Electronic and magnetic properties of the (001) surface of hole-doped manganites

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The electronic and magnetic properties of ferromagnetic doped manganites are investigated by means of model tight-binding and ab initio self-interaction corrected local spin density approximation calculations. It is found that the surface alone by breaking the cubic symmetry induces a difference in the occupation of the two $e_g$ orbitals at the surface. With ab initio calculations we found surface localisation of one orbital and hence a change in the Mn valency from four in the bulk to three at the sub-surface. Different surface or disordered interface induced localisation of the orbitals are considered too with respect to the nature and the strength of the magnetic exchange coupling between the surface/interface and the bulk-like region.

I. INTRODUCTION

The half-metallic properties of $La_{1-x}Sr_xMnO_3$ ($x$~0.3) (LSMO) are of great importance for applications in spintronics. The tunnel magnetoresistance (TMR) of LSMO/STO junction shows a magnetoresistance ratio in excess of 1800% and was, by these authors, attributed to half-metallicity. While the magnetic impurities which might diffuse to the insulating layer could play an important role in the tunnelling process through the spin flip effects, antiferromagnons at the interface due to an antiferromagnetic interlayer coupling with the subsurface (or bulk) are found also to affect the MR in manganites tunnel junctions. The magnetic properties of these materials are highly sensitive to local crystal properties. The extrinsic strain field induced by lattice mismatch with the substrates or tunnel barriers can be sufficient to severely degrade the magnetic order in the surface layers which are critical for tunneling. Although other defects such as segregation of a particular species, like Sr in LSMO, at the interface alters the desired electronic and magnetic properties we have not addressed the issue in this work. Good TMR is expected if the material is fully polarised and half-metallic. Thus the occurrence of an antiferromagnetic layer or a localised layer at the surface will be very detrimental to tunneling. There is then a strong case for demanding to have both half-metallicity and ferromagnetic exchange at the interfaces between manganites and insulating barriers. Understanding the spin polarisation at the surface is then of major importance assuming that growing techniques could fabricate sharp well-defined interfaces and low diffusion rates of the magnetic ions into the insulating layer. In this paper we investigate the conditions required for surface antiferromagnetism and/or localised surface states so as to make clear the physical conditions for avoiding them.

On the basis of local spin density (LSD) band theory calculations, the origin of half-metallic character of manganese perovskites was discussed in several papers. These LSD calculations failed to obtain a half-metallic state and subsequently the possibility of transport half-metallicity was raised by Nadgorny et al. It could equally well be argued that the fascinating electronic and magnetic properties of LSMO, including colossal magnetoresistance (CMR), might indicate that the electronic structure is more complex than the standard band theory picture (see reviews and might necessitate a better treatment of correlation effects. Of particular importance would be to see if these correlation effects confirmed the half-metallicity of these materials.

Recently two of us described how upon Sr doping of LaMnO$_3$ (LMO) the Mn valence increases from 3+ to 4+ by delocalizing the $e_g$ electron. These results therefore suggested that, in LMO, Sr hole doping favours band formation instead of localisation. With this Sr doping no half-metallic state was obtained in LMO. Rather, the calculations suggested, half-metallicity is the consequence of remaining local Jahn-Teller distortions from the LMO parent material. This did go hand in hand with a mixed valence $Mn^{3+}/Mn^{4+}$ ground state which was discovered for Sr concentrations less than 20%.

The importance of the local distortions in LSMO does suggest that the surface properties of LSMO might be different from the bulk properties. This could possibly have important consequences for the magnetoelectronic transport through an LSMO/STO interface. Surfaces of manganese perovskites were studied before. Filippetti and Pickett used a pseudopotential method to study the magnetic properties of the surface of CaMnO$_3$ (CMO) and La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) in the (001) direction, Evarestov et al. used the Hartree-Fock approach to study the surface (110) in LaMnO$_3$. In particular the work of Filippetti and Pickett stressed the importance of spin flip processes at the surface for the transport properties.

