

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 self-interaction corrected local spin density (SIC-LSD) 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. We found surface localization of one orbital and hence a change in the Mn valency from four in the bulk to three at the subsurface. Different surface or disordered interface induced localization of the orbitals are considered too with respect to the nature and the strength of the local orbital ordering and magnetic exchange coupling between the surface/interface and the bulklike region. We predict that better tunneling can be achieved in tunnel barriers that favor slightly the occupancy of the Mn $e_{g(3z^2-r^2)}$ at the interface.

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I. INTRODUCTION

Mixed valence manganites have attracted much attention because of the colossal magnetoresistance (CMR) effect they exhibit in the bulk whereby the electrical resistance changes drastically upon application of a magnetic field. But the magnitude of the magnetic fields needed is much higher than those available in technological applications. A similar effect is found to occur in manganites-based tunnel junctions and in manganites polycrystals called tunneling magnetoresistance (TMR). In the latter smaller fields are needed to induce a change of orders of magnitude in the tunneling resistance. Unlike the CMR effect which is observed around room temperature the TMR effect vanishes at much lower temperatures indicating that important changes occur at the interfaces of the manganites with the insulating layers. Understanding of surface properties is of relevance since tunnel magnetoresistance (TMR) in excess of 1800% for LSMO/SrTiO₃/LSMO junctions was attributed to half-metallicity of the manganites at the interface.¹ While the magnetic impurities which might diffuse to the insulating layer could play an important role in the tunneling process² through the spin flip effect,³ antiferromagnons at the interface² 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 ferromagnetic order in the surface layers which are critical for tunneling.^{4,5} 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 polarized and half-metallic. Thus the occurrence of an antiferromagnetic layer or a localized layer at the surface will be very detrimental to tunneling. There is then a strong case for demand-

ing to have both half-metallicity and ferromagnetic exchange at the interfaces between manganites and insulating barriers. Understanding the spin polarization at the surface is then of major importance assuming that growing techniques could fabricate sharp well-defined interfaces¹ 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 localized 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.⁶⁻¹¹ These LSD calculations failed to obtain a half-metallic state and subsequently the possibility of transport half-metallicity was raised by Nadgorny *et al.*¹⁰ and Mazin.¹¹ 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 Refs. 12 and 13) 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 us¹⁴ described how upon Sr doping of LaMnO₃ (LMO) the Mn valence increases from 3+ to 4+ by delocalizing the e_g electron. These results therefore suggested that, in LSMO, Sr hole doping favors band formation instead of localization. With this Sr doping no half-metallic state was obtained in LSMO. 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 Mn³⁺/Mn⁴⁺ ground state which was discovered for Sr concentrations less than 20%.¹⁴

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: Phillipetti and Pickett used a pseudopotential method to study the magnetic properties of the surface of CaMnO_3 (CMO)¹⁵ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO)¹⁶ in the (001) direction; Evarestov *et al.*¹⁷ used the Hartree-Fock approach to study the surface (110) in LaMnO_3 . In particular the work of Phillipetti and Pickett^{15,16} stressed the importance of spin flip processes at the surface for the transport properties.

In this paper we deal with finite slabs of $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R and A are trivalent and divalent ions, respectively) to study the surface in a tight-binding model and self-interaction corrected^{18,19} (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 ferromagnetic (FM) metallic phase we use the Kondo-lattice type model Hamiltonian^{20,21} using the two e_g orbitals:

$$H = -\frac{1}{2} \sum_{\mathbf{ia}\gamma\gamma'\sigma} t_{\gamma\gamma'}^{\mathbf{a}} d_{\mathbf{i}\gamma\sigma}^\dagger d_{\mathbf{i}+\mathbf{a}\gamma'\sigma} - J_h \sum_{\mathbf{i}} \mathbf{s}_i \cdot \mathbf{S}_i + J_{AF} \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

The Hamiltonian consists of the kinetic energy of the e_g electrons with anisotropic hopping integrals $t_{\gamma\gamma'}^{\mathbf{a}}$ (γ and γ' denote the two e_g orbitals, \mathbf{i} and \mathbf{a} index the sites and the first neighbors, respectively), a Hund coupling which favors the alignment of their spins (\mathbf{s}_i) with the corelike t_{2g} moments (\mathbf{S}_i) and superexchange interaction between the classical t_{2g} spins.

