Can we prevent the “dead layer” formation at manganite interfaces?

Ayşegül Begüm Koçak,1,2,3,4 Julien Varignon,3 Sébastien Lemalet,3 Philippe Ghosez,3 and Marie-Bernadette Lepetit1,4

1Institut Néel, CNRS UPR 2940, Grenoble, France
2Institut National Polytechnique de Grenoble, France
3Theoretical Materials Physics, Q-Mat, CESAM, Université de Liège, 4000, Sart Tilman, Belgium
4Institut Laue Langevin, Grenoble, France

The present work theoretically studies the possibility to hinder the formation of a “dead” layer at the interfaces in manganite superlattices. We showed that this goal can be reached by using alkaline-earth simple oxides as alternating layers in very thin superlattices. Indeed, such alternating layer promotes the contraction of manganite layers at the interfaces and $d_{x^2−y^2}$ preferred $e_g$ orbital occupancy, while Boltzman’s transport calculations show an increase in conductivity. This result hold for different manganites, different alkaline-earth simple oxides as well as different thicknesses of the two layers.

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Interfases between perovskite oxides have been the subject of intense research over the last decade. The first reason is the outstanding properties discovered in such interfaces: let us only cite the superconductivity discovered at the interface between two band insulators such as SrTiO$_3$ (STO) and LaAlO$_3$ [1]. Another reason is the potential applications of such properties. Manganite-based devices using tunnel junctions are actually studied for the design of spin valves or spin injectors. Such junctions present a high degree of spin polarization and robust magnetic properties at the interface between the manganite and the barrier. The main problem that has hindered the development of such devices is the formation of a so-called ”dead-layer” [2,3], below a critical distance to the interface. In such layers the magnetotransport properties are strongly depressed. The present paper proposes a possible solution to this critical problem with not only a set of criteria to design appropriate barriers, but also a detailed study of a realistic example.

Manganites are known to be ferromagnetic metals over a large range of their phase diagram, and to present colossal magneto-resistance effects. Indeed, the record value is of over 14 orders of magnitude in resistivity change under magnetic field [4]. Their transport and magnetic properties are controlled by small atomic displacements, allowing potential pathways to tune their properties using interfaces in very thin films and heterostructures (see for instance Ref. [5,8] and Ref. [9] for a recent review). Unfortunately, a loss of magnetization and metallicity, also called “dead layer”, is observed over a thickness of few unit cells (u.c.) at the interface of ferromagnetic manganites, such as La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) or La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO), and most perovskite substrates or combined layers [2,3]. This “dead layer” phenomenon has been the subject of many interpretations such as (i) homogeneous substrate strain [10], (ii) electronic and/or chemical phase separation [11] related to structural inhomogeneities at the interface [12] or uncontrolled stoichiometry [13], (iii) manganese $e_g$ orbital reconstruction that may induce C-type antiferromagnetism [14,15] and can be attributed to a weak delocalization at the interfaces [16].

Ferromagnetic manganites (and related heterostructures) of general formula La$_{1−x}$A$_x$MnO$_3$ ($A$ a divalent cation, $x$ in the approximate range $0.2 < x < 0.45$) crystallize in a ABO$_3$ perovskite structure [22,23], with the Mn occupying the B site. The Mn atom is thus in an octahedron environment, which induces an energetic splitting of the Mn 3$d$ orbitals into a $^3$T$_2g$ — threefold degenerated — low energy set, and a $^3$E — twofold degenerated — high energy one (ideal case). Moreover, the Mn atoms are in a mixed valence ionic state (Mn$^{3+}$+$x$), with a 3$d^{4−x}$ high spin orbital occupancy. As a result, the two $e_g$ orbitals, $d_{x^2−y^2}$ and $d_{z^2}$, are partially occupied by $1−x$ electron which may delocalize (the $d_{z^2}$ electrons along the $c$ direction and the $d_{x^2−y^2}$ ones in the $(a,b)$ plane). This delocalization is energetically very favorable, but will only occur when the spins of neighboring Mn ions are ferromagnetically aligned. In such a case the delocalization energy gain overcomes the antiferromagnetic exchange interaction between localized ions, and imposes a ferromagnetic ordering (double exchange mechanism) [17].

In bulk materials the $e_g$ electrons are shared between the two orbitals with equivalent occupancies. It results
in magnetic ordering and delocalization occurring in all directions. In very thin films, however, the out-of-plane direction, c, spans only over a few u.c., and thus the thermodynamic limit is only obtained in the in-plane, \((a, b)\), directions. It is thus of crucial importance for the magnetic and transport properties to maximize the \(d_{x^2−y^2}\) orbital occupancy, responsible for the in-plane delocalization and thus magnetic and transport properties.