In this paper we deal with finite slabs of $R_{1-x}A_xMnO_3$ (where R and A are trivalent and divalent ions respectively) to study the surface in a tight-binding model and Self-Interaction Corrected (SIC) LSDA calculations. The first allows us to study larger systems and more complicated magnetic configuration using a few parameters whereas the latter is parameter free and therefore more accurate but limited by the number of atoms that can be simulated.
II. TIGHT-BINDING METHODOLOGY

The active orbitals in a model calculation on manganites are the two degenerate $e_g$ orbitals separated by a "strong" ligand field from the three low-lying $t_{2g}$ states. As we are concerned with a region of the phase diagram where most manganites are found to be in the FM metallic phase we use the Kondo-lattice type model Hamiltonian\(^{20,21}\) using the two $e_g$ orbitals:

$$H = -\frac{1}{2} \sum_{\gamma, \gamma'} \sum_{\sigma, \sigma'} t_{\gamma \gamma'} d_{\gamma \sigma}^d \left( d_{\gamma' \sigma}^d + d_{\gamma' \sigma}^\dagger \right) - J_h \sum_i s_i \cdot s_i + J_{AF} \sum_{\langle i,j \rangle} s_i \cdot s_j. \quad (1)$$

The Hamiltonian consists of the kinetic energy of the $e_g$ electrons with anisotropic hopping integrals $t_{\gamma \gamma'}$ ($\gamma$ and $\gamma'$ denote the two $e_g$ orbitals, $i$ and $a$ index the sites and the first neighbours respectively), a Hund coupling which favours the alignment of their spins ($s_i$) with the core-like $t_{2g}$ moments ($S_i$) and superexchange interaction between the classical $t_{2g}$ spins.

The transfer integrals between two orbitals $e_g(3z^2−r^2)$ (orbital 1) and $e_g(x^2−y^2)$ (orbital 2) on adjacent Mn ions are given by:

$$t_{\gamma \gamma'} = -t_0 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{along } z,$$

$$t_{\gamma \gamma'} = -\frac{t_0}{4} \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & 3 \end{pmatrix} \quad \text{along } x \quad (2)$$

$$t_{\gamma \gamma'} = -\frac{t_0}{4} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & 3 \end{pmatrix} \quad \text{along } y,$$

and $t_0 = \frac{V_{pdz}}{e_p-e_d}$ where $V_{pdz}$ is the Slater-Koster parameter and $e_p$, $e_d$ are the energies of the O $2p$ and Mn $3d$ states. This parameter takes into account the hybridisation with O which does not appear explicitly in the model.

As shown above an electron in the state $e_g(3z^2−r^2)$ cannot hop along the $z$ direction whereas its hopping integral along $x$ and $y$ is larger than for the $e_g(x^2−y^2)$. This fact will be important in the determination of the occupancy of the two orbitals in the presence of the surface and/or an interlayer antiferromagnetic coupling. The strong on-site Hund coupling will favour the alignment of neighbouring core spins via the itinerant $e_g$ electrons. Competing with this tendency is the superexchange which acts between core spins on neighbouring sites. This interaction is responsible for the observed G-AF phase in the end members AMnO$_3$ where the $e_g$ electrons are absent and thus only the superexchange operates. The superexchange also wins over when there are not enough carriers to lower the total energy by a gain in kinetic energy or in case where hopping is suppressed due to other factors as is the case in the presence of a surface as we will see below. In order to keep the number of parameters to a minimum we did not include the Coulomb on-site repulsion between $e_g$ electrons nor the Jahn-Teller coupling\(^{21}\). On the other hand we added a shift\(^{21}\) $\Delta$ of the on-site energy for the orbitals at the surface in order to take into account the change in energy of the states at the surface due chemical shifts and/or strain fields. This may be the case at interfaces with grain boundaries or with insulating barriers in tunneling devices as explained above. One of the major effects of the surface is the occurrence of a charge transfer to or from the bulk region inducing a loss of local neutrality and creation of electrostatic dipoles. We treat these interactions in the Hartree approximation\(^{21}\) by solving the Poisson equation with $\epsilon = 5$. The coupled Schrödinger-Poisson equations are solved self consistently until the relative change in energy and charge is less than 0.05%.

III. RESULTS AND DISCUSSION

A. Orbital ordering and surface magnetism

We will consider three possible magnetic configurations namely ferromagnetic (FM), A-type antiferromagnetic (A-AF) and a configuration where all the moments on the inner layers are parallel and the surface one flipped (DUUD, where D is for down and U is for up) in order to look at the interplay between magnetic ordering and orbital ordering and the effect of the surface. In section III.C we evaluate the energy of a reversed layer. We assume an in-plane ferromagnetic ordering so that we have one inequivalent atom per plane. We show in Fig. 11 the occupancies of the $e_g(3z^2−r^2)$ and $e_g(x^2−y^2)$ orbitals in these three configurations. There is a noticeable correlation between the type of magnetic and orbital orderings. The $e_g(x^2−y^2)$ is more populated than the $e_g(3z^2−r^2)$ on those planes which are antiparallel to their neighbours. Whereas the two are equally occupied when the coupling is FM. The surface layer is an exception however but this is not surprising having in mind the anisotropy of the transfer integrals defined above.

