that the change of the direction of polarization in the ferroelectric film may be used in order to control the carrier concentration at the interface. As a result, it may be possible to control both conductivity and magnetism by an electric field in the heterostructures similar to BTO/LMO. Therefore, it opens the possibility of designing of new electronic devices with ferroelectric control of the ferromagnetism on the interface.

Recently, we presented experimental investigations for Ba₀.₈Sr₀.₂TiO₃/LaMnO₃ heterostructure [46]. In particular, four-probe measurements of the electrical resistance versus temperature indicate that the resistivity exhibits the activation-type of behavior within the whole temperature range for the sample in the configuration with the c-axis of LaMnO₃ single crystal directed parallel to the interface. In contrast, in the second sample with c-axis of LaMnO₃ single crystal directed perpendicular to the interface at high temperatures the resistance shows an activation like behaviour, whereas at temperatures below 160 K, it passes to the regime characteristic for a metallic behaviour. The total electrical resistance of the sample is several times lower than the electrical resistance for the sample without the film. The drastic decrease in the electrical resistance at low temperatures is a signature of the transition to the conducting state. Thus, experimental investigation of the Ba₀.₈Sr₀.₂TiO₃/LaMnO₃ heterostructure confirms our conclusion. Besides, we have investigated the effect of magnetic field on the conducting properties of our heterostructure. We found that when the magnetic field is applied along to the magnetic axis of the LaMnO₃ the conductivity strongly and irreversibly decreases in the low-temperature phase.
5. Conclusion

We have explored different types of BaTiO$_3$/LaMnO$_3$ heterointerface by means of ab initio calculations within the GGA+$U$ approach and found that for the LaO/TiO$_2$ interface type conducting state in the heterostructure may occur. Besides, the ferromagnetic order in the LaMnO$_3$ central slab arises which correspond mainly to the Mn atoms. The possibility to switch the interface magnetism by an electric field in the BTO/LMO heterostructure is discussed. Optical properties of BaTiO$_3$/LaMnO$_3$ heterostructure were also discussed. We expect that a high photon absorption will take place at the interface, especially at the terahertz spectrum range.

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ORCID iDs

V V Kabanov https://orcid.org/0000-0002-3663-5855

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