The transfer integrals between the 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

$$\begin{aligned} t_{\gamma\gamma'} &= t_0 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \text{ along } z, \\ t_{\gamma\gamma'} &= \frac{t_0}{4} \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & 3 \end{pmatrix} \text{ along } x, \\ t_{\gamma\gamma'} &= \frac{t_0}{4} \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & 3 \end{pmatrix} \text{ along } y, \end{aligned} \quad (2)$$

and $t_0 = V_{pd\sigma}^2 / (e_p - e_d)$ where $V_{pd\sigma}^2$ 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 hybridization with O which does not appear explicitly in the model. In the present calculations we use²⁰ $t_0 = 0.6$ eV and $J_h = 8t_0$. The orbits are

defined so that the z direction is perpendicular to the surface of the finite slab.

As shown above an electron in the state $e_{g(x^2-y^2)}$ cannot hop along the z direction whereas its hopping integral along x and y is larger than for the $e_{g(3z^2-r^2)}$. 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 favor the alignment of neighboring core spins via the itinerant e_g electrons. Competing with this tendency is the superexchange which acts between core spins on neighboring 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 the 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 shift²¹ Δ 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 to 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 approximation²¹ by solving the related Poisson equation with $\epsilon = 5$.²² Including the Coulomb interaction, one finds in the mean-field (MF) approximation that the on-site energy of the orbital a becomes

$$\epsilon_{new}^a = \epsilon_0^a + U' \langle n_b \rangle, \quad (3)$$

where ϵ_0^a is the bare on-site energy and $\langle n_b \rangle$ is the occupation of the other orbital b . Only the interorbital term U' appears here because the double occupation of one orbital is already forbidden by the strong Hund's coupling J_h . In the bulk $\langle n_a \rangle = \langle n_b \rangle = n/2$ and therefore $\epsilon_{new}^a = \epsilon_{new}^b = \epsilon_0 + U' n/2$. At the surface, however, $\langle n_a \rangle$ is in general different from $\langle n_b \rangle$ but because of the strong electrostatic interactions mentioned earlier we have $\langle n_a \rangle + \langle n_b \rangle = n$. The Coulomb term, which is similar to the electron-lattice interaction,²³ acts to enhance the orbital ordering which is found to occur at the surface but has no major effect in the bulk due to the cubic symmetry which favors equal occupation of both e_g orbitals. The effect of the Coulomb interaction is then the renormalization of the parameters²⁴ ϵ_0 and a further splitting of the levels at the surface. 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 Sec. 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. 1 the occupancies of the $e_{g(x^2-y^2)}$ and $e_{g(3z^2-r^2)}$ 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 neighbors. 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 localized. 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 this orbital is independent both of the position in the slab and the magnetic orientation of the neighboring 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 Fig. 1. 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 localize as we will see below in the SIC calculations. Inside the bulklike 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 penalized 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 disfavored near the surface 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

