Polarization-dependent angle-resolved photoemission spectroscopy study of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ M. C. Falub,^{1,*} M. Shi,^{1,†} P. R. Willmott,¹ J. Krempasky,¹ S. G. Chiuzbaian,¹ K. Hricovini,² and L. Patthey¹¹Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland²Laboratoire de Physique des Matériaux et des Surfaces, Université de Cergy-Pontoise, 95011 Neuville, France

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We present angle-resolved photoemission spectroscopy results on thin films of the three-dimensional manganite perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, with $T_c=240$ K. In the low-binding energy region, we found two energy bands, one dispersing along the (100) sample surface and the other along the surface normal. Through a detailed polarization-dependent analysis, we have determined the symmetries of the two bands. The initial states associated with the band that disperses along the surface are dominantly odd with respect to the (110) mirror plane and even with respect to the (010) mirror plane. Based on this investigation, we have derived the expression of the spatial term for the wave functions describing these low-energy states.

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I. INTRODUCTION

The discovery of the colossal magnetoresistance effect in manganite perovskites has stimulated considerable interest in their electronic and magnetic properties.^{1,2} The system $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) has a very rich phase diagram.^{3,4} The parent compound LaMnO_3 is an antiferromagnetic insulator that becomes, upon Sr doping, a ferromagnetic metal. An external magnetic field greatly reduces the resistivity near the transition temperature (T_c), an effect known as colossal magnetoresistance (CMR). The ferromagnetic phase was explained in the double-exchange (DE) model⁵ by taking into account the combined effect of the e_g electrons hopping between the nearest-neighbor sites and the strong Hund's exchange with the localized t_{2g} electron spins. Later, it was shown that one has to consider the electron-phonon interaction in order to explain the high resistivity above T_c or the large drop in resistivity just below T_c .⁶

For a complete understanding of the rich physics of the manganites, it is of great importance to study their electronic structure, particularly the low binding energy states and their associated wave functions, which are used to determine important physical quantities. Angular-resolved photoelectron spectroscopy (ARPES) is a unique surface-sensitive spectroscopic tool capable of revealing the $\mathbf{k}$ -resolved electronic structure.^{7,8} So far, the main difficulty encountered in using ARPES to study the three-dimensional (3D) manganites has been the preparation of smooth surfaces at an atomic level, because of the lack of a natural cleavage plane. At the Swiss Light Source, it has been possible to grow high-quality epitaxial thin films of LSMO with submonolayer roughness and investigate their $\mathbf{k}$ dependent electronic structure by *in situ* ARPES.⁹

Here we report an *in situ* ARPES study of thin films with $T_c=240$ K, close to the lowest transition temperature from the paramagnetic to ferromagnetic metallic phase.^{3,4} Whereas a vanishing or very small spectral weight at the Fermi level (E_F) was reported for the similar layered (2D) manganites,^{10,11} a finite step at E_F was observed for the 3D manganites.

Compared to our earlier ARPES results on LSMO films with high transition temperatures ($T_c=313$ K),⁹ we show

here that a similar sharp step at E_F appears only in the vicinity of the (001) axis in normal or near-normal emission. On the other hand, the dispersive band along the sample surface always lies below E_F . We have varied the matrix elements by changing the polarization of the incoming light. In this manner, we have determined the symmetries of the two energy bands with respect to the reflections in different mirror planes and derived the spatial term of the corresponding wave functions.

II. EXPERIMENT

LSMO samples were obtained by growing *in situ* 130-nm-thick films heteroepitaxially on $\text{SrTiO}_3(001)$ substrates by pulsed laser deposition.^{12,13} The surface roughness was checked by *in situ* reflection high-energy electron-diffraction patterns and Kiessig fringes in *ex situ* x-ray reflectivity curves and found to be less than one monolayer. No surface reconstruction was observed, the low-energy electron-diffraction analysis indicating a clear (1×1) pattern. The sample used in this study has $T_c=240$ K, which is close to the lowest transition temperature from paramagnetic (PM) to ferromagnetic (FM) states in this system.

ARPES measurements were performed at the Surface and Interface Spectroscopy (SIS) beamline at the Swiss Light Source.^{14,15} During measurements, the base pressure always remained below 1×10^{-10} mbar. The ARPES spectra were recorded with a Gammadata Scienta 2002 analyzer. The energy resolution was relaxed to 40 meV to obtain a high photon flux. All measurements were performed at 20 K.

In our experimental setup the propagation vector of the incident light, the surface normal to the sample, and the direction of the outgoing photoelectrons lie in the same horizontal plane (HP). The vector potential ($\mathbf{A}$) of the light with linear vertical (LV) polarization is perpendicular to HP, while it lies in HP and is 45° to the surface normal in the case of linear horizontal polarization (LH). The (010) and (110) mirror planes can be brought into HP by rotating the sample about the surface normal. The polar angles (between the surface normal and the direction of the outgoing photoelectrons) were in the range of $-5^\circ < \theta < 12^\circ$.

FIG. 1. (Color) (a) and (b) ARPES intensity maps at 20 K with photons energy $E_{ph}=101$ eV; the corresponding paths in the Brillouin zone are indicated in (d). (c) EDCs taken at $E_{ph}=33$ eV (blue), 38 eV (red), and 43 eV (green) with corresponding $\mathbf{k}$ points indicated by filled circles in (d).

