Double exchange-driven spin pairing at the (001) surface of manganites

Alessio Filippetti* and Warren E. Pickett
Department of Physics, University of California at Davis, Davis, California 95616

The (001) surface of La$_{1-x}$Ca$_x$MnO$_3$ system in various magnetic orderings is studied by first principle calculations. A general occurrence is that $z^2$ dangling bond charge – which is "invisible" in the formal valence picture – is promoted to the bulk gap/Fermi level region. This drives a double-exchange-like process that serves to align the surface Mn spin with its subsurface neighbor, regardless of the bulk magnetic order. For heavy doping, the locally "ferromagnetic" coupling is very strong and the moment enhanced by as much as 30% over the bulk value.

Although most efforts on the colossal magnetoresistance (CMR) materials typified by the La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) system are still concentrated on bulk properties, growing interest is being shown in the surface behavior [1,2]. Knowledge of surface properties is essential not only to develop a perovskite manganite-based technology but also to determine fundamental phenomena and mechanisms of magnetoelectronic behavior. Indeed, the CMR effect occurs at high temperature, around the magnetic ordering temperature, and a magnetic field of several Tesla is required to suppress the thermal magnetic disorder and produce the change in resistivity. Since high magnetic fields are generally unavailable in applications, alternative ways to trigger large low-field MR were considered, such as with trilayer junctions [3] and polycrystalline samples [4]. The junctions are epitaxially grown along the [001] direction, and are made of a central insulating thin film of SrTiO$_3$ (the barrier), sandwiched by two metallic layers of La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO). Applying a low magnetic field, the tunneling conductivity can be switched by inducing a parallel (switch on) or anti-parallel (switch off) spin-orientation in the two electrodes. Taking advantage of their half metallicity gives a very large tunneling MR (TMR).

Large low-field intergrain MR (IMR) [4] over a large temperature range has been observed in polycrystalline samples of LSMO, CrO$_2$, Cr$_2$O$_3$, and the double perovskite systems Sr$_2$Fe(Mo,Re)O$_6$, all of which are expected to be half metallic magnets. Magnetotunneling across grain boundaries, in which the relative orientation of the magnetization of neighboring grains is manipulated by an applied field, is believed to be the mechanism. In the IMR process, which may be the most promising for MR applications, there is mounting evidence that the state of the surfaces of the grains is important in the intergrain tunneling process [5,6]. For TMR it has long been clear that tunneling characteristics are strongly influenced, perhaps even dominated, by the electronic and magnetic structure at the interface, and for IMR surface states have been suggested to play the central role.

In the few experimental works present in the literature intrinsic difficulties have been reported in the process of obtaining clean, bulk-truncated surfaces, due to surface segregation that occurs during growth at high temperature [7,8], and strain effects induced by film-substrate mismatch [9]. Structural and electronic properties of the low-index surfaces (including the possibility of reconstructions) are still unknown, in spite of their importance in establishing the half metallic nature of the CMR materials using photoelectron emission [10]. However, advancements in epitaxial growth and surface uniformity are being reported, so a first fundamental step towards describing real surfaces consists in understanding how the intrinsic properties of the ideal unreconstructed surfaces differ from the respective bulk properties, i.e. how the bulk truncation in itself modifies the physics of this compounds. First-principle calculations are ideally suited for this aim, and in this paper we focus on surface spin ordering of the Mn-terminated (001) surface of La$_{1-x}$Ca$_x$MnO$_3$. Although this system shows an extremely rich variety of magnetic phases for different level of doping [11,12], we identify a general, robust mechanism that should dominate the surface spin order for any doping level $x$. In the regime of heavy doping $x \sim 1/2$, the surface-to-subsurface magnetic coupling is much stronger than in bulk, and the surface moment is enhanced by as much as 30%.

