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Electronic-structure modifications induced by surface segregation in $La_{0.65}Pb_{0.35}MnO_3$ thin films

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PACS. 73.20.-r – Electron states at surfaces and interfaces.
PACS. 68.35.Fx – Diffusion; interface formation.
PACS. 75.25.+z – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-ray scattering, etc.).

Abstract. – Using spin-polarized inverse photoemission and X-ray absorption spectroscopy techniques, we show that the electronic structure of $La_{0.65}Pb_{0.35}MnO_3$ thin films depends on the composition at the surface. With a gentle annealing procedure, the surface provides a maximum of 80% spin asymmetry at 0.5 eV above the Fermi level in spite of extensive Pb segregation. A heavily annealed (restructured) surface exhibits a reduced surface "ordering" temperature of 240 K (compared to the approximately 335 K bulk value) as well as a reduced spin asymmetry value of 40% at 0.5 eV above Fermi energy.

Recently, there has been a surge of interest in transition metal oxides due to their unique physical properties, *e.g.*, colossal magnetoresistance (CMR) [1,2] and extremely high degree of spin polarization [3,4]. Band structure calculations of $La_{0.65}Sr_{0.35}MnO_3$ —a material almost identical in electronic and structural properties with $La_{0.65}Pb_{0.35}MnO_3$— predict that this system is very close to being half-metallic [5,6]. Several recent studies focused on determining the spin-polarization, in doped lanthanum perovskites, using mainly spin-polarized tunneling measurements [3,4,7]. Proof of 100% polarization is still sadly absent in manganese oxides [8], in spite of one claim of 100% polarization [9].

There are theoretical problems with abstracting the correct spin polarization in transport measurements [10], and there is, so far, no evidence that the resistance of the spin-down channel goes to infinity for $D_{\downarrow}(E_F) = 0$. Proof of half-metallicity through spin-asymmetry in angle-resolved photoemission and inverse photoemmision is complicated by the surface sensitivity of these two techniques as composition or electronic structure are often modified in the surface region. In addition, electron spectroscopies must sample the density of states

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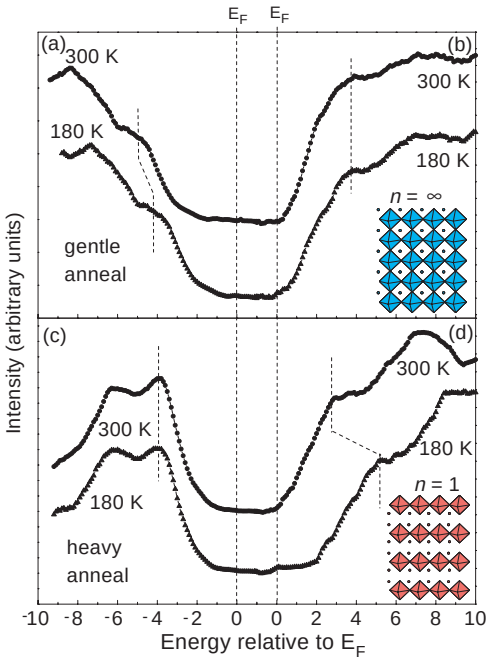

Fig. 1 – Valence band spectra ((a) and (c)) and conduction band spectra ((b) and (d)) at 300 K and 180 K, for the gently annealed surface ((a) and (b)) and for the heavily annealed (restructured) surface ((c) and (d)) of $La_{0.65}Pb_{0.35}MnO_3$. The insets in panels (b) and (d) show the schematic layer sequence structure of the gently and heavily annealed surfaces, correspondingly.

at wave vectors near the Fermi level crossings, not just one $\boldsymbol{k}$-point, to provide conclusive proof. Here we illustrate the importance of the surface and near-surface region in the study, primarily, of the unoccupied band structure of a CMR perovskite material.