When an interface “dead layer” is present, the \(d_{x^2}\) electrons of the manganite delocalize in the empty \(d_{z^2}\) orbitals of the substrate or of the alternating layer (typically SrTiO\(_3\), BaTiO\(_3\) or similar compounds). Even if weak (about one or two tenth of an electron \([16]\)), at the interfaces this delocalization energetically favors the \(d_{z^2}\) orbital occupancy over the \(d_{x^2−y^2}\) one. It results in a Jahn-Teller distortion of the MnO\(_6\) octahedron, with a splitting of the \(e_g\) degeneracy \([18]\) \((\varepsilon_{z^2} < \varepsilon_{x^2−y^2})\). The in-plane delocalization is thus hindered (at least by carrier density reduction). Consequently, the characteristics of the “dead layer” phenomenon appear, (reduced ferromagnetic spin arrangement and conductivity \([3, 19]\)).

Such a Jahn-Teller distortion induces a small increase of the \(c\) parameter \([16, 20]\), that can be fully attributed to the delocalization mechanism at the interfaces, as strain effects tend to reduce \(c\). Indeed, on a STO substrate, manganites such as LSMO or LCMO are under tensile strain \((a_{\text{STO}} = 3.905\text{Å} \ [21], \ a_{\text{LSMO}} = 3.880\text{Å} \ [22], \ a_{u\text{CMO}} = 3.86\text{Å} \ [23] \) yielding a 1% strain on LSMO and 2% on LCMO), known to favor a reduction of \(c\). In order to prevent the formation of a “dead layer”, one thus needs to interface the manganite with an alternating layer material hindering the delocalization between the different layers.

The purpose of this work is thus to investigate, using first-principle calculations, possible candidates for such alternating layers. We will focus on LSMO-based heterostructures over a SrTiO\(_3\) substrate.

The first idea that may come to mind, is to use alternating layers with totally-filled \(d\)-shells, and a tetragonal structure. Indeed, the latter was shown to be crucial in order to prevent the rhombohedral distortion in the manganite layer, but rather favor a tetragonal one \([18]\). Let us remember that a tetragonal distortion, associated with a \(c\) parameter contraction, allows an enhancement of the \(d_{x^2−y^2}\) orbital occupancy and thus of the desired properties. One could therefore think of materials such as the BaSnO\(_3\) compound.

Unfortunately, our test calculations on such hetero-structures exhibited a weak electron delocalization, from the Sn filled \(d_{x^2}\) orbitals towards the Mn partially occupied ones, very similar to what we observed in our calculations on BTO/LSMO \([18]\) or STO/LSMO heterostructures (that exhibit a JT distortion of \(\sim 1.04\) in the interface layer, a dominant \(d_{z^2}\) occupancy and a weak \(d_{z^2}\) delocalization in the Ti orbitals.). This delocalization is associated with an increase of the Mn \(d_{z^2}\) orbital occupancy, and a Jahn-Teller distortion. One can thus expect such hetero-structures to exhibit a “dead layer” phenomenon.

Another way to prevent the inter-layers delocalization of the LSMO Mn \(d_{z^2}\) orbitals is to totally avoid \(d\) orbitals, in the alternating layer material. The requirement for the alternating layer should thus be i) no \(d\) orbitals, ii) a tetragonal or cubic structure, and iii) a compound allowing perfect epitaxy with the manganite layer. Fulfilling all those requirements are the simple alkaline-earth oxides, and more specifically the BaO compound. Indeed, the mismatch between BaO and LSMO is only of 0.7\%, and between BaO and the STO substrate 0.3\%. Of course the epitaxy imposes a BaO unit cell \((Fm\overline{3}m\) cubic group \([24]\) rotated in-plane by an angle of \(45°\) \([25]\), compared to the manganite unit cell (see figure \([1]\)).

We thus studied, using first-principles calculations, \([\La_{2/3}\Sr_{1/3}\MnO_3]_n[\BaO]_p\) superlattices on a STO substrate, alternating a few u.c. of manganite and of simple Barium oxide. Superlattices with other alkaline-earth oxides were also investigated to see whether the results are resilient to a change in the alternating layer, despite their unrealistic strain values \([26]\).

