

## Unoccupied electron states of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

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### Abstract

We present a spin-resolved inverse photoemission study from  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$  thin films grown by pulsed laser deposition. The low temperature half-metallicity of such a material is evident in the empty electron density of states, as it results from the spin-resolved spectra taken at 100 K. © 2002 Elsevier Science B.V. All rights reserved.

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The field of 100% spin-polarized materials is a vital research area for spin electronics. In this sense manganites appear very promising systems, and in the particular case of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) a half-metallic behavior at low temperature has been observed by means of spin polarized photoemission spectroscopy (SPES) [1] and tunneling [2] experiments. Despite these encouraging results, the electronic structure of this oxide is still not well known. In particular there is no experimental confirmation of theoretical calculations for the unoccupied density of states which predict a gap for the minority states along with a delayed onset of the  $t_{2g}$  minority band. This point is critical to research underway on magnetic tunneling junctions, which incorporate a half-metallic electrode such as LSMO, to better understand the tunneling magneto resistance (TMR) effect and its bias dependence.

In this work we present an analysis of the electronic states of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  just above the Fermi level, performed by means of spin polarized inverse photoemission at different temperatures.

A 350 Å thick film of LSMO(001) was grown by pulsed laser deposition on a  $\text{SrTiO}_3(001)$  substrate in a multitarget LDM 32 Riber machine using a frequency tripled Nd:YAG laser (B.M. Industries 503 DNS) with a pulse length of 10 ns at a repetition rate from 1 to 5 Hz.

It delivers a laser beam at 355 nm wavelength with a power density from 50 to 300 MW/cm<sup>2</sup> depending on focussing the laser beam on the target. In this work, the growth parameters have been set in order to obtain a deposition rate of 0.22 nm/s at a repetition rate of 2.5 Hz and a substrate-target distance of 35 mm. The LSMO target, which is stoichiometric with a density higher than 0.9 of the theoretical one, is continuously moved to ensure a uniform ablation rate. Before the growth, the  $\text{SrTiO}_3$  substrates are cleaned by heating in pure oxygen up to 800°C for 10 min at a pressure of 45 Pa. After this procedure, cleanliness and flatness of the surface are verified by reflection high-energy electron diffraction before starting the growth procedure. The growth temperature is around 700°C as measured at the surface of the substrate holder. The growth is carried out under a pressure of 45 Pa of research graded oxygen, and the sample is then cooled to room temperature within 45 min including an intermediate temperature plateau at 400°C for 15 min under  $4 \times 10^4$  Pa of oxygen.

The sample, once removed from the growth chamber, was exposed to atmosphere and introduced in the machine for spin polarized inverse photoemission (SPIPE) [3]. No system bake-out was carried out in order to reduce further sample contamination. The base pressure during measurements was below  $2 \times 10^{-10}$  Torr. Experimentally, a major problem when performing electron spectroscopies on complex oxides is that any cleaning procedure, such as ion sputtering or heating in the presence of reactive gases,

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can significantly alter the surface chemical composition. As a consequence the surface of samples prepared ex situ often exhibits contamination and the electron spectroscopy data are difficult to interpret, due to the high surface sensitivity of such techniques.

In the following we present two sets of data taken on the same sample in different conditions: (i) as received, i.e. without any treatment after insertion in vacuum, (ii) after a procedure aiming to remove any surface contaminants arising from exposure to atmosphere. The film was magnetized in remanence by means of a pulsed field of amplitude 1500 Oe.