The $La_{0.65}Pb_{0.35}MnO_3$ thin films (1000 Å in thickness) were grown on (100) $LaAlO_3$ substrates by rf sputtering [11]. The films are highly oriented along the substrate normal and single phase, with a very small mosaic spread. Detailed studies of the surface composition in ref. [12] show that gentle annealing (up to 250 °C) of the sample induces a large amount of Pb segregation to the surface, while a heavy anneal at higher temperatures (250 °C) completely changes the surface and selvedge structure and results in Pb evaporation. We first annealed the samples up to 250 °C in an oxygen atmosphere of 1×10^{-6} torr for 10–15 hours. A clear four-fold symmetric low-energy electron diffraction (LEED) pattern, together with a negligible amount of C (less than 3% of a monolayer) monitored using X-ray photoemission (XPS), were taken as good indicators of a clean surface, with a high degree of crystallinity across the entire area of the sample. After careful analysis of this "gently annealed" surface, the sample was further annealed in vacuum at 250 °C for 10–15 hours. The heavily annealed surface goes through a restructuring transition characterized by the formation of a Ruddlesden-Popper $(La_{1-x}Pb_x)_2MnO_4$ phase with a possibly embedded MnO columnar phase. These measurements have been repeated on a number of different samples. The schematic representations of the surface region layer stacking sequences of the two surfaces are presented as insets in fig. 1.

The occupied valence bands are due mostly to hybrid MnO states in photoemission studies of $La_{0.65}D_{0.35}MnO_3$ (D = hole dopant) perovskites [13], but some modifications, induced by

surface restructuring and segregation, are evident near the Fermi level. The valence band spectra (fig. 1(a) and (c) for the gently and heavily annealed $La_{0.65}Pb_{0.35}MnO_3$ surfaces, respectively) are dominated by features at 3–5 eV and ~ 6 eV below the Fermi level. The first feature is generally ascribed to the Mn $3d$-$t_{2g\uparrow}$ states while the latter has more O $2p$ weight [14, 15]. Although very low, the emission intensity between the Fermi level and approximately 2 eV binding energy is generally attributed [13–15] to the occupied $e_{g\uparrow}$ electronic band. For the restructured surface (formed after heavy annealing), we find that at the spectral feature at about 4 eV the binding energy decreases in intensity compared to the same band corresponding to the gently annealed surface. Such spectral weight transfer is related to the increase in hole doping levels of the surface region [14, 15]. The experimental valence band structure obtained from the gently annealed surface (fig. 1(a)) corresponds to a high Pb doping level, while the restructured surface (fig. 1(c)) displays a valence band indicative of low Pb content, consistent with the Pb concentration profiles found for the surface region of gently and heavily annealed thin films of $La_{0.65}Pb_{0.35}MnO_3$ [12].

The effect of different surface compositions can also be seen in the unoccupied electronic band structure of the surface probed by inverse photoemission spectra on gently and heavily annealed surfaces, as seen in fig. 1(b) and (d). The Mn $3d$-O $2p$ nonbonding or antibonding-like states [16, 17] are centered around 3.6 eV above E_F for $La_{0.65}Pb_{0.35}MnO_3$ gently annealed surfaces. In the case of the $La_{0.65}Pb_{0.35}MnO_3$ surface, formed after heavy annealing, the unoccupied peak corresponding to La $5d$ states is enhanced, while the Mn $3d$-O $2p$ shoulder moves towards the Fermi level (to 2.4 eV) at 300 K, as shown in fig. 1(d). These changes are again consistent with Pb depletion of the surface region and formation of a Ruddlesden-Popper (or $n = 2$ layered perovskite) surface phase in the well-annealed sample, as demonstrated in [12]. A similar surface was obtained for $La_{0.84}Sr_{0.16}MnO_3$ [16, 17].