We performed geometry optimizations for the different superlattices, using periodic density functional calculations. Since epitaxial films normally follow the structure of the substrate, we imposed to our optimizations to keep the substrate in-plane lattice constants (optimized using the same computational parameters). The alkaline-earth oxides are strong insulators, while the manganite layers are expected to be metallic, one thus needs to choose a functional that properly positions the metal Fermi level with respect to the insulator gap. We used the B1WC hybrid functional \([27]\), that was specifically designed to properly treat both gaps and weak distortions, two key components in the present systems. The calculations were done using the CRystal package \([28]\), with the basis sets and effective core pseudopotentials (ECP) of ref. \([29]\). As the LSMO A-site cations disorder is difficult to treat within periodic calculations, we run a set of calculations with different orderings, using true atoms or average ones. The average ions were modeled as in reference \([18]\) that is using ordered cations ECPs but with averaged effective nuclear charges. The effect of these average charges is to hinder possible electronic localization induced by the cation orders. Unless specified, we will only present results that are independent of the cation order or model. Finally we used a \(\sqrt{2}a \times \sqrt{2}a \times c\) unit cell in order to allow octahedra rotations and in-plane antiferromagnetic (AFM) ordering (see figure \([1]\)).

We first studied the \([\La_{2/3}\Sr_{1/3}\MnO_3]_3[\BaO]_6\) superlattice, using all 6 cations models and different magnetic orders ; that is ferromagnetic (FM), A-type AFM (in-plane FM and out-of-plane AFM), C-type AFM (in-plane AFM and out-of-plane FM) and G-type AFM (in-plane and out-of-plane AFM).

Notice that in what follows we consider superlattices
with stoichiometric layers yielding, in most cases, asymmetric interfaces as it would be in real heterostructures. As it will be discussed in the last Section, this has however no direct impact on our conclusions.

Our calculations showed that the magnetic ground state always imposes a FM in-plane order and a total net magnetic moment. The two out-of-plane magnetic arrangements are quasi-degenerate within DFT error bars. Indeed, the energy difference per LSMO u.c. (or equivalently per Mn), between FM and A-type AFM orders, is in average 8 meV/u.c., with a mean deviation of 16 meV. This is smaller than the room temperature \( k_B T \sim 25 \text{ meV} \). Whether the DFT ground state is the FM or the A-type AFM configuration depends on the specific cation ordering. The in-plane AFM ordered states are much higher in energy, ranging between 130 meV and 210 meV above the ground states.

Figure 2 pictures the statistics of both the Jahn-Teller distortion (JTd) (measured as \( d_{\text{OO}}/\alpha - 1 \), with \( d_{\text{OO}} \) the out-of-plane O-(Mn)-O distance) and \( c/\alpha \) (\( c \) being measured as the perovskite A-sites distance). Red and pink symbols refer to the interfacial mono-layers, blue symbols to the central ones. Diamonds are for the FM order and stars for the A-type AFM one. The green dashed squares show the experimental values of LSMO over STO for 6 m.l. thin films exhibiting a dead layer. The Jahn-Teller distortion and \( c/\alpha \) ratios are extracted from the cumulative displacements in Ref. 20 and the \( \eta(d_{z^2-y^2})/\eta(d_{z^2}) \) ratio is extracted from linear dichroism experiments of Ref. 14. Bulk LSMO corresponds to the cross point between the dashed lines.

One sees immediately that all three layers are compressed along the \( c \) direction, except for the central layer in two AFM calculations. Similarly, the Mn-octahedra of the interface mono-layers are compressed along \( c \) and display a dominant \( d_{x^2-y^2} \) orbital occupancy, favorable to the searched magnetic semi-metal behavior. Only the central monolayer exhibits sometimes an elongation of the Mn-octahedra, with a dominant \( d_{z^2} \) occupancy. This behavior is the exact opposite of what is found in [LSMO]_3[BTO]_3 superlattices [18 30], in which the interface layers are elongated with a dominant \( d_{z^2} \) occupancy, responsible for the dead layer behavior. One should also point out that octahedra rotations are essentially negligible in these hetero-structures (rotation values less than 1°).