The higher occupancy of the $e_g(x^2−y^2)$ orbital at the surface is explained by the absence of interlayer hopping for the electrons in this state which do not lose kinetic energy in the presence of the surface. Whereas the $e_g(3z^2−r^2)$ electrons are more sensitive to the presence of the surface which limits their hopping and as a result this orbital is more occupied in the bulk where the levels are broadened than at the surface where the level is more localised. As mentioned above the anisotropy of the hopping integrals leads to no direct electron transfer from $e_g(x^2−y^2)$ orbitals between planes. Hence in the current model the local density of states (DOS) projected on to this orbital is independent both of the position in the slab and the magnetic orientation of the neighbouring planes. On the other hand there is transfer between $e_g(3z^2−r^2)$ orbitals along $z$. This means that the local $e_g(3z^2−r^2)$ DOS will be narrowed at the surface because the transfer is only to one plane instead of two and this is true also if there is AF order. We see this effect clearly in
finite transfer integral in this direction the hopping is partially suppressed because of the narrowing of the local DOS. The electrons would rather go to the wider $e_g(x^2-y^2)$ DOS. Thus there is an orbital order induced at the surface and is present in all of the three configurations but is stronger when there is a local AFM coupling between the surface and subsurface layers as is the case in (b). The effect is even bigger in (c) where the AF coupling all through the slab causes a narrowing of the $e_g(x^2-y^2)$ and no significant change to the $e_g(x^2-y^2)$ DOS so that we found orbital order throughout the film. The total electron density shown by the sum, $d_{3\pm x_2}+d_{x_2-y^2}$, is almost unchanged at 0.7. This is due to the suppression of charge imbalance by including the electrostatic interactions solved for in the Poisson equation. Without this extra electrostatic term the electrons in the absence of a shift of the surface levels would transfer to the inner part of the slab raising the density above the bulk level independently of the slab thickness. We see however from Fig. 1 that we get the bulk properties for three layers away from the surface.

We have studied the effect of introducing the shift $\Delta$ for both orbitals and for only one of them at the surface. As explained earlier, this parameter is used to mimic the effect of structural (like lattice mismatch) and chemical (like charged surfaces) on the on-site energy level of the orbitals. Here we look at the effect on the orbital ordering and in Section III.C we will consider the changes in the relative stability of the two solutions FM and DUUD. The orbital occupancies are given in Fig. 2 as a function of the strength $\Delta$ for the two magnetic solutions corresponding to (a) and (b) of the Fig. 1. We found that when both orbitals are shifted by a small $\Delta$ the occupation of the $e_g(x^2-y^2)$ remains higher and is explained from the simple kinetic energy gains argument explained earlier. Increasing $\Delta$ results in a crossover to higher occupancy of the $e_g(x^2-y^2)$ orbital but this is explained also from the anisotropy of the transfer integrals argument. As is depicted schematically in Fig. 3 the LDOS of the $e_g(x^2-y^2)$ orbital is broader than that of $e_g(3z^2-r^2)$ so that when the Fermi level is well below the centre of the bands the occupation of the first is higher. With increasing $\Delta$ the Fermi level lies at the centre and the two orbitals are equally filled. Increasing further $\Delta$ will favour the occupation of $e_g(3z^2-r^2)$ which has higher number of states available in a much smaller energy window. The crossover occurs for smaller values of $\Delta$ in the FM solution than in the DUUD case, in agreement with our earlier finding that the occupation of $e_g(3z^2-r^2)$ favours FM coupling. Shifting one orbital only will favour its occupation in both solutions and for values of $\Delta$ larger than 2$t_0$ the other orbital is completely depleted.

