Abstract. We have performed first principles calculations of the electronic properties and the magnetic order at the interface of La$_{0.7}$Sr$_{0.3}$MnO$_3$ and SrTiO$_3$. The results are analysed in order to give the strength of the exchange between the surface MnO$_2$ layer and the bulk and also the degree of the polarization of the bands. It is shown that these properties depend on the way the interface is grown. Two different interface terminations are identified and modelled. The results of the calculations compare favourably with recent experimental data.

Spintronic devices use the information carried by the spin of electrons as well as their charge, and spin-dependent tunnelling lies at the heart of their operation. They depend on having a strongly polarized or half-metallic ferromagnet from which polarized carriers can tunnel. The rare earth manganites, particularly La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO), are good candidates for tunnel devices because there is evidence that they have a high spin polarization $P \sim 1$ [1]–[3]. There are three factors that should be considered for a good tunnelling device. Firstly the magnetism of the surface layer should not be much lower than the bulk, secondly the electronic spin polarization, $P$, at the surface should be high, and thirdly if $P < 1$ the velocities of the majority carriers should be high and that of the minority carriers should be low [4]. A perfect tunnelling magnetoresistance (TMR) device can be obtained either if $P = 1$ so the density of states (DOS) is 100% polarized at the Fermi level or if the minority spin states at the interface are actually localized.

Insulating SrTiO$_3$ (STO) is one of the most promising materials to use as a tunnel barrier in LSMO-based junctions. It is a good lattice match to LSMO and also has a small band gap so that the tunnelling rates are high. Hence the importance of understanding the nature of the interface between these two perovskites. The AO and BO$_2$ layers of a perovskite ABO$_3$ grow alternately.
In pulsed laser deposition (PLD) one should regard the process as depositing unit cells, i.e. equal numbers of A and B ions [5]. The junction between two perovskites ABO3 and CDO3 can occur in two ways keeping the provision that the size differential between the ions means that A or C ions do not go on to the B or D sites or vice versa. These are ABABCDC and ABADCDC. They differ by having an extra B or an extra D layer at the interface respectively. Even if the interface is not flat this imbalance will still occur. In the case of an interface between LSMO and STO the extra layer can be either MnO2 or TiO2 (see figure 1). Recent experiments [6, 7] show that there is a dramatic difference between the TMR of the two interfaces. We show here that this difference can be well understood from first principles.

There have recently been studies [6]–[12] of the magnetic properties of the LSMO/STO interface when it is grown as La0.7Sr0.3O/TiO2 and as MnO2/SrO. It is convenient to refer to these as TiO2 and SrO interfaces respectively. Bowen et al [6, 8] grew tunnel structures in which both interfaces were of the TiO2 type and obtained a value of the TMR of 1800%. Yamada et al [7] showed that the magnetism and TMR at the SrO interface were enhanced when two layers of undoped LaO were grown adjacent to the SrO layer, however even then the magnitude of the observed TMR (170%) is far below what was observed for the TiO2 interface.

In this paper we give the first microscopic analysis of the nature of the magnetism for LSMO at TiO2 and SrO interfaces, when zero, one and two layers of undoped LaMnO3 (LMO) are grown adjacent to the interface. We address the three important issues: the magnitude of the magnetic exchange between the surface layer and the bulk, the DOS at the Fermi level both in the bulk and at the surface and the value of the spin polarization, P, at the surface and finally the relative mobility of the majority and minority carriers at the surface.

We address all the terminations in a self-consistent self-interaction corrected LSD (SIC-LSD) [13] calculation by means of sufficiently large supercells (8–10 unit cells of LSMO and 8 unit cells of STO). The SIC-LSD method has been applied successfully to a variety of problems where competition occurs between localization and delocalization of electrons in strongly correlated systems such as transition metal oxides [14].

In the present study we have used the experimental lattice parameter of STO, 7.38 a.u., for the whole system which has a cubic perovskite structure. To model the LSMO system we use a
We first apply our method to calculating the electronic structure for bulk LSMO and STO. The calculated band structure and DOS of bulk LSMO are shown in figure 2. We find LSMO to be nearly half-metallic with the Fermi level ($E_F$) lying at the bottom of the minority conduction band as shown in figure 2. In the ground state the three $t_{2g}$ orbitals are localized and the total magnetic moment in the unit cell is $3.47 \mu_B$ (experimental moment is $\sim 3.60 \mu_B$). Note that in a half-metal the total moment should be $3.70 \mu_B$. It is however not completely clear whether LSMO is really a half-metal [2, 3], [15]–[17]. Bulk STO is known to be a band insulator and in our LDA calculation we find that it has a gap of 2.09 eV, smaller than its experimental value of 3.25 eV. In STO no self-interaction correction is subtracted because the Ti 3d levels are unoccupied.