The unoccupied bands of $La_{0.65}Pb_{0.35}MnO_3$ were explored further using X-ray absorption spectroscopy (XAS). Once the core level binding energy has been taken into account for the O $1s$ (or Mn $2p$) core level, the XAS and inverse photoemission spectra can be roughly compared, as shown in refs. [18, 19], though there is an expected energy shift from the perturbation caused by the photo-excited core hole in XAS. In both inverse-photoemission and XAS, the joint density of states just above E_F is largely $e_{g\uparrow}$ (at 531 eV in O $1s$ XAS) plus $t_{2g\downarrow}$ (at 532 eV in O $1s$ XAS) in origin, while the enhanced shoulder at 3 eV above E_F (534 eV in O $1s$ XAS) has an $e_{g\downarrow}$ provenance and originates from the nonbonding or antibonding-like states with Mn $3d$-O $2p$ hybridized character. The feature at 6.5 eV above E_F corresponds to the La(Pb) $5d$-O $2p$ states (at 538 eV in O $1s$ XAS). This is summarized in fig. 2 ($\uparrow$ and $\downarrow$ describing majority and minority spin), consistent with previous assignments of the inverse photoemission [16, 17, 20] and XAS [21] features for the manganese perovskites. A clear distinction between the majority e_g and minority t_{2g} bands, in the XAS spectra, requires enhanced resolution, as suggested by the spin-polarized inverse photoemission (fig. 2(a)). The spin-integrated inverse spectra in figs. 1 and 2 are generally similar to other CMR-manganite materials where the Mn $3d$-O $2p$ antibonding-like states are positioned at approximately 2 eV above the Fermi level for both $La_{0.65}Ca_{0.35}MnO_3$ and $La_{0.65}Ba_{0.35}MnO_3$, and at about 4 eV above Fermi level for the $La_{0.65}Sr_{0.35}MnO_3$ [20], but the similarity of the unoccupied inverse photoemission spectra for all doped manganites argues in favor of the model proposed by Taguchi and Shimada [22], that the bonding is generally covalent, for moderately doped manganite species.

The comparison between spin-polarized inverse-photoemission and X-ray absorption (fig. 2(a), (b), (d), (e)) of the unoccupied density of states for the gently and heavily annealed surfaces reveals (even more clearly than in fig. 1) that the $e_{g\downarrow}$ minority band is enhanced in case of the Ruddlesden-Popper restructured surface (the heavily annealed surface of $La_{0.65}Pb_{0.35}MnO_3$), relative to the surface with the $n = \infty$ layered perovskite structure.

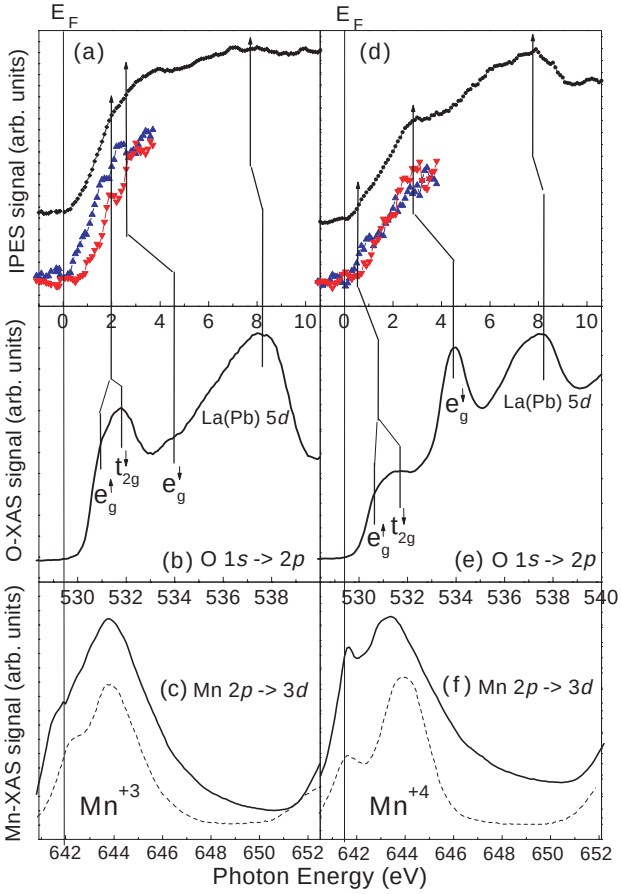

Fig. 2 – Inverse photoemission spectra ((a) and (d)) at normal incidence and X-ray absorption thresholds of oxygen ((b) and (e)) and manganese ((c) and (f)), acquired at 300 K, on a gently annealed LPMO surface ((a), (b), (c)), as well as on a heavily annealed (restructured) surface ((d), (e), (f)). The dotted lines in panels (c) and (f) are reproduced after ref. [21] and they represent the theoretically obtained spectra for (c) Mn^{+3} and (f) Mn^{+4}, respectively.