B. Ab initio study of charge and orbital ordering

As mentioned above we report also on results using the SIC-LSDA to study the surface of a a representative system, La$_{0.7}$Sr$_{0.3}$MnO$_3$. This method has already been used with success in studying the bulk properties of this material. It allows for a parameter-free total energy

![FIG. 1: Occupancy of the $e_g(3z^2-r^2)$ and $e_g(x^2-y^2)$ and their sum as a function of the distance from the surface for a 21-layer TB model of R$_{0.7}$A$_{0.3}$MnO$_3$. The configurations are in order FM, FM with the surface layer flipped (DUUD) and A-AF. Conversely, the decrease in the kinetic energy of the $e_g(3z^2-r^2)$ electrons at the surface results in the weakening of the double exchange and a tendency to an AF coupling between the surface and subsurface layers. The higher occupancy of the $e_g(x^2-y^2)$ orbital at the surface makes it more likely that it will want to localise as we will see below in the SIC calculations. Inside the bulk-like region of the slab the two orbitals are equally likely to be occupied as long as the coupling between layers is FM. The strong on-site Hund’s coupling will always act to align the $e_g$ electron’s spin to the $t_{2g}$ one and in order for the system to gain from the kinetic energy of the electrons, the core spins ought to be parallel. If this is not the case then the hopping is partially suppressed and the superexchange wins over. This suppression occurs between layers and as the only orbital which has a finite transfer integral in this direction the $e_g(3z^2-r^2)$ will be penalised and hence depopulated as can be seen from Fig. 1. In Fig. 1 where no shift of the surface levels is introduced the $e_g(3z^2-r^2)$ is disfavoured near the surface because of the narrowing of the local DOS. The electrons...
The shifts are for:
- \( d_{3z^2-r^2} \) (filled circles)
- \( d_{x^2-y^2} \) (open circles)

The shifts are for:
- \( d_{3z^2-r^2} \) (dotted)
- \( d_{x^2-y^2} \) (dashed)
- both (full)

FIG. 2: Evolution of the occupancies of the \( e_g(3z^2-r^2) \) and \( e_g(x^2-y^2) \) orbitals at the surface versus the shift \( \Delta \). Two configurations are considered: FM(a) and DUUD (b).

FIG. 3: Schematic representation of the evolution of the occupancy of the \( e_g(3z^2-r^2) \) (narrow) and \( e_g(x^2-y^2) \) (broad) orbitals at the surface when shifted by an amount \( \Delta \) with respect to their common bulk level. The area below the two curves is the same. The horizontal line represents the Fermi energy. When the Fermi level is above the centre of the two bands the occupation of \( e_g(3z^2-r^2) \) becomes higher.

minimisation with respect to the localised/itinerant state of the Mn \( d \) electrons in our case. The number of electrons allowed for band formation is found by comparing total energies in the two configurations where the electron is itinerant and where it is localised. The valency of the Mn ions is then found by subtracting the localised electrons from the total number of valence electrons. It has been applied successfully to systems where there is strong tendency to localisation of the valence electrons that could not be accounted for using the conventional LSDA functionals.

Here the focus is put on the changes brought about by the surface on the charge and orbital orderings. The valence of Mn in LSMO was calculated to be tetravalent in the bulk material. However we find here that this valence is reduced to trivalent when the Mn is on the subsurface layer. We report on calculations in which we include a virtual La/Sr atom to account for the mixed valence. All the layers are either MnO\(_2\) or La\(_{0.7}\)Sr\(_{0.3}\)O. This is a type of rigid band model. First we studied a supercell consisting of four layers of MnO\(_2\) with three and four layers of La\(_{0.7}\)Sr\(_{0.3}\)O. The second system is considered in order to check the effect of the stoichiometry which is not respected in the system with three La\(_{0.7}\)Sr\(_{0.3}\)O layers only. This non-stoichiometric system is symmetric and the calculations are much less involved than in the stoichiometric but non-symmetric case. The slabs are separated by seven and six layers of empty spheres in the symmetric and non-symmetric case respectively. The non-symmetric system has two surface terminations, i.e MnO\(_2\) and La\(_{0.7}\)Sr\(_{0.3}\)O whereas in the symmetric case the termination is MnO\(_2\).

In the LSDA calculations we found an energy difference of 8.04 mRy/(MnO\(_2\) layer) between the ground-state FM configuration and the configuration where the surface moment is antiparallel to the bulk ones (DUUD) in the symmetric case. For the non-symmetric case the
ground state is also FM and the difference in energy with the flipped surface moment configuration is of 5.59 mRy/(MnO$_2$ layer). The surface and subsurface Mn magnetic moments in the ground state are of 3.26 and 3.16$\mu_B$ in the symmetric system and of 3.28 and 3.12$\mu_B$ in the non-symmetric system. The results are indeed in good agreement. We then studied different orbital localisation scenarios. These are the localisation of the $3t_{2g}$ orbitals all through the slab and localisation of an extra $e_g$ orbital at the surface, which gives three possible scenarios for each of the magnetic configurations. In both systems the ground state is the FM phase with the $3t_{2g}$ orbitals only localised on all the Mn ions. The FM configuration with an extra $e_g(x^2−y^2)$ localised at the surface is 6.67 mRy/(MnO$_2$ layer) higher in the symmetric case and is of 6.21 mRy/(MnO$_2$ layer) in the non-symmetric case. The surface and subsurface Mn magnetic moments are of 3.30 and 3.31$\mu_B$ in the symmetric system and of 3.32 and 3.27$\mu_B$ in the stoichiometric system.