We have considered both interface terminations (TiO$_2$ and SrO) by performing two separate calculations with symmetric supercells so that in each case we have only one kind of termination present. Using the following notation: L for La$_{0.7}$Sr$_{0.3}$O, M for MnO$_2$, T for TiO$_2$ and S for SrO, the first supercell is LM[LM]$_6$LT[ST]$_6$ST which has two TiO$_2$-type interfaces. The second is M[LM]$_6$LMST[ST]$_6$S which has two SrO-type interfaces. The subscript is for the number of formula units. We also consider the cases where one and two La$_{0.7}$Sr$_{0.3}$O layers at the SrO interface are replaced by undoped LaO layers. Within the layers we have assumed ferromagnetic (FM) coupling and therefore we have used one Mn atom per layer. This is a reasonable assumption since both $e_g$ ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$) orbitals have significant hopping integrals within the layers and it is known from the double-exchange model that the kinetic energy mediates the FM coupling. Between the layers, on the other hand, only the $d_{3z^2-r^2}$ hopping integral is nonzero, and...
Table 1. Exchange energies and magnetic moments in the bulk and at TiO\textsubscript{2}, SrO and SrO + 1(2) LaO interfaces. The energies are given in mRyd and the moments in units of $\mu_B$.

|        | Bulk | TiO\textsubscript{2} | SrO | SrO + 1 LaO | SrO + 2 LaO |
|--------|------|----------------|-----|-------------|-------------|
| $E_{AF} - E_{FM}$ | 6.0  | 3.5            | −6.3| −5.5        | 3.0         |
| Moment | 3.47 | 3.21           | 3.31| 3.34        | 3.31        |

this has a significant effect on the interlayer magnetic coupling [18]. Bulk LSMO is FM so we investigate the magnitude of the exchange interaction between the interface MnO\textsubscript{2} layer and the bulk by considering the energy difference $E_{AF} - E_{FM}$ of the supercell between when the interface MnO\textsubscript{2} layer is ferromagnetically (FM) and antiferromagnetically (AF) aligned with the bulk, and compare this to the bulk value. Experimentally, this corresponds to the differences observed between the interface and bulk Curie temperatures ($T_C$) [19]. We find that the exchange estimated in this way depends on the interface termination. We can make a simple estimate of the energy required to turn over one layer in the bulk as $E_{AA-F} - E_{FM}$. The A-AF solution corresponds to alternating FM layers coupled antiferromagnetically along the [001] direction.

The values of the exchange energies are given in table 1. In the case of TiO\textsubscript{2} interfaces we find a value of the surface exchange $E_{AF} - E_{FM}$ which is 58% of the difference $E_{A-AF} - E_{FM}$ in the bulk indicating that the FM coupling between the interface layer and the bulk is reduced. However, for SrO interfaces we find that $E_{AF} - E_{FM}$ is negative, i.e. the surface layer is coupled antiferromagnetically to the bulk; this is clearly not a good candidate for a large TMR. The fact that AF is the ground state destroys completely the TMR effect because in this case electrons of both spins can tunnel and there would therefore be no difference if the magnetizations of the electrodes were parallel or antiparallel. This is in qualitative agreement with experiments where suppression of ferromagnetism at the SrO interface is found [17, 11, 12]. However, a low magnetoresistance effect was also found [7] which means that the coupling between the interface and the bulk is probably not collinear AF. The magnitude of the antiferromagnetic coupling is reduced if one undoped layer of LaO is inserted as the penultimate layer to the interface. However, the coupling becomes FM when two layers of undoped LaO are grown next to the surface. In this case the value of $E_{AF} - E_{FM}$ is 50% that of the bulk indicating that the surface magnetism is comparable to that of the TiO\textsubscript{2} interface. Coupling between the interface and bulk for both terminations is comparable to half the bulk value. In both cases the interface will be expected to disorder at lower temperature than the bulk [19, 20].

