Surface Magnetic Phase Diagram of Tetragonal Manganites

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Abstract

To gain insights into the fundamental and characteristic features of the surface of doped manganites, we constructed a general magnetic phase diagram of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (001) surfaces in the plane spanned by \(x\) and the bulk tetragonal distortion \(c/a\), from the first-principles calculations. We found that the surfaces are quite different from the bulk in the sense that both the (La, Sr)O and MnO\(_2\) terminated surfaces show strong tendency toward antiferromagnetism (A-type and C-type respectively). The basic physics governing the phase diagram can be understood in terms of the surface orbital polarizations. It is also found that the strong surface segregation of Sr atoms is mostly caused by the electrostatic interaction and will further enhance the tendency to surface antiferromagnetism.
I. INTRODUCTION

Over the last half a decade, the perovskite colossal magneto-resistive (CMR) manganites have attracted intensive attention due to the remarkably rich variety of structural, magnetic, transport and optical properties and are regarded as potentially important materials for the next generation technology. Such possibility may be a strong motivation for the study of thin films and superlattices of the manganites and the related materials. In these systems surfaces and interfaces will play important roles. However, even without appealing to thin films and superlattices, surfaces and interfaces are involved in various aspects. The enhanced low-field magnetoresistance has been reported in the polycrystalline samples due to the spin-dependent behaviors across the grain boundaries. The photoemission data, which provide evidence for the half-metallicity, and the scanning tunneling spectroscopy (STS) or microscopy (STM), which provide evidence for the spatial phase-separation, are all surface sensitive. Therefore, the basic understanding of the surfaces of doped manganites is an urgent and challenging problem. It is already established that one of the most important implications in the physics associated with the CMR manganites is the key roles of orbital degrees of freedom (ODF), which couple strongly with the lattice, charge and magnetic degrees of freedom (MDF). We expect that the ODF will play even more important roles on the surfaces due to the lowering in symmetry and dimensionality.

Detailed experimental and theoretical studies on the surfaces of CMR manganites have started only very recently and the results obtained so far are not yet sufficient to establish any general picture about the surface phase diagram. In the experimental side, it is still difficult to prepare well defined surfaces. In the theoretical side, on the other hand, only some limited phase space and limited conditions have been taken into account. Although it is not possible to consider the complete phase space and all possible complications conceivable in real systems, it is very important to construct a general qualitative picture for the surface phase diagram by taking account of possible phases and some important experimental conditions. This is what we aim in the present work by taking \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \)
(LSMO) as a canonical system of doped manganites.

First, since it is possible to control the terminations by chemical treatment of the surface or by controlling the chemical potential, consideration of two possible terminations of (001) surface is important. It is natural to expect that the surface effect will be strong for the MnO\textsubscript{2} termination, but weak for the (La, Sr)O termination, due to the loss of part of the ligand of Mn in former case. Although the expectation is qualitatively true, the change in the electrostatic potential for SrO termination can also produce significant change in the electronic structure. Second, the lattice deformation induced by the substrates can produce cooperative stabilization of orderings in ODF and MDF, leading to strong anisotropy in the thin film. Therefore, in the present work, we will present a general surface phase diagram of LSMO, for both the (La, Sr)O and MnO\textsubscript{2} terminated (001) surfaces, as functions of the hole doping $x$ and the bulk tetragonal distortion $c/a$ ratio induced by the substrates. We found that the (La, Sr)O terminated surface shows strong tendency toward the A-type antiferromagnetic (AF) state, while the surface phases of MnO\textsubscript{2} termination are dominated by the C-type AF state. The basic physics behind is the ordering in the surface ODF of Mn $e_g$ states. Third, we found that the Sr atoms should seriously segregate towards the surfaces due to the electrostatic interaction. The general tendency of surface segregation will further favor the surface AF states.