The spin-polarized unoccupied bands also differ for the gently and heavily annealed surfaces as shown in fig. 2 ((a) and (d)), as is evident in the spin-polarized inverse photoemission spectra. The spin asymmetry of the gently annealed surface reaches 80% above background, while the heavily annealed surface shows a maximum of 40% above background, at an energy of 0.5 eV above the Fermi level.

To identify the ground state of the Mn ion, we have compared our spectra in fig. 2(c) and (f) with the theoretical calculation performed by Abbate *et al.* in ref. [21]. The shape of the Mn spectrum in $LaMnO_3$ corresponds to a $3d^4$ ($t_{2g}^3 e_g^1$) ground state, while the Mn spectrum for the heavily Sr doped manganite $La_{0.1}Sr_{0.9}MnO_3$ has a $3d^3(t_{2g}^3)$ ground state, as shown in ref. [21]. The change of shape, specifically the development of a second peak in the low-energy part of the L_3 and L_2 edges, is caused by holes (Sr^{2+}) induced by substitution in the $La_{1-x}Sr_xMnO_3$ compound. On this basis, we suggest that the ground state for the Mn ion in the surface region is more Mn^{3+} for a lightly annealed surface (corresponding to the

surface with high levels of Pb doping), while for the well-annealed sample (corresponding to the reconstructed surface with low Pb dopant) the Mn ion resembles more the Mn^{4+} one. The Mn spectrum characteristic of the heavily annealed surface is quite similar to the Mn $2p$ core level in MnO_2, with Mn^{4+} in an octahedral symmetry [23]. Similar results, showing double-peak structure in the Mn $2p$ spectrum, have been published in refs. [24,25]. Both Mn $2p$ and O $1s$ absorption spectra indicate that the heavily annealed restructured surface is dominated by a columnar MnO_2 phase, in combination with a perovskite tending more towards La_2MnO_4, in agreement with the STM and LEED measurements presented in ref. [12], and that Pb segregation cannot be the sole cause of the changes in the shape of the absorption spectra. It is quite probable that the XAS and MCD techniques are not strictly probes of the bulk, as the results differ considerably with surface preparation [26], but XAS does probe deeper in the bulk than IPES.

The temperature dependence of the valence band structure shows an approximate 0.8 eV binding energy shift in case of the gently annealed surface, while the restructured surface remains largely unchanged between 300 K and 180 K. For the lightly annealed sample, the presence of an energy shift towards the Fermi level indicates an increasingly more metallic state at low temperatures, consistent with the dramatic decrease in resistivity with decreasing temperature [11, 12, 18].

The temperature dependence of the unoccupied levels is quite pronounced for the restructured surface, in comparison with the lightly annealed surface. Figure 1(a) shows a slight shift towards the Fermi level as the temperature is lowered to 180 K, while fig. 1(d) presents a 2.5 eV energy shift of both bands at 180 K compared to the spectrum acquired at 300 K. In both Sr- [27] and Pb- (present work) doped perovskite structures, the dramatic decrease in density of states at E_F with a reduction of the temperature is one of many indicators that the surface becomes insulating at low temperatures. For this Pb-doped perovskite surface, the energy shift in fig. 1(d) also indicates the onset of the insulating character and, from spectra acquired at several temperatures, this phase transition occurs at 240 ± 20 K. This is similar in temperature to the surface insulating transition observed in $La_{0.65}Sr_{0.35}MnO_3$ surfaces [27]. The surface transition to insulating behavior is confirmed by the X-ray flux dependence of the O $1s$ core level binding energy. The shift towards higher binding energies, in XPS, for both perovkites also indicates the onset of the insulating character below 240 K. It is to be noted here that in case of the gently annealed surface, there was no evidence of a core level energy shift with temperature, regardless of the source power used. We infer that this gently annealed surface of $La_{0.65}Pb_{0.35}MnO_3$ does not go insulating at low temperatures, in the vicinity of 150 K to 400 K.