Based on the growing understanding of the double exchange (DEX) process in bulk manganites, it can be expected that the surface spin alignment will be strongly dependent on the Mn $e_g$ occupation. At the (001) surface, however, the $e_g$ degeneracy is broken: the $x^2 - y^2$ orbital remains very strongly $d_{xy}$ hybridized with neighboring (in surface layer) O ions, but the $z^2$ orbital is left "dangling." The implications of this symmetry breaking were first glimpsed in the simple, undoped $x=1$ member

*Present address: Materials Research Lab, Univ. of California, Santa Barbara, Ca 93106
CaMnO$_3$, which has G-type AFM bulk ordering due to standard AFM superexchange between filled $t_{2g}$ shells. These $t_{2g}$ shells contain the nominal three electrons assigned to Mn$^{4+}$ in the formal valence picture, with the $e_g$ formally empty. As it has been pointed out in other contexts, $[13]$, the amount of actual $d$ charge is not at all identical to the formal $d^n$ charge. For bulk phenomena however, this idealization usually gives a reliable broad picture of general behavior, including spin, charge, and orbital order. For the CaMnO$_3$ (001) surface, however, G-type spin order does not survive at the surface. Instead, a flip of all spins in the surface layer occurs, driven by the appearance of Mn $z^2$ charge $[4]$ that drives a double exchange (DEX) process that strives to align spins. This $z^2$ charge is present in the bulk, resulting from $dp\sigma$ mixing that draws a truly significant amount of $e_g$ charge into the “O 2$p$” bands: the 18 O $p$ bands actually contain on the order of 1.5-2 electrons of Mn $e_g$ character. Some of this becomes a dangling bond at the surface, lying in the bulk gap and driving the surface spin to flip. What we show in this paper is that this mechanism survives, and in fact is enhanced, as doping occurs.

First-principles calculations have been performed within local-density approximation (LDA), employing a plane wave basis and Vanderbilt pseudopotentials $[15]$. A 30 Ryd cut-off energy and the exchange-correlation potential of Perdew and Zunger $[16]$ was used. For the La$_{1-x}$Ca$_x$MnO$_3$ (001) surfaces we have studied, we used slab of nine atomic layers. For $x=1/2$, the stacking along $\hat{z}$ is made by alternating layers of La and Ca (see Fig. 1), retaining a mirror symmetry with respect to the central Mn layer. The artificial ordering of La and Ca layers (which must be done somehow in a finite supercell) should not affect our conclusions, since they simply become ionized by contributing their valence electrons to the O and Mn bands. For the planar lattice constant of bulk La$_{1/2}$Ca$_{1/2}$MnO$_3$ we obtain by energy minimization $a_0=7.21$ a.u. which is a reasonable value between the experimental 7.35 a.u. for La$_{2/3}$Ca$_{1/3}$MnO$_3$, and 7.05 a.u. for CaMnO$_3$. We find the AFM phase favored by 15 meV/Mn over the FM, which has a nearly half-metallic density of states.

In Table 1 the calculated relative surface energies for $x=1/2$ are reported. As can be seen from Fig. 1, there are two kinds of Mn-terminated surfaces, i.e. one with La in the subsurface layer (indicated as Mn-La), and one with Ca instead (Mn-Ca). Since (Table I) they give equivalent results, we will quote specific results for just one of them (La-Mn). Treating an inner region with the true spin, charge, and orbital order for $x=1/2$ $[17]$ is well beyond computational capabilities, but the behavior we identify is so robust that we expect it to be independent of bulk order. For each of the geometries of our nine layer surface, four spin arrangements on Mn are possible, labeled in Table I by arrows on central (C), subsurface (SS) and surface (S) Mn, in this order. These are: surface and subsurface parallel, aligned or antialigned to the central layer, and surface and subsurface antiparallel, with the subsurface aligned or antialigned with the central layer. We find that S-SS spin alignment is strongly favored, with the most stable configuration having both the surface and subsurface layer spins antiparallel to the central Mn spin: (from third to top layer) $\uparrow\downarrow\downarrow$.

The energies can be mapped onto an interlayer Ising model with three independent effective exchange constants: $J_{S-SS}$, $J_{SS-C}$ and $J_{S-C}$, the latter being a second neighbor coupling. $J_{SS-C} = -18$ meV (AFM) is close to the exchange parameter obtained directly from the bulk calculation ($J_{bulk} = -15$ meV). The interaction between Mn on first and third layers, $J_{C-S} = 8$ meV, is FM in sign and is related to the $d_{xz}$ the surface state discussed below.