**II. CALCULATION METHODS**

The present work is based on the first-principles electronic structure calculations, which adopt the PBE version of generalized gradient approximation (GGA). The Kohn-Sham equation is solved by using the pseudopotential technique. The Mn(3d) and the O(2p) states are treated by the ultra-soft pseudopotential, while the norm-conserving scheme is used for other states. The cutoff energies for the plane-wave expansions of wavefunction and charge density are 30 Ry and 200 Ry respectively. La\textsubscript{x}Sr\textsubscript{1-x} is treated as a virtual atom by the virtual crystal approximation (VCA). In present systems, the valence electronic
states near and below the Fermi level are contributed mostly by Mn and O, the states coming from La and Sr are far above the Fermi level. Therefore, the simple VCA can provide a reasonable description of the systems. The validity of these techniques was well demonstrated in our previous calculations for the bulk. We use a repeated slab geometry, which includes five MnO$_2$ layers with mirror symmetry in the central MnO$_2$ layer. As the MnO$_2$ layer and the (La, Sr)O layer are stacked alternately along the surface normal, i.e., z-axis, nine and eleven atomic layers in total are included in the unit cell for the MnO$_2$ and (La, Sr)O terminations, respectively. A vacuum region of 12 ~ 13Å is included to separate the slabs. Several magnetic states, i.e., ferromagnetic (FM), A-type AF and C-type AF states, are calculated in the present study. In the A-type AF state, the magnetic moment of Mn are aligned ferromagnetically in the $ab$-plane (slab plane) and these FM layers are coupled antiferromagnetically along the $c$ direction (surface normal). In the C-type AF state, on the other hand, the FM chains along the $c$ direction are coupled antiferromagnetically. In the surface phase diagrams in Fig.1, the above definition is applied to the slab. A simple schematic description about the spin configurations of surface A- and C-type AF states can be found in Fig.2. To accommodate the C-type AF states, we use the planar c(2x2) unit cell. The atomic positions and magnetic states are fully optimized for each of given $ab$-plane lattice constants, which define the bulk $c/a$ ratio since the bulk volume is given for each doping $x$. By choosing the lowest energy state among FM, A-type AF and C-type AF states for each $ab$-plane lattice constant and each doping $x$, we can construct the surface phase diagram.

III. RESULTS AND DISCUSSION

We show the calculated surface phase diagrams in Fig. 1 compared with the bulk phase diagram which was obtained in our previous calculations. The surface phase diagrams for the (La, Sr)O and MnO$_2$ terminations are indicated by the red and green lines respectively. Clearly for the MnO$_2$ termination, the surface phases are dominated by the C-type AF state.
for a wide range of doping $x$ and $c/a$ ratio, except a tiny FM region in the very small $c/a$ ratio and low doping case. On the other hand for the (La, Sr)O termination, the surface shows rich phases similar to the bulk case but with a significant shift. Compared with the bulk phase diagram (indicated by black lines and characters), the main change for the surfaces is the up- and downward shifts of the phase boundaries for (La, Sr)O and MnO$_2$ termination respectively. It should be noted that, since non-equivalent numbers of (La, Sr)O and MnO$_2$ layers are included in our unit cell, the effective doping $x_{\text{eff}}$ of the central MnO$_2$ layer is slightly different from the formula doping $x$. By calculating the number of $e_g$ electrons, we estimate that the $x_{\text{eff}}$ is smaller (larger) than $x$ by about 0.04 (0.05) for (La, Sr)O (MnO$_2$) termination. For the sampling point ($x = 0.5$ and $c/a = 1.0$, indicated by the blue star in Fig. 1), the calculated total energies and some physical parameters are summarized in Tables I and II. It should be also noted here that the presence of interfaces between the surface and bulk regions may modify our calculated phase diagram slightly. If the penetration of the perturbation in the magnetic state on surface is deeper than half of the slab thickness, the surface phase diagram may depend on the slab thickness. In order to check these effects, we performed calculations in which the spin structures of the central MnO$_2$ layer are constrained to be the bulk ones. We found that the spin structures in the first two surface layers (of both sides of the slabs) are little affected by the constraint in the central layer. We should also point out that the possible non-collinear magnetic configurations are not taken into account in the present calculation. However, even if we confine ourselves to collinear spin configurations, we can still gain important valuable insights into the basic trend in surface magnetic states by our calculated phase diagram.