The fact that the FM and A-type AFM orders are found so close in energy tells us that, in real systems such superlattices may present one or the other spin arrangement as the ground state, according to the specific cation disorder. In any way at room temperature both state can be expected to be occupied with similar probabilities. Our results thus show that such superlattices should display a net total magnetization (even-though reduced compared to the FM state), and more importantly a large magnetic moment for the interface layers. Concerning the transport properties we computed the conductivity tensor for the [LSMO]_3[BaO]_6 and the [LSMO]_3[BaTiO]_3 systems using the Boltztrap code. Figure 3 clearly shows a strong increase in the in-plane conductivity for the system with BaO alternating layers. The dominant \( d_{x^2-y^2} \) orbital occupancy at the interfaces, supported by the conductivity

\[ \text{FIG. 1: (color online) Schematic representation of the [La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_6[\text{AO}]_6 \text{ and } [\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_6[\text{AO}]_2 \text{ superlattices.} \]

\[ \text{FIG. 2: (color online) } \eta(d_{x^2-y^2})/\eta(d_{z^2}) \text{ ratio of the } d_{x^2-y^2} \text{ and } d_{z^2} \text{ orbitals.} \]
calculations, lead us to think that using simple oxides as alternating layers is indeed a promising way to prevent the “dead layer” phenomenon.

One can however wonder if this conclusion will remain valid if one increases the size of the manganite layer. In order to check this point we increased the size of the LSMO layer to 6 mono-layers, and performed the calculations for one typical cation configuration. To keep this calculation to a reasonable size, we needed to simultaneously decrease the BaO layer thickness. We thus first checked whether such a reduction would affect the results. For this purpose we run test calculations on the preceding superlattice with only two mono-layers of BaO (i.e. on [LSMO]$_3$[BaO]$_2$). These calculations showed a similar behavior to the calculations with 6 BaO mono-layers, and thus validate 2 BaO mono-layers model.

Our calculations on the [LSMO]$_6$[BaO]$_2$ superlattices showed that the ground state again imposes in-plane ferromagnetism. The spin arrangement in the c direction displays a ↑↑↓↓↑↑ pattern (“ nueedu”) with a total net magnetization for the system. This ground state is again very close in energy to the FM state and the A-type AFM state. The latter does not however correspond to a full AFM state, since it exhibits a non null net total magnetization of about 1/10 of an electron per Mn atom.

The dominant $e_g$ orbital occupancy in the different LSMO mono-layers is found qualitatively independent of the out-of-plane spin ordering (see table I for an example). Indeed, as in the [LSMO]$_3$[BaO]$_6$ calculations, the mono-layers at the interfaces are contracted and strongly dominated by the $d_{x^2-y^2}$ orbital occupancy. In fact only the inner most mono-layer is still elongated and dominated by $d_{z^2}$ orbital occupancy. As it can be seen in Table I, the Mn magnetic moments and the amplitude of the Jahn-Teller distortion exhibit a strong correlation. The Mn-octahedra in the inner most mono-layer exhibit a strong elongation and the largest Mn magnetic moment. This specificity of the inner most mono-layer is responsible for the non-vanishing total magnetization in the A-type AFM state. These results show that, when increasing the thickness of the LSMO layer, one essentially increases the thickness of the interface layers and not of the central one. The former being contracted along c and dominated by $d_{x^2-y^2}$ orbital occupancy, it confirms that the use of BaO alternating layers hinder the formation of a “dead layer” at the LSMO interfaces.

Finally we checked whether this result is resilient to a change in the simple oxide and manganite compounds. We thus performed a set of calculations using BaO, SrO and MgO as alternating layers, and LSMO or LBMO as manganite layers ([La$_2$/3Sr$_{1}$/3MnO$_3$]$_3$[BO]$_6$, for a typical cation disorder model [26]. Table II summarizes the $e_g$ orbital occupancies for those calculations. One may notice that the (LBMO)$_3$(BaO)$_6$ and (LSMO)$_3$(SrO)$_6$ superlattices have in theory equivalent interfaces, unlike all the other superlattices we studied. One sees in table II

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**TABLE I:** Mulliken spin population of the Mn $e_g$ orbitals, $c/a$ ratio, JTd (Jahn-Teller distortion) and $\mu_{Mn}$ (Mn magnetic moment) in the [La$_2$/3Sr$_{1}$/3MnO$_3$]$_3$[BaO]$_6$ ground state of one typical cation order. Values for the two other low energy states (FM and A-type AFM) are qualitatively equivalent.