The most striking result for $x=1/2$ (Table I) is the positive, unusually large value of $J_{S-SS} = 53$ meV, more than three times larger than, and opposite in sign to, the bulk AFM coupling. For comparison, for CaMnO$_3$ ($x=1$) the interlayer exchange constant at the surface was 29 meV. (The bulk coupling for $x=1$ is also different from $x=1/2$, with $J_{bulk} = -26$ meV.) This large FM coupling, for both $x=1$ and $x=1/2$, is the consequence of a very general characteristic of (001) surface formation. In Fig. 2 the orbital-resolved density of states (DOS) of the Mn ions for the (001) surface in the most stable spin configuration (i.e. $\uparrow\downarrow\downarrow$) is shown. Two surface Mn $d_{xz}$ DOS peaks straddle the Fermi energy ($E_F = 0$), with a tail of occupied states that extends down to $\sim -1.5$ eV. These states are also visible on subsurface Mn and, for the occupied peak, on central Mn as well. Thus the surface has a deep surface $d_{xz}$ resonance extending to the fifth layer below the surface. In the majority channel of the central (‘bulk’) Mn ion, $d_{xz}$ and $d_{xy}$ orbitals contribute to the DOS at $E_F$, whereas in the minority channel the only contribution comes from $t_{2g}$ states. The $d_{xz}$ dangling bond discussed above leads to the formation of the surface resonance as it does in CaMnO$_3$. It is also apparent that the $d_{xy}$ bands are shifted upward in energy, so that the minority channel is depleted (i.e. the Mn at surface is fully polarized) and the $d_{xy}$ surface bands contribute to the DOS at $E_F$. The magnetic moment on the surface Mn (3.23 $\mu_B$) is 10% larger than on subsurface Mn (2.97 $\mu_B$) and 30% larger than in ‘bulk’ central Mn (2.50 $\mu_B$), but the total charge on Mn ($\sim 5.3$ electrons using our definition) is nearly the same at surface and in the bulk. The increase of magnetization is due mostly to the $d_{xz}$ polarization with some contribution from the depletion of $d_{yz}^\uparrow$ states around $E_F$. Also, a small intratomic charge readjustment occurs from $d_{x^2-y^2}^\uparrow$ to the polarized $d_{xz}$ orbital on the surface Mn ion.

The resulting surface polarization can be visualized from the isosurfaces of the magnetization displayed in Fig. 3. Contributions coming from states that lie in the region within 0.3 eV below $E_F$ are shown, i.e. the “core”
The change of the Mn d_{z^2} orbital from broad, strongly dπσ hybridized in the bulk to an atomic-like, narrow in energy, surface state is a very specific feature of this (001) surface formation, and this surface dehybridization generally should be described well by LDA. We suggest that this effect is strong enough to turn the AFM spin coupling into FM for any doping level. At least two arguments support this hypothesis. First, the spin-pairing occurs for the (001) surface of CaMnO₃ that should be the most unfavorable case, since in the bulk (nominally) only the majority t_{2g} orbitals are occupied, thus their AFM character is dominant. Nevertheless, the partially occupied d_{z^2} surface state reverses the magnetic coupling. Second, the very large change of exchange interaction parameter (from -15 meV in bulk to +53 meV at the surface) would overcome AFM bulk coupling even stronger than the one considered here.

A crucial case is the x=0 member LaMnO₃, which is A-type AFM in the bulk. The spin-pairing argument applied to the surface parallel to the FM (001) layers predicts a spin-flip of the surface Mn layer. The AFM spin coupling along the \( \hat{z} \) axis is robust and explained by a well established picture: the in-plane FM coupling is stabilized by the ordering of Mn \( e_g \) orbitals, so that occupied \( d_{x^2} \) (\( d_{y^2} \)) orbitals alternate with empty \( d_{x^2} \) (\( d_{y^2} \)) orbitals on neighboring Mn. Thus, all the \( e_g \)-type charge fills in-plane orbitals, and the \( d_{z^2} \) orbitals are empty and higher in energy. As a consequence, the AFM interactions between neighboring \( t_{2g} \)'s dominates in the orthogonal direction. A realistic first-principle calculation of the LaMnO₃ surface is beyond the possibility of detailed calculations, since it would require a \( \sqrt{2} \times \sqrt{2} \) lateral enlargement of the cell as well as additional thickness to treat the tilting of the MnO₆ octahedra [27], and the Jahn-Teller distortion at the surface would have to be determined. However, the formation of the \( d_{z^2} \) surface state within bulk LaMnO₃ gap seems to be beyond doubt, based on the behavior of the \( d_{z^2} \) dangling bond for \( x=1 \) and \( x=1/2 \). The question is whether this would be able to overcome the \( t_{2g} \) AFM contribution. In Ref. [19] it is shown that the \( t_{2g} \) contribution for bulk LaMnO₃ increases linearly in magnitude with the distortion between in-plane and inter-planar lattice constants at fixed volume, i.e. the AFM coupling between (001) planes increases linearly by shortening the interplanar distance, likely due to the electrostatic repulsion that further depletes the \( d_{z^2} \) orbitals. The \( t_{2g} \) contribution to \( |J|_{\text{bulk}} \) has been calculated in Ref. [19] as a function of the lattice distortion. It is in the range of \( \approx 20-30 \) meV, i.e. not large enough to overcome the value of \( J_{S-S} \), thus we definitely expect the occurrence of a spin-flip process at the (001) LaMnO₃ surface.