The occupation imbalance between two $e_g$ orbitals, namely $3z^2 - r^2$ and $x^2 - y^2$ orbitals in doped manganites, is the key concept to understand the rich phase diagrams. On the surfaces, the orbital polarization is certainly very important because of the change in crystal field, hybridization and surface lattice relaxation. For the (La, Sr)O termination, the environment of the 2nd surface Mn changes only from the 2nd nearest neighbor layer, which is negatively charged MnO$_2$ layer. Missing of this layer in the vacuum side produces
an attractive potential leading to downward shift of the 2nd surface Mn 3d bands. However, the strengthened $pd\sigma$ hybridization due to the missing Mn atom on top of the surface O atom will cause the upward shift of the $3z^2 - r^2$ state compared with the $x^2 - y^2$ state. Although the surface relaxation in the interlayer distance, which is very small, will modify the details quantitatively, it will not affect the qualitative features. For the sampling structure in Fig. 1, the Mn-O bond length between the 1st and 2nd layers changes only by $-0.2\%$ (see Table II). For the MnO$_2$ termination, the most dramatic effect is the significant downward shift of the $3z^2 - r^2$ state due to the reduction in $pd\sigma$ hybridization caused by the missing ontop oxygen. For other orbitals, missing of the positively charged (La, Sr)O layer produces repulsive potential. In this case, the surface relaxation is very large because of the loss of ligand oxygen atoms. However, the atoms are relaxed in such a way that the topmost Mn-O bond length along surface normal direction is elongated to further push down the $3z^2 - r^2$ orbital. Therefore the net effect of surface orbital polarization is that the occupation of the $x^2 - y^2$ ($3z^2 - r^2$) orbital is enhanced for (La, Sr)O (MnO$_2$) termination. The orbital population ratio $n_{3z^2-r^2}/n_{x^2-y^2}$ for the sampling structures in Fig. 1 are estimated as 0.74 and 2.16 for the surface Mn sites of (La, Sr)O and MnO$_2$ terminations respectively. The surface orbital polarization of MnO$_2$ termination is much stronger than that of (La, Sr)O termination. Figure 2 shows the charge distributions (from the Fermi level to 0.8 eV below) for two different terminations of the sampling point. The surface orbital polarizations are clearly seen in each case.

The change in occupation will change the competition between the double exchange (DE) and the superexchange (SE). For the less than half-filled majority-spin $e_g$ bands, the more (less) populated are the orbitals, the stronger (weaker) are the DE interactions among these orbitals. Therefore, the region of the A-type (C-type) AF state becomes wider for the (La, Sr)O (MnO$_2$) termination because of higher population of the $x^2 - y^2$ ($3z^2 - r^2$) orbital. A. Filippetti and W. E. Pickett studied the magnetic properties of MnO$_2$ terminated (001) surface of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) with particular doping $x$ ($=0.5$). Their observation of the stability of the FM state is due to the use of the (1x1) surface unit cell. Our calculations
for LSMO with the same doping \((x = 0.5, c/a = 1.0)\) give the same order of total energy difference between the surface FM and A-type AF states (Table I). However, the surface C-type AF state has much lower energy compared with the above two states.