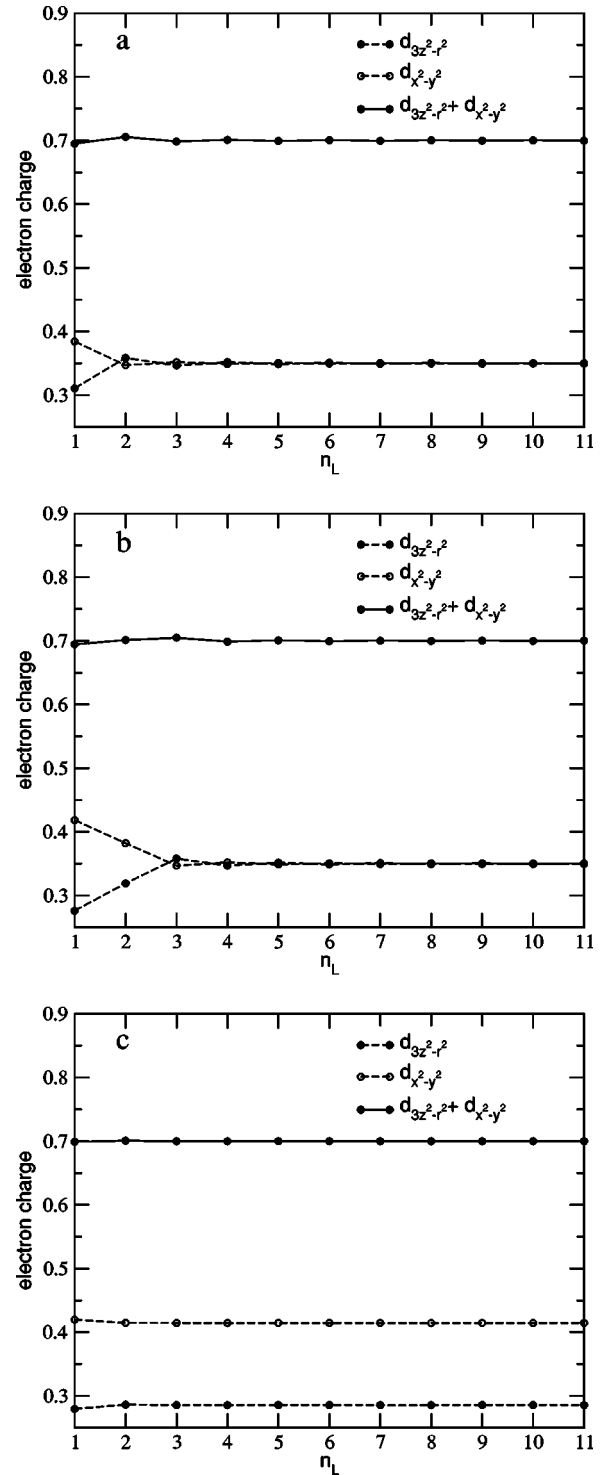


FIG. 1. Occupancy of the $e_{g(3z^2-r^2)}$ and $e_{g(x^2-y^2)}$ and their sum as a function of the distance from the surface for a 21-layer TB model of $R_{0.7}A_{0.3}MnO_3$. The configurations are in the order FM, FM with the surface layer flipped (DUUD), and A-AF.

all through the slab causes a narrowing of the $e_{g(3z^2-r^2)}$ 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, $d_{3z^2-r^2} + d_{x^2-y^2}$, 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 Δ for both orbitals and for only one of them at the surface. The parameter Δ depends on the symmetry lowering at the surface or interfaces and on changes in the type, number, and distance to neighboring atoms. These changes in the energy levels (both core and valence) are almost unavoidable at interfaces.²⁵⁻²⁷ We have made an approximate estimation of Δ by looking at the position of the center-of-mass of the d orbitals at the surface compared to the bulk in our LSDA calculation for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ system. This is given, for an orbital a , by

$$\epsilon_c^a = \int \rho^a(\epsilon) \epsilon d\epsilon, \quad (4)$$

where $\rho^a(\epsilon)$ is the density of states at energy ϵ projected on the orbital a .

We have evaluated the orbital energies in the FM case and we found that both e_g levels at the surface are shifted from their bulk position. The center-of-mass of the $e_{g(x^2-y^2)}$ level is shifted upward by 0.21 eV whereas that of the $e_{g(3z^2-r^2)}$ level is shifted by 0.12 eV. Since the surface d levels are expected to shift upward following the upward core-level shifts, as given by the core eigenenergy differences between the bulk and the surface,²⁹ one can argue that the smaller shift of the $e_{g(3z^2-r^2)}$ level is due to the reduced electrostatic repulsion on its lobe directed to the missing surface oxygen as pointed out by Calderon *et al.*²¹ This electrostatic gain compensates then for the upward shift of this orbital. The $e_{g(x^2-y^2)}$ orbital on the other hand which is not sensitive to the absence of the oxygen ion has a larger shift. The parameter Δ is positive and of the order of 0.2 eV, about $t_0/3$ ($t_0=0.6$ eV in the model calculations), for the $e_{g(x^2-y^2)}$ orbital. This value is, however, likely to change both in sign and magnitude when the terminating manganese ions have neighboring oxygens (in samples grown on substrates such as SrTiO_3 , AlO_3 , ...) and when Mn-O distances change as a result of lattice mismatch. This reminds us of the splitting of the e_g levels due the presence of short and long Mn-O bonds in the parent compound LaMnO_3 , that is the Jahn-Teller splitting. The shift Δ , however, is expected to be smaller as only one Mn-O bond length undergoes changes at the interface.