In order to extract magnetic information from our two types of surfaces, we have monitored the MCD signal from the Mn $2p$ core hole as a function of temperature. As can be seen in fig. 3 from the L_3 edge-integrated MCD signal, the Curie temperature remains close to the bulk value of 340 K for the gently annealed surface, while for the restructured surface the ordering temperature in MCD drops to approximately 240 K (close to the surface insulating phase transition temperature).

The shift in T_C observed in MCD may be caused by the tilting of the surface region MnO_6 octahedra, a structural distortion induced as the vacancy rate increases [28]. Another possibility that would explain the shift in T_C is the occurrence of a surface region reordering transition below 240 K, as expected for a double-layer structure [29]. The total magnetic moment, extracted from the SQUID measurements at a lowest temperature (5 K), is 10% reduced in absolute value in the heavily annealed (restructured) sample relative to the gently (as-deposited) thin film, suggesting that the restructured surface region is not ferromagnetic. The shape of the temperature dependence of the magnetic moment obtained from SQUID

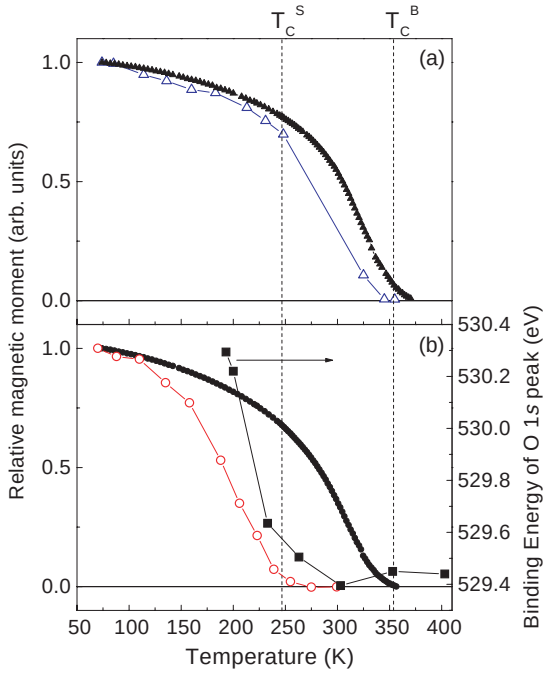

Fig. 3 – Relative magnetic moment obtained from SQUID measurements (filled symbols) and Mn-MCD (open symbols) for gently (a) and heavily (b) annealed surfaces. The binding energy of the oxygen 1*s* peak as a function of temperature is shown on the right axis for the restructured surface, in panel (b), and provides one of several indicators for the onset of insulating behavior in the surface with the Ruddlesden-Popper phase (heavily annealed surface).

is similar for the two types of samples, as is the temperature-dependent resistance, with no evidence of a reduced surface Curie temperature at 240 K. We conclude that the bulk (not surface region material) perovskite structure is preserved. Note that the in-plane temperature dependence of magnetization was measured in an applied external field of 1000 Oe, so the out-of-plane contribution of the magnetic moment cannot be detected.

In addition to the temperature-dependent relative moments derived from both MCD and SQUID, fig. 3(b) shows the temperature dependence of the O 1*s* photoemission core level for the restructured (heavily annealed) sample. This 240 K phase transition at the surface of the heavily annealed sample is not a simple ferromagnetic transition. The reduction of the magnetization of the sample where a surface Ruddlesden-Popper phase has been formed suggests that the surface region and phase transition at 240 K is not related to intrinsic ferromagnetic ordering by itself —the spin-polarization of 40% away from E_F in inverse photoemission may be induced by the original perovskite structure below. The phase transition at 240 K is not easily observed in bulk (SQUID) measurements or bulk resistivity measurements.

The results obtained here are of great importance not only in explaining the lower than expected polarization values found in the literature, but also because they underscore the importance of characterizing the interface in any effort to understand the properties of spin-electronics junctions. We present clear evidence that changes in surface composition greatly affect the electronic structure of the surface. Throughout this work, the photoemission, using a He I source (21.3 eV), and inverse photoemission spectra were undertaken at normal emission

or incidence, corresponding to the center of the surface Brillouin zone ($\bar{\Gamma}$). The surface Brillouin zone is the $\boldsymbol{k}$-point representative of long-range magnetic order in real-space, but is not a test of the half-metallic character by itself.

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