| Mono-layer | $e_g$ orb. spin pop. | $d_{x^2-y^2}$ | $d_{z^2}$ |
|------------|---------------------|---------------|------------|
| LSMO       | $c/a-1$             | JTd  | $\mu_{Mn}$ |
| 1          | 0.46 0.32           | -0.032 | 0.017 3.55 |
| 2          | 0.47 0.24           | -0.028 | -0.034 3.43 |
| 3          | -0.46 -0.25         | -0.021 | -0.038 -3.45 |
| 4          | -0.30 -0.74         | 0.013 0.070 | -3.89 |
| 5          | 0.48 0.22           | -0.027 | -0.035 3.44 |
| 6          | 0.50 0.29           | -0.043 | -0.012 3.57 |

**TABLE II:** Mulliken spin population of the Mn $e_g$ orbitals in the [La$_2$/3A$_1$/3MnO$_3$]$_3$[BO]$_6$ ground state (A=Sr, Ba ; B=Ba, Sr, Mg). The shown example was chosen as the cation ordering associated with the lowest ground state energy.

| Mono-layer | $e_g$ orb. spin pop. | $d_{x^2-y^2}$ | $d_{z^2}$ |
|------------|---------------------|---------------|------------|
| LBMO-BaO   | 1                   | 0.44 0.29     |
|            | 2                   | 0.38 0.54     |
|            | 3                   | 0.51 0.26     |
| LBMO-BaO (P4/mmm) | 1 | 0.48 0.27 |
|            | 2                   | 0.24 0.66     |
|            | 3                   | 0.48 0.27     |
| LSMO-SrO   | 1                   | 0.48 0.26     |
|            | 2                   | 0.40 0.52     |
|            | 3                   | 0.48 0.26     |
| LSMO-SrO (P4/mmm) | 1 | 0.48 0.25 |
|            | 2                   | 0.40 0.53     |
|            | 3                   | 0.48 0.25     |
| LSMO-MgO   | 1                   | 0.35 0.17     |
|            | 2                   | 0.23 0.70     |
|            | 3                   | 0.60 0.26     |
| LBMO-MgO   | 1                   | 0.35 0.17     |
|            | 2                   | 0.24 0.70     |
|            | 3                   | 0.59 0.32     |
that this symmetry is kept in the (LSMO)$_3$(SrO)$_6$ superlattice. Indeed, the two calculations with and without imposed symmetry yield equivalent results within error bars. For the (LBMO)$_3$(BaO)$_6$ superlattice however, this is not the case. Indeed, a spontaneous symmetry breaking occurs along the c axis, associated with a small energetic stabilization ($37 \text{ meV} \simeq 430 \text{ K}$) per LBMO u.c. This induces a symmetry breaking in the $e_g$ orbitals occupancies as can be seen in table [11]. Nevertheless, all manganite interface mono-layers are favoring a $d_{x^2−y^2}$ occupancy over a $d_{z^2}$ one, as was the case for the (LSMO)$_n$(BaO)$_p$ compounds. This result thus seems to remain valid independently of the manganite compound and of the simple oxide chosen for the alternating layer.

As a conclusion one may recall that thin films and superlattices of [La$_{2/3}$A$_{1/3}$MnO$_3$] ($A=$Sr, Ca) manganite compounds, over an SrTiO$_3$ substrate, have been extensively studied in the hope to find a good material for electronic and spintronics applications. Indeed, on such an STO, the LSMO is under tensile strain, so one is entitled to expect that the elastic energy will favor a contraction of the mono-layers along the c direction. Due to the degeneracy of the $e_g$ orbitals, such a contraction would have enhanced the occupation of the $d_{x^2−y^2}$ over the $d_{z^2}$ and thus the ferromagnetic and metallic behavior through the double exchange mechanism. Unfortunately the formation of a non-magnetic and insulating layer (called “dead layer”) at the interface prevents to reach this goal. This “dead layer” originates in a weak delocalization of the Mn layer) at the interface prevents to reach this goal. This consequence a preferred occupancy of the Mn orbitals in the empty Ti ones. The energy gain in this phenomenon overvalues the elastic energy loss [10]. As a consequence a preferred occupancy of the Mn $d_{z^2}$ orbitals associated with an elongation (along the c direction) of the interface mono-layers takes place.

In this paper, we theoretically studied different possibilities to hinder the interface delocalization using suitable alternating layers in superlattices. Our first principle calculations show that superlattices alternating manganite and alkaline-earth simple oxides efficiently prevent inter-layer delocalization, promote mono-layers contraction at the interfaces and a preferred $d_{x^2−y^2}$ occupancy over the $d_{z^2}$ one, and finally strongly increase the in-plane conductivity. Our studies show that this result should hold for different manganite and alternating layer thicknesses. One can thus reasonably expect that such superlattices may present the long searched magnetic and electric properties.

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