The SIC calculations indicate that the most favourable state has the Mn $t_{2g}$ states localized and the $e_g$ states delocalized. This means that in both cases the valency of Mn remains unchanged at the interface. However, we can infer from the results presented in table 2 that the energy required to localize a further $e_g$ electron depends on the symmetry of the electron state, the magnetization and the nature of the interface. All the localization energies for the $e_g$ states are higher for the SrO interface than for the TiO\textsubscript{2} interface due to the lower electron density in the MnO\textsubscript{2} layer adjacent to the SrO interface. In the SIC formalism, one treats electrons as either localized or band-like and probes the energy required to localize an electron. One of the criteria for an orbital to localize is that it has an occupation of $\sim 1$ electron. Hence the difference in the localization energy between the TiO\textsubscript{2} termination which has $\sim 0.7$ electrons and the SrO termination which has $\sim 0.4$ electrons (table 3).

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Table 2. Total energy differences for the different localization scenarios and magnetic coupling at TiO$_2$ and SrO interfaces. The energy is given in nRyd per interface.

| Coupling at interface | SIC correction | TiO$_2$ | SrO |
|-----------------------|----------------|--------|-----|
| FM                    | $t_{2g}$       | 0.0    | 0.0 |
| FM                    | $t_{2g} + (3z^2 - r^2)$ | 12.9  | 39.8|
| FM                    | $t_{2g} + (x^2 - y^2)$ | 23.5  | 37.9|
| AF                    | $t_{2g}$       | 3.5    | -6.3|
| AF                    | $t_{2g} + (3z^2 - r^2)$ | 8.9   | 46.0|
| AF                    | $t_{2g} + (x^2 - y^2)$ | 22.4  | 30.6|

Table 3. Electronic charge on MnO$_2$ layers in the bulk and near the TiO$_2$ and SrO interfaces. SrO + 1(2) LaO means 1(2) layers of LaO inserted at the SrO interface. Indices C and I stand for the centre and the interface respectively. Mn$_{I-1}$ is the neighbouring layer to the interface.

| Interface and doping | Calculated charge | Ionic charge |
|----------------------|-------------------|--------------|
| TiO$_2$: Mn$_C$      | 0.64              | 0.70         |
| TiO$_2$: Mn$_{I-1}$  | 0.65              | 0.70         |
| TiO$_2$: Mn$_I$      | 0.68              | 1.05         |
| SrO: Mn$_C$          | 0.67              | 0.70         |
| SrO: Mn$_{I-1}$      | 0.62              | 0.70         |
| SrO: Mn$_I$          | 0.41              | 0.35         |
| SrO + 1 LaO: Mn$_C$  | 0.65              | 0.70         |
| SrO + 1 LaO: Mn$_{I-1}$ | 0.71            | 0.85         |
| SrO + 1 LaO: Mn$_I$  | 0.54              | 0.50         |
| SrO + 2 LaO: Mn$_C$  | 0.65              | 0.70         |
| SrO + 2 LaO: Mn$_{I-1}$ | 0.75            | 1.00         |
| SrO + 2 LaO: Mn$_I$  | 0.50              | 0.50         |

The DOS projected onto the four layers making up the interfaces are shown in figure 3 for the TiO$_2$ termination and in figure 4 for the modified SrO termination. The differences between the minority DOS on the MnO$_2$ layers in figures 3 and 4 is striking. In figure 3 there is a sharp peak in the minority DOS just below the Fermi energy. Following Mazin [4] and Pickett and Singh [17] we may identify this as a localized state so that the very high TMR seen in this case is due to transport half-metallicity. As for the insulating barrier, we see in figure 3 that some electrons occupy the conduction Ti 3d band near the interface due to the proximity to the ‘electron donor’ La$_{0.7}$Sr$_{0.3}$O layer. This is not the case for the SrO type of termination where the barrier remains insulating up to the interface.

The change in the magnetic coupling at the interface is related to two key ingredients: the doping level and the mobility (kinetic energy) of the $e_g$ electrons. In order to compare the amount of $e_g$ electrons on each MnO$_2$ layer we have integrated the layer-projected DOS from the bottom of the conduction band up to $E_F$ bearing in mind that these bands originate from the