In Fig. 4 we show the \( e_g \) orbitals on surface and subsurface layers, and indicate the expected filling and orbital ordering after the formation of the surface state. The orbitals are ordered in “FM” fashion both in-plane and orthogonally to the surface, as a result of the surface formation that fills the Mn surface \( d_{z^2} \) orbital no longer degenerate with the \( d_{z^2} \) orbital of the underlying subsurface Mn.

To summarize, we have found that terminating the (001) surface of La₁₋ₓCaxMnO₃ surfaces with the Mn ion exposed, results in partial filling of the \( d_{z^2} \) orbital that drives a double-exchange-like ordering of the surface and subsurface layers of Mn ions. We have shown this effect explicitly for \( x=1/2 \) and (previously) for undoped CaMnO₃. A comparison between these two cases indicates that it is stronger in doped systems. This result has important implications (1) for surface studies, where this effect tends to insure that surfaces of the CMR materials \( (x \approx 1/3) \) will remain ferromagnetically aligned and half metallic as well, as supported by photoemission studies, and (2) for the intergrain magnetoresistance effect, where the magnetic structure of the grain surfaces can strongly affect the device characteristics. This behavior, which is strongly related to band filling but much less dependent on ion size effects, should also hold for the La₁₋ₓSrₓMnO₃ and La₁₋ₓBaₓMnO₃ systems.

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TABLE I. Energies (in meV) for different spin configurations on Mn atoms. Each of them is labeled by the three arrows indicating the spin direction of central-subsurface-surface Mn. Mn-La is the Mn-terminated (001) surface with La on second layer, Mn-Ca is that one with Ca on second layer. All energies refers to that one of the most stable arrangement, i.e. ↑↓↓.

| Configuration | Mn-La | Mn-Ca |
|---------------|-------|-------|
| ↑↓↑ (001)     | 23    | 17    |
| ↑↑↓ (001)     | 144   | 142   |
| ↑↑↑ (001)     | 91    | 88    |
| ↑↑↑ (001)     | 0     | 0     |
| ↑↑↓ (001)     | 53    | 53    |
| ↑↓↑ (001)     | -18   | -18   |
| ↑↓↓ (001)     | 8     | 9     |

FIG. 1. Structure of the (001) surface of tetragonal La$_{1/2}$Ca$_{1/2}$MnO$_3$. Arrows indicate spin orientations for the stable ↑↓↓ ordering (see text), which we find for this compound and for CaMnO$_3$. Parallel alignment of the surface and subsurface layers is expected to be true generally. Note that the surface oxygen ions are also polarized.
FIG. 2. Orbital-resolved Mn d DOS for the (001) Mn-La surface in the spin configuration $\uparrow \downarrow \downarrow$ (i.e. AFM bulk and flipped spin at surface). The panels refer to the 3 unequivalent Mn layers in the slab.

FIG. 3. Isosurfaces of the valence magnetization for the (001) Mn-La surface in the spin configuration $\uparrow \downarrow \downarrow$. The magnetization shown is due to states below, and within, 0.3 eV of $E_F$ (see the corresponding DOS in Fig.2). Dark and light isosurfaces are of same magnitude but opposite sign, i.e. they represent up and down spin densities, respectively.
FIG. 4. Orbital ordering at LaMnO$_3$ (001) surface: filling of $d_{z^2}$ orbital (indicated by shading) at the surface produces FM spin coupling perpendicular to the surface. Planar orbital ordering in the subsurface and other buried layers leads to FM layers alternating in spin direction, except at the surface.