Having confirmed that the stoichiometry has negligible effect on the overall relative stability of different orbital and magnetic configurations we applied this method to symmetric five-MnO$_2$ layers supercell of LSMO surface which included four unit cells of empty spheres (see Fig. 4). In this case the MnO$_2$ layer is at the sub-surface rather than the surface which we studied previously. The TB model does not include the La$_{0.7}$Sr$_{0.3}$O layers and therefore cannot differentiate between these cases. However a phenomenological shift $\Delta$ of the on-site energies at the surface could capture this. We found that terminations by the La$_{0.7}$Sr$_{0.3}$O layer leads to the localisation of one more electron on the Mn atoms in the MnO$_2$ layer under surface. The ground state configuration has localised $3t_{2g} + 1e_g(x^2−y^2)$ electrons under the surface and $3t_{2g}$ electrons on the manganese in the bulk in agreement with the model calculations when the shift $\Delta$ is applied to the surface $e_g(x^2−y^2)$ orbital (see Fig. 5). Since the MnO$_2$ layer is not the termination, the $e_g(x^2−y^2)$ could not be said to be favoured as was the case in earlier calculations. There is however an electrostatic interaction with the surface $O^{2−}$ ion which means that the energy level of this orbital should increase in comparison to the case when the MnO$_2$ layer is at the surface. Whereas this is not true for the $e_g(x^2−y^2)$ orbital which is less sensitive to the presence of the extra La$_{0.7}$Sr$_{0.3}$O layer. The situation can then be modelled by shifting the on-site $e_g(x^2−y^2)$ level downwards which is equivalent to shifting the other level upwards. The calculated ground state configuration has the total energy of 37 mRy lower than the system with all Mn$^{3+}$ configured manganese. From the LDOS of the first layer we can see small contributions of electronic states from the vacuum region. The La$_{0.7}$Sr$_{0.3}$O surface layer becomes insulating with a band gap of about 1 eV. The LDOS for the first MnO$_2$ layer with Mn$^{3+}$ valence shows a nearly half-metallic character with a nearby pseudo-gap of 1.7 eV. This shows that localisation of the $e_g(x^2−y^2)$ electron, forced by the surface, leads to near half-metallic properties at the LSMO surface as was mentioned before. The change of the symmetry of the localised electron to $e_g(3z^2−r^2)$ increases the total energy by about 23 mRy. This is a substantial energy, 62% of the energy needed for delocalizing this $e_g$ electron. Additionally, the rotation of $e_g(3z^2−r^2)$ orbitals by 90° into the $x−y$ plane makes this configuration unfavourable by only 10 mRy in comparison with the ground state configuration of a localised $e_g(x^2−y^2)$ electron. Localisation of $e_g$ electrons on the other Mn atoms, inside the bulk, increases the total energy of the system.