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Mn $e_g$ orbitals with a small hybridization with O 2p orbitals. These values are given in table 3 for the four scenarios considered: TiO$_2$ interface, SrO interface and the two cases when one or two La$_{0.7}$Sr$_{0.3}$O layers are substituted by LaO at the SrO interface. The calculated charges are also compared with estimates from an ionic picture. The latter are obtained by assuming a contribution of $(1 - x)/2$ electrons from each neighbouring La$_{1-x}$Sr$_x$O layer to a particular MnO$_2$ layer. If we consider the SrO interface for instance then the ionic value is $0.7/2 + 0/2 = 0.35$, given that the MnO$_2$ layer is sandwiched between a La$_{0.7}$Sr$_{0.3}$O layer which contributes $0.7/2$ and a SrO layer which contributes 0 electrons. As expected there are deviations from the ionic values because of band formation and hybridization. The largest of these deviations occurs at the TiO$_2$ interface where we find 0.68 electrons whereas from the ionic picture we have 1.05 electrons. In this case, however, and as can be seen from figure 3, there are a few electrons (0.21) in the conduction band of the interface TiO$_2$ layer. The effect of the number of $e_g$ carriers on magnetic coupling is seen when comparing the charge on the interface MnO$_2$ layer between the two types of interfaces. The charge at the SrO interface (0.41) has been reduced below the bulk value (0.67). This difference accounts for the observed AF coupling for the SrO interface whereas the FM solution is stable for the TiO$_2$. All the other layers have roughly the same charge. However, the effect of the number of carriers cannot be separated completely from the effect of their mobility.

The effect of the mobility of the $e_g$ electrons can be seen by comparing the number of carriers in $e_g$ bands in the bulk and at the TiO$_2$ interface. These are given by $M_{nc}$ and $M_{nl}$ in table 3 respectively. Although this value is indeed slightly larger at the interface, we find that FM

Figure 3. Layer-projected DOS (states/layer/Ryd) for the La$_{0.7}$Sr$_{0.3}$O/TiO$_2$ type of interface. Shown are the four layers making up the interface.
Figure 4. Layer-projected DOS (states/layer/Ryd) for the MnO$_2$/SrO type of interface with two LaO layers substituted for La$_{0.7}$Sr$_{0.3}$O near the interface. Shown are the four layers making up the interface.

exchange is smaller at the interface as compared to the bulk. This is attributed to the fact that the carriers at the interface are confined to a two-dimensional (2D) motion which, normally, favours antiferromagnetism whereas in the bulk the interlayer hopping mediates a stronger FM coupling. The effect of the 2D confinement of the electrons at the interface has been seen in multilayers of LaAlO$_3$(LAO)/LSMO and STO/LSMO [21]. LAO has a gap of $\sim$6 eV and confines the electrons more effectively than STO which has a gap of $\sim$3 eV. As a result, the multilayer containing LAO has a lower $T_C$ than that containing STO [21]. In the case of the SrO interface the charge on the interface MnO$_2$ layer is 0.41, much smaller than the bulk value of 0.67. This corresponds to a doping $x = 0.65$ in the ionic picture. With this amount of doping, well above 0.5, even the bulk material is in an AF, and possibly charge ordered, state. This high level of doping combined with the confinement of electrons due to the interface leads to a very strong tendency to AF coupling to the bulk as found from our total energy calculation (see table 2). Upon inserting one LaO layer, the charge at the interface MnO$_2$ increases from 0.41 to 0.54, its ionic value being 0.50 in this case. The coupling is, however, still AF. Introducing a second LaO layer we see indeed that the charge at the interface remains $\sim$0.50. The excess charge goes to the MnO$_2$ layers adjacent to the interface. On these layers the electrons have more mobility and as a result lead to stronger FM coupling between the bulk and the interface. We see then that increasing the number of carriers at, but not limited to, the interface MnO$_2$ layer leads to FM coupling between the interface and the bulk and also to the preservation of transport half-metallicity. From the exchange energies
and the DOS, given above, we expect the modified SrO interface to have a TMR effect as large as that of the TiO\textsubscript{2} interface. Considering only the case of two layers of LaO inserted at the SrO interface of a STO/L\textsubscript{0.4}Sr\textsubscript{0.6}MnO\textsubscript{3} junction, an increase of TMR (50–170\%) was reported \cite{7}.

In summary, we have studied the two possible interface terminations of a LSMO/STO/LSMO junction and found that the TiO\textsubscript{2} interface preserves the ferromagnetism and the transport half-metallicity, characteristic of bulk LSMO, both of which are very important for a high TMR. For the SrO interface, on the other hand, it is necessary to add carriers to the interface and also to the neighbouring MnO\textsubscript{2} layers in order to recover these properties. The modified SrO interface is expected to yield comparable TMR values to those of the TiO\textsubscript{2} type of termination. The number of carriers and their mobility are crucial for enhancing ferromagnetism at the interface. This work has provided a consistent interpretation of two different sets of experimental data on LSMO/STO interfaces. It is hoped that it will serve as a guide to experimentalists in order to improve the efficiency of manganite-based tunnel junctions.

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