Here we look at the effect on the orbital ordering and in Sec. 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 Δ for the two magnetic solutions corresponding to (a) and (b) of Fig. 1. We found that when both orbitals are shifted by a small Δ 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 Δ results in a crossover to higher occupancy of the $e_{g(3z^2-r^2)}$ orbital but this is explained also

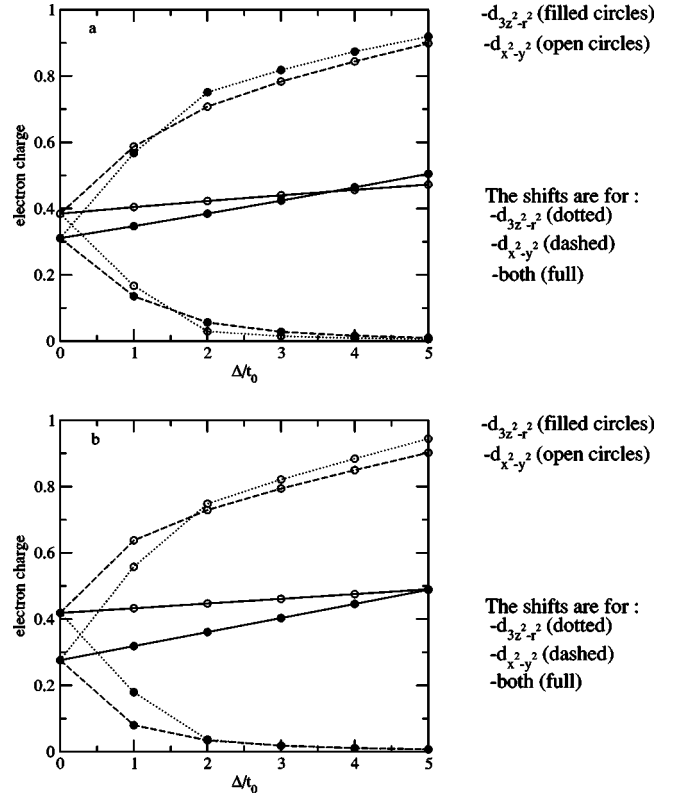


FIG. 2. Evolution of the occupancies of the $e_{g(3z^2-r^2)}$ and $e_{g(x^2-y^2)}$ orbitals at the surface vs the shift Δ . Two configurations are considered: FM(a) and DUUD (b).

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 center of the bands the occupation of the first is higher. With increasing Δ the Fermi level lies at the center and the two orbitals are equally filled. Increasing Δ further will favor the occupation of $e_{g(3z^2-r^2)}$ which has a higher number of states available in a much smaller energy window. The crossover occurs for smaller values of Δ in the FM solution than in the DUUD case, in agreement with our

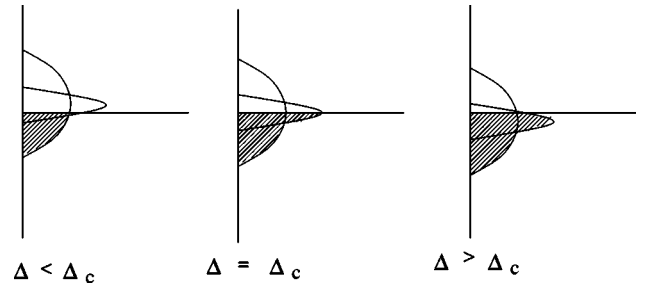


FIG. 3. Schematic representation of the evolution of the occupancy of the $e_{g(3z^2-r^2)}$ (narrow) and $e_{g(x^2-y^2)}$ (broad) orbitals at the surface when shifted by an amount Δ with respect to their common bulk level. The area below the two curves is the same. The horizontal line represents the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

earlier finding that the occupation of $e_{g(3z^2-r^2)}$ favors FM coupling. Shifting one orbital only will favor its occupation in both solutions and for values of Δ larger than $2t_0$ the other orbital is completely depleted.

B. SIC-LSD study of charge and orbital ordering

As mentioned above we report also on results using the SIC-LSDA to study the surface of a representative system, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. This method has already been used with success in studying the bulk properties of this material.¹⁴ It allows for a parameter-free total energy minimization with respect to the localized/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 localized. The valency of the Mn ions is then found by subtracting the localized electrons from the total number of valence electrons. It has been applied successfully to systems where there is a strong tendency toward localization of the valence electrons that could not be accounted for using the conventional LSDA functionals.²⁸