**C. Energetics**

Depending on the surface/interface termination several scenarios are possible which will allow for a particular orbital to be favoured. It has been argued that a termination with MnO$_2$ plane will favour the occupation of the $e_g(3z^2−r^2)$ orbital which has its lobe oriented toward the missing oxygen ion and hence has lower electrostatic energy than the $e_g(x^2−y^2)$ which still see the oxygen present in the plane. A phase diagram in the parameter space has been obtained where it is shown clearly that a large shift $\Delta$ of the $e_g(3z^2−r^2)$ with respect to $e_g(x^2−y^2)$ and the bulk levels will favour an inplane antiferromagnetism at the surface and a canted configuration with respect to the “bulk”. First principles calculations.
on the other hand found that the surface-subsurface exchange coupling in La$_2$Ca$_{1-x}$MnO$_3$ is FM independently of the “bulk” magnetic configuration. The authors argued that this is due to the dangling $e_{g}(3z^2-r^2)$ bond again which favours this ferromagnetism. Whereas in the present ab initio study we have found that it is rather the $e_{g}(2x^2-y^2)$ that is localised as the MnO$_2$ layer is the subsurface rather than the terminating layer. We present below results concerning the competition between FM and AFM surface-subsurface coupling as a function of the symmetry of the localised orbital and the amount $\Delta$ by which the levels are shifted. We considered shifts of both levels simultaneously and of one orbital at a time and calculated the band energies (kinetic plus Hartree) when the surface-subsurface coupling is either FM or AFM. The superexchange energy difference between them is of $2J_{AF}$ per surface Mn ion. The results are shown on Fig. where the energies are given in units of the hopping integral $t_0$ and the Hund’s coupling constant $J_H$ is taken equal to $6t_0$. As can be seen from the figure while localising both orbitals does not change the relative energies, localising the $e_{g}(2x^2-y^2)$ will affect strongly the surface-subsurface ferromagnetism. This is due to the depletion of the other orbital on the surface and hence the weakening of the double exchange mechanism mediated by $e_{g}(3z^2-r^2)$ electrons hopping between the layers. In the case where both orbitals are shifted it is the reduction in the subsurface occupation of the $e_{g}(3z^2-r^2)$ orbital which limits the gain in kinetic energy that would result from the higher occupation of the surface $e_{g}(3z^2-r^2)$ orbital. The relative stability of the two configurations remains unaltered as a result. Shifting the $e_{g}(3z^2-r^2)$ will enhance the FM coupling with the bulk as found in the ab initio study of the MnO$_2$-terminated system. But this is true only if the $e_{g}(2x^2-y^2)$ is not strongly disfavoured as found in the previous model calculations. If the occupation of the latter orbital is low at the surface in-plane anti-parallel coupling of the spins would result as a consequence of the weakening of the double exchange at the surface which is mediated mostly by $e_{g}(2x^2-y^2)$ electrons.

IV. CONCLUSION

We have considered what light our calculations have shed on the ideal hole-doped-manganite-insulator interface such that tunneling magnetoresistance (TMR) is optimal. We have studied changes that are induced by the lack of cubic symmetry at the surface as well as different chemical environments which favour the formation of localised states, through a realistic double exchange model and first principles calculations. In the model calculation we have taken account of the different scenarios by adding a shift $\Delta$ to the surface on-site energy of the orbitals. If a surface/tunnel barrier has net positive charge $\Delta$ will be negative for both orbitals. If this is too large we get localisation which is bad for tunnelling. Equally a strong negative charged termination is also bad because a positive $\Delta$ will deplete both orbitals leading to magnetic disorder at the surface. If the in-plane lattice constant of the barrier is smaller than that of the manganite crystal there will be a strain field which gives a negative $\Delta_{3z^2-r^2}$ tendency to favour the $e_{g}(3z^2-r^2)$ orbital. For small values of $\Delta_{3z^2-r^2}$ surface ferromagnetism is enhanced. However large values of this strain will deplete the $e_{g}(2x^2-y^2)$ orbital and favour in-plane antiferromagnetism at the surface MnO$_2$ layer which is detrimental to TMR. On the other hand strains favouring $e_{g}(2x^2-y^2)$ always suppresses ferromagnetic ordering and hence TMR. In the absence of any chemical shift of the atomic levels at the surface only a small amount of charge is transferred to the bulk because of the resulting electrostatic forces tendency to restore local charge neutrality. Shifting both levels or one of them however will result in charge transfer to the surface for large values of $\Delta$. This leads to the formation of Mn$^{3+}$ at the surface. These findings are confirmed by the more accurate ab initio SIC-LDA calculation on a model system La$_{0.7}$Sr$_{0.3}$MnO$_3$. In these calculations we found no localisation of the surface orbitals when the slab is terminated by a MnO$_2$ layer and the coupling is ferromagnetic. We studied the LaSrO-terminated system were the subsurface $e_{g}(3z^2-r^2)$ still sees an oxygen ion on the surface and interacts strongly with it. This orbital is then disfavoured and we found that the $e_{g}(2x^2-y^2)$ is localised at the subsurface layer changing the valency of the Mn ion from tetravalent in the bulk to trivalent at the surface. The magnetic coupling then becomes antiferromagnetic as would be expected from the correlation between orbital and magnetic ordering. However if the interlayer distance is increased at the surface, which amounts to favouring the $e_{g}(3z^2-r^2)$, we found that the energy differences between competing orderings decrease significantly. This relates the ab initio results to the model ones. In summary we predict that the best TMR will come from tunnel barriers that are neutral or weakly positive. There should be a minimal surface strain although a small in-plane compressive strain favouring the $e_{g}(3z^2-r^2)$ is actually beneficial.

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