Just after the insertion in the SPIPE system, the X-ray photoemission spectroscopy (XPS) spectra revealed the presence of some carbon and an excess of oxygen that can be attributed to the presence of a disordered CO overlayer, as confirmed by the absence of a detectable low energy electron diffraction (LEED) pattern. The presence of such a contamination does not seem to be so critical for the present SPIPE study, since we succeeded in detecting a clear spin polarization at the Fermi level ( $E_F$ ). In Fig. 1 we present normal incidence SPIPE results referring to this surface, taken at different temperatures. LSMO is a ferromagnet with a Curie temperature ( $T_C$ ) around 350 K; however, on the basis of the small value of the surface magnetization at 300 K [1,4], we consider the spectra taken at this temperature as representative of the paramagnetic insulating behavior above  $T_C$ . The spin integrated spectrum taken at  $T = 300$  K (see inset), displays two structures, B and C, barely emerging from the background, without angular dependence. This fact, in connection with the absence of a LEED pattern, suggests the possibility of interpreting the data in terms of the unoccupied density of states. The overall lineshape does not change upon cooling the sample down to 100 K. However a temperature-dependent change occurs near  $E_F$ , as seen in Fig. 1. At 300 K (bottom curve) there is no trace of spin polarization: the delayed onset of the spectrum, with respect to  $E_F$ , clearly indicates the insulating behavior of the LSMO film at room temperature. On the other hand, at low temperature the film becomes metallic and two distinct line-shapes for the majority-(full dots) and minority-spin channels (open dots) are visible. Here the spin-resolved spectra have been rescaled by means of a standard procedure to take into account the incomplete polarization of the incident electron beam [3]. Despite the sizeable data scattering in these spectra, due to the very low counting rate close to  $E_F$  and to the effect of the rescaling procedure, the signal-to-noise ratio is good enough to confirm the half-metallicity of LSMO, which has been already demonstrated by SPPEs [1]. By taking into account the energy resolution of our apparatus ( $\sim 700$  meV), the majority-spin onset is found at  $\sim 200$  meV below  $E_F$ , while the minority-spin one is definitely above  $E_F$ . On the basis of theoretical

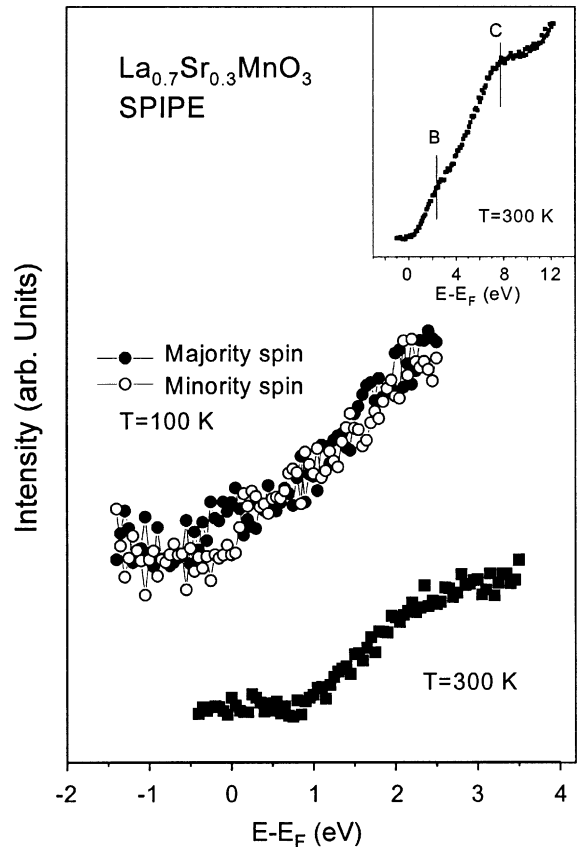


Fig. 1. Inverse photoemission spectra from as received  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ : data taken at 300 K (squares) and spin resolved data taken at 100 K (dots). Inset: data taken at 300 K in a wider energy range.

expectations the onset of the minority spin channel can be related to the  $t_{2g}$  minority states which we found to be centered at  $\sim 0.3$  eV above  $E_F$ . This is also in fair agreement with the TMR bias dependence of LSMO-based tunnel junctions, which displays a strong decrease in the case of transport towards the unoccupied state of LSMO near  $E_F$  [5].

Next, in order to clean the sample surface we performed many cycles of exposure to 100 L of  $\text{O}_2$  ( $1 \text{ L} = 1 \times 10^{-6}$  Torr s) and subsequent flash-heating up to 850 K, while monitoring the surface chemical composition by XPS. As a result we obtained a clean surface with no trace of carbon and the proper oxygen concentration, together with the appearance of a well-resolved square LEED pattern compatible with the cubic structure of LSMO. However, it is worth noting that a change in the oxygen concentration of a few percent, i.e. below the XPS sensitivity, can significantly alter the magnetic properties of manganites [6]. Thus, it is possible that the results obtained after cleaning are affected by a slight surface oxygen deficiency.