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 tetravalent¹⁴ 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 $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$. This is a type of rigid band model. First we studied two systems with supercells consisting of four layers of MnO_2 with three, for the first, and with four layers of $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ for the second. The second system is considered in order to check the effect of the stoichiometry which is not respected in the system with three $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ layers only. This nonstoichiometric system is symmetric and the calculations are much less involved than in the stoichiometric but nonsymmetric case. The slabs are separated by seven and six layers of empty spheres in the symmetric and nonsymmetric case, respectively. The nonsymmetric system has two surface terminations, i.e., MnO_2 and $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$, 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 nonsymmetric 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 μ_B in the symmetric system and of 3.28 and 3.12 μ_B in the nonsymmetric system. The results are indeed in good agreement. We then studied different orbital localization scenarios. These are the localizations of the $3t_{2g}$ orbitals all through the slab and localization 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 localized on all the Mn ions. The FM configuration with an

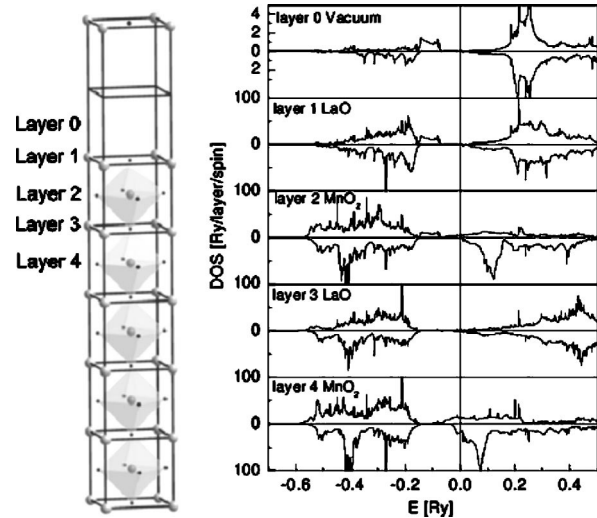


FIG. 4. LDOS, in the rigid band model, for a five unit supercell ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$)₅. The Mn in layers two and ten have localized $3t_{2g} + 1e_{g(x^2-y^2)}$ electrons and the other Mn have localized $3t_{2g}$ electrons only. The left-hand-side picture shows the supercell.

extra $e_{g(3z^2-r^2)}$ localized at the surface is 6.67 mRy/(MnO_2 layer) higher in the symmetric case and is of 6.45 mRy/(MnO_2 layer) in the nonsymmetric case. The surface and subsurface Mn magnetic moments in the ground state are of 3.30 and 3.31 μ_B in the symmetric system and of 3.32 and 3.27 μ_B in the stoichiometric system.

Having confirmed that the stoichiometry has a negligible effect on the overall relative stability of different orbital and magnetic configurations, we applied this method to a symmetric five- MnO_2 layer supercell of the LSMO surface which included three layers of empty spheres (see Fig. 4). In this case the MnO_2 layer is at the subsurface rather than the surface which we studied previously. The TB model does not include the $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ layers and therefore cannot differentiate between these cases. However, a phenomenological shift Δ of the on-site energies at the surface could capture this. We found that terminations by the $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ layer leads to the localization of one more electron on the Mn atoms in the MnO_2 layer under the surface. The ground state configuration has localized $3t_{2g} + 1e_{g(x^2-y^2)}$ electrons under the surface and $3t_{2g}$ electrons on the manganese in the bulk. The magnetic order changes from FM in the bulk to a local antiferromagnetic arrangement. Localization of the $e_{g(x^2-y^2)}$ orbital favors antiferromagnetism as is found in the model calculations when the shift Δ 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 $e_{g(3z^2-r^2)}$ could not be said to be favored as was the case in earlier calculations.^{16,21} 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 $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ layer. The situation can then be modeled by shifting the on-site $e_{g(x^2-y^2)}$ level downward which is equivalent to shifting the other level upward. The calculated ground state configuration

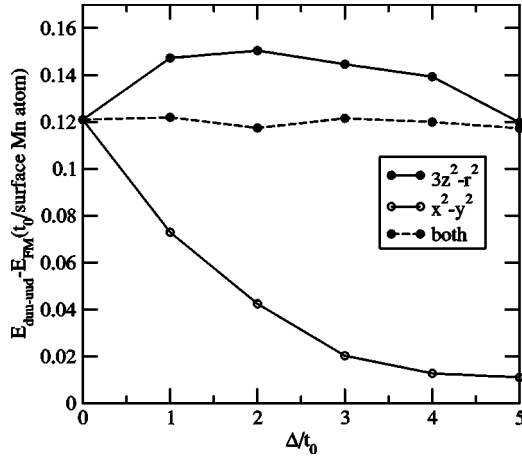


FIG. 5. Energy differences between the two configurations where the surface-subsurface coupling is AFM or FM in units of the hopping parameter t_0 per surface Mn ion vs the amount Δ of the shift added to one or both surface levels. The Hund's coupling parameter is $J_h = 8t_0$.