On the real surfaces of CMR manganites, the surface segregation on the perovskite A-sites may be another important factor. It was experimentally suggested that the Ca content in the surface layers of LCMO is dramatically enhanced\(^\text{13}\) for both terminations. The basic questions here are: 1) why does surface segregation happen? 2) how will it affect our phase diagram? In the analysis of surface segregation, we need the bulk part as a particle reservoir. The present type slab calculation has, therefore, rather severe restriction in this context. In the following, we will do a simple analysis in order to gain insight into the fundamental aspects of the problem. We artificially locate a pure SrO layer at different positions in our unit cell keeping the Sr content \(x\) in all other (La, Sr)O layers as a given value and calculate the total energy as a function of the SrO layer position. The calculated results shown in Fig. 3 clearly suggest that the stable position of the SrO layer is the surface for the (La, Sr)O termination or the 2nd surface for the MnO\(_2\) termination. The result is qualitatively consistent with the experimental observation for LCMO\(^\text{13}\). The main reason for the stability of the surface (or subsurface) SrO layer is the electrostatic interaction. SrO layer is nominally charge neutral, while the nominal charge of LaO is +1. In the bulk the ionized object is stabilized by the electrostatic interaction with the counter ions. This stability mechanism is weakened on the surface. Therefore, the neutral object tends to be located on the surface keeping the charged objects inside the bulk. For the MnO\(_2\) termination, the presence of SrO layer at the 2nd surface will make the surface MnO\(_2\) layer nearly neutral also. In Fig. 3(b), we show that the contribution coming from the electrostatic energy is responsible to the stability of the SrO layer at the surface. As the nominal doping \(x\) increases, the effect of Sr segregation should be weakened as is actually demonstrated in Fig. 3. Although the present analysis is only for limited configurations in which one particular layer of the system has full Sr segregation. Nevertheless, the above consideration about the mechanism of the stability of surface SrO layer clearly suggests a rather general tendency of surface segregation of the
neutral objects. By taking account of the surface segregation of Sr, the effective doping on the surface becomes larger than the bulk doping. This will again lead to stronger stability of surface AF ordering.

IV. SUMMARY

In summary, we calculated the surface magnetic phase diagram of tetragonal manganite LSMO as functions of hole doping $x$ and the bulk tetragonal distortion $c/a$. The (001) surfaces of tetragonal manganites show clear tendency towards A-type and C-type AF states for (La, Sr)O and MnO$_2$ terminations respectively though the surface A-type AF state may be hard to distinguish experimentally from the surface FM state. The basic physics governing the phase diagram is explained in terms of the orbital polarization induced by surface effects. Strong surface segregation of Sr atoms is caused by the electrostatic interaction and further favors the tendency to surface antiferromagnetism.

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FIG. 1. The calculated phase diagrams of La$_{1-x}$Sr$_x$MnO$_3$ in a plane of hole doping $x$ and $c/a$ ratio. Here the $c/a$ ratio can be defined by the $ab$-plane lattice constant as the bulk volume is given for each doping $x$. The red and green colors correspond to the surface phase diagrams for the (La, Sr)O and the MnO$_2$ terminations respectively, while the black color corresponds to the bulk phase diagram. The denotations F, A, C and G mean FM, A-type AF, C-type AF and G-type AF states respectively.
FIG. 2. The occupied (0.8 eV below the Fermi level) electronic charge distributions for the two terminations corresponding to the sampling point in Fig. 1. Red color denotes high charge density. Between two neighboring Mn sites, there is small charge density from oxygen sites. The spin configurations of Mn sites are indicated by the red arrows.
FIG. 3. The calculated total energies as a function of SrO layer position keeping the Sr content $x$ in all other (La, Sr)O layers as a given value. The zero in the numbering of layers corresponds to the center of our unit cell, while MnO$_2$ layers are located on even number of layers.
TABLES

TABLE I. The calculated total energies, per surface (1x1) cell, for the sampling point (x = 0.5, c/a = 1.0) in Fig. 1.

|                  | Surface F | Surface A | Surface C |
|------------------|-----------|-----------|-----------|
| (La,Sr)O termination | 22 meV    | 0 meV     | 61 meV    |
| MnO$_2$ termination | 124 meV   | 203 meV   | 0 meV     |

TABLE II. Some calculated parameters corresponding to the sampling point in Fig. 1 for the two terminations. $\Delta d_{\text{Mn-O}}$ means the change of the topmost Mn-O bond length along surface normal; $M_c$ and $M_s$ denote the magnetic moments of Mn sites at the central and the surface layers respectively; $n_{3z^2-r^2}/n_{x^2-y^2}$ defines the ratio of occupation numbers for two $e_g$ orbitals of surface Mn.

|                  | $\Delta d_{\text{Mn-O}}$ | $M_c$  | $M_s$  | $n_{3z^2-r^2}/n_{x^2-y^2}$ |
|------------------|--------------------------|--------|--------|----------------------------|
| (La,Sr)O A-AF    | -0.2%                    | 3.11   | 3.12   | 0.74                       |
| MnO$_2$ C-AF     | +2.7%                    | 2.87   | 3.17   | 2.16                       |