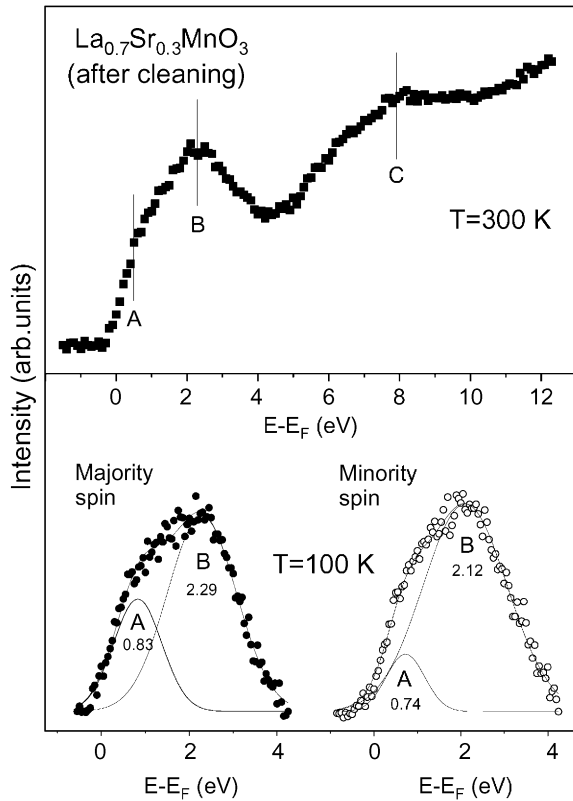


Fig. 2. Inverse photoemission spectra from  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  after cleaning. Top: data taken at 300 K. Bottom: spin resolved data taken at 100 K after a linear background subtraction in the region of A and B peaks, along with spectral decomposition resulting from a Gaussian fit.

In Fig. 2 we present normal incidence SPIPE spectra from  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$  after cleaning. At 300 K we did not find any spin polarization and in the top panel we plot the spin-integrated spectrum. The overall lineshape is quite similar to that of the spectrum before cleaning, except for the large intensity increase of structures B and C and the appearance of a shoulder A at lower energy. In the bottom of Fig. 2 we present SPIPE spectra taken at 100 K close to  $E_F$  after a linear background subtraction, along with a spectral decomposition which gives the peak positions for the two spin channels. We find a splitting of 100 meV for A and 170 meV for B, respectively, reflecting the ferromagnetic behavior of the film at low temperature. On the other hand it is quite difficult to unambiguously detect a spin polarization at  $E_F$ . At variance with the findings for the sample before cleaning, the presence of the two

prominent structures A and B prevents us from accurately investigating the onset behavior. Furthermore, after the cleaning procedure a LEED pattern is clearly visible, indicating a well ordered structure. In such a case, since we are working with angular resolution,  $\mathbf{k}$ -parallel conservation has to be considered and the spectra must be interpreted in terms of transitions between unoccupied bands. This is confirmed by the angular dispersion of the structures observed in the SPIPE spectra (not shown). Moreover in this case we do not observe any variation in the spectra onset when going from 300 to 100 K, at variance with expectations based on the insulator–metal transition accompanying the evolution towards the ferromagnetic state. This is due to the fact that the spectra of Fig. 2 do not reflect the density of states, but the band structure above  $E_F$  along the  $\Gamma X$  direction. In this sense the two features A and B correspond to transitions towards final states at 0.8 and 2.2 eV above  $E_F$ , respectively, in fair agreement with the band structure calculation of Livesay et al. [7].

In conclusion, the present study confirms the low temperature half-metallic behavior of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . The transition from the paramagnetic room-temperature insulator state to the low-temperature half-metallic one shows up in the onset of the unoccupied density of states, with a delayed onset of  $\sim 0.3$  eV for minority-spin electrons at low temperature. Surprisingly enough, this observation is prevented when a clean and well ordered surface is studied, due to the appearance of strong features at slightly higher energies and possibly to some surface oxygen deficiency.

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