has the total energy of 37 mRy lower than the system with all Mn^{4+} configured manganese. From the LDOS of the first layer we can see small contributions of electronic states from the vacuum region. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}$ 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 pseudogap of 1.7 eV. This shows that localization 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.¹⁴ This is, however, not good for TMR because the half-metallicity occurs in the wrong spin channel. The change of the symmetry of the localized 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 unfavorable by only 10 mRy in comparison with the ground state configuration of a localized $e_g(x^2-y^2)$ electron. Localization of e_g electrons on the other Mn atoms, inside the bulk, increases the total energy of the system. The LDOS for the next LaO layer shows metallic character with a small number of electrons at the Fermi level but each of the MnO_2 layers including the Mn^{4+} has a clear metallic character. The LDOS for the layers below these are similar to the ones for the bulk.

C. Energetics

We now turn our attention to a quantitative assessment of the importance of the shift Δ to the magnetic ordering at the surface induced by a related orbital ordering. Depending on the surface/interface termination several scenarios are possible which will allow for a particular orbital to be favored. It has been remarked that a termination with a MnO_2 plane will favor the occupation of the $e_g(3z^2-r^2)$ orbital²¹ 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 sees

the oxygens present in the plane. Our present LSDA calculation confirmed that when the MnO_2 layer is at the surface the $e_g(3z^2-r^2)$ on-site energy is lower than that of $e_g(x^2-y^2)$, even though the actual occupancy of the latter may still be larger because of it being broader. In junctions or at grain boundaries, however, the last MnO_2 is always in the presence of other layers and the bare surface picture has to be modified. In fact we found in the present calculation that by adding one monolayer between the MnO_2 plane and the surface the $e_g(x^2-y^2)$ orbital becomes localized in contrast with the scenario where the MnO_2 is at the surface and where the $e_g(3z^2-r^2)$ is favored. A phase diagram in the parameter space has been obtained²¹ where it is shown clearly that a large shift Δ of the $e_g(3z^2-r^2)$ with respect to $e_g(x^2-y^2)$ and the bulk levels will favor an in-plane antiferromagnetism at the surface and a canted configuration with respect to the "bulk." LSDA pseudopotential calculations¹⁶ on the other hand found that the surface-subsurface exchange coupling in $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ is FM independently of the "bulk" magnetic configuration. The strong FM coupling at the surface was ascribed¹⁶ to the dangling $e_g(3z^2-r^2)$ bond which when occupied favors this ferromagnetism.

Here we present results concerning the competition between FM and AFM surface-subsurface coupling as a function of the symmetry of the localized orbital and the amount Δ 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 $2J_{\text{AF}}$ per surface Mn ion. The results are shown in Fig. 5 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 $8t_0$. As can be seen from the figure, while localizing both orbitals does not change the relative energies, localizing the $e_g(x^2-y^2)$ 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 LSD study of the MnO_2 -terminated system. But this is true only if the $e_g(x^2-y^2)$ is not strongly disfavored as found in the previous model calculations.²¹ 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 $e_g(x^2-y^2)$ 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 favor the formation of localized 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 Δ to the surface on-site energy of the orbitals. If a surface/tunnel barrier has net positive charge Δ will be negative for both orbitals. If this is too large we get localization which is bad for tunneling. Equally a strong negative charged termination is also bad because a positive Δ 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 $\Delta_{3z^2-r^2}$ tending to favor 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 $e_{g(x^2-y^2)}$ orbital and favor in-plane antiferromagnetism at the surface MnO_2 layer which is detrimental to TMR. On the other hand strains favoring $e_{g(x^2-y^2)}$ always suppress 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 Δ . This leads to the formation of Mn^{3+} at the surface. These findings are confirmed by the more accu-

rate SIC-LSD calculation on a model system $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. In these calculations we found no localization 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 where 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 disfavored and we found that the $e_{g(x^2-y^2)}$ is localized 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. We are then in the presence of two limiting cases regarding the shift Δ applied to $e_{g(3z^2-r^2)}$ orbit in the ideal surface case. This relates the SIC-LSD 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 favoring the $e_{g(3z^2-r^2)}$ is actually beneficial.

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²⁹This is the simplest approximation to account for surface core-level shifts and is called the initial state model (see Ref. 26).