To determine $k_{\perp}$, which is not conserved across the sample surface, several specific experimental methods¹⁶ have been developed for absolute three-dimensional band mapping. In ARPES experiments one can calculate the value of $k_{\perp}$ by assuming the nearly free-electron description for the Bloch states and determine the inner potential V_o from the observed periodicity of the dispersion $E(k_{\perp})$.¹⁷ We used the reduced zone scheme to indicate the wave vectors ($\mathbf{k}$) in reciprocal space. To determine paths or $\mathbf{k}$ points in reciprocal space, we used $(V_o - \varphi) = 10.16$ eV, where φ is the work function.⁹

III. RESULTS

Figures 1(a) and 1(b) show the ARPES spectral intensity as a function of the wave vector ($\mathbf{k}$) and binding energy (E_b) obtained in the (110) and (010) mirror planes, respectively. The corresponding paths in $\mathbf{k}$ space are indicated in Fig. 1(d). As the sample was rotated between these two planes (and using the appropriate polarization of the incoming light), the dispersion could be seen to monotonically evolve from Fig. 1(a) to Fig. 1(b). This indicates that these dispersions belong to the same energy band. Except for a shift to higher binding energy, this energy band has a similar width and dispersive feature as the one observed in a LSMO sample with higher $T_c=313$ K.⁹ When we follow a path parallel to the (001) direction (surface normal) with a fixed $\mathbf{k}$ component along the sample surface, the ARPES peak does disperse along the surface normal, as similarly found for LSMO films with higher T_c [Fig. 2c in Ref. 9]. This indicates that the ARPES peaks shown in Figs. 1(a) and 1(b) originate

FIG. 2. ARPES spectra taken with $E_{ph}=101$ eV at 20 K with linear vertical (LV) and linear horizontal (LH) light, respectively. The spectra in (a) and (b) correspond to paths in the Brillouin zone varying from $\mathbf{k}=(0.14,0.14,0.7)\pi/a$ to $\mathbf{k}=(0.76,0.76,0.7)\pi/a$ (top to bottom), as marked in (d) (top). Similarly, in (e) and (f), the top spectrum corresponds to $\mathbf{k}=(0.2,0,0.7)\pi/a$ and the bottom spectrum to $\mathbf{k}=(1.08,0,0.7)\pi/a$, respectively, as shown in (d) (bottom). The EDCs shown in (c) and (g) were measured at $\mathbf{k}=(0.5,0.5,0.7)\pi/a$ and $\mathbf{k}=(0.7,0,0.7)\pi/a$.

from the bulk. The dispersion in the direction of surface normal is much weaker than that along the sample surface, giving this band a 2D-like character.¹⁸

Figure 1(c) shows that when the wave vector approaches the $\mathbf{k}$ point $(0, 0, 0.4\pi/a)$ from both sides along the (001) direction, the step at E_F becomes sharper. As for LSMO samples with $T_c=313$ K,⁹ we observed a similar trend for any path parallel to (001) with $|k_{\parallel}|=(k_x^2+k_y^2)^{1/2} < 0.4\pi/a$. It should be noted that we found a nonvanishing intensity at E_F only in the vicinity of $k_z=0.4\pi/a$ and $|k_{\parallel}| < 0.4\pi/a$, where the other band disperses to higher binding energies. The finite spectral weight at E_F might explain why the 3D manganites have a much higher T_c than the layered manganites, for which only vanishing or very small spectral weights at E_F were reported.^{10,11}

The dispersive ARPES features strongly depend on the polarization of the photon beams. In the (110) mirror plane a clear peak disperses along a path parallel to the surface when using the LV light [Fig. 2(a)]. However, when we used LH light, there is only a little residual intensity of the dispersive peak on a sloped background [Fig. 2(b)]. Figure 2(c) shows the comparison of the energy distribution curves (EDCs) taken at $\mathbf{k}=(0.5,0.5,0.7)\pi/a$ with LV and LH lights, respectively. An opposite behavior was found for the spectra taken in the (010) mirror plane [Figs. 2(e) and 2(f)]. Here we observed a clear dispersive feature in the case of LH light, but none when using LV light. A comparison of the EDCs taken at $\mathbf{k}=(0.7,0,0.7)\pi/a$ with LV and LH lights is presented in Fig. 2(g).

The photoemission spectral weight is proportional to the square of the matrix element $M_{if} = \langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle$, where $|i\rangle$ and $|f\rangle$ are the initial and final states, and $\mathbf{p}$ is the momentum operator. In our experimental configuration, $\mathbf{A}$ is odd (even) with respect to HP for LV (LH) light. If HP is a mirror plane of the sample, then the final states in the photoemission process must be even with respect to the reflection in the same mirror plane. Thus to have nonzero matrix elements the symmetry of $\mathbf{A}$ and that of the initial state $|i\rangle$ must be the same.^{19,20} Namely, $|i\rangle$ must be odd with respect to the mirror plane for LV light, and even for LH light. Although it is difficult to determine whether there are some residual dispersive features in Figs. 2(b) and 2(e), our polarization-dependent analysis indicates that the symmetries of the initial states associated with the dispersion along the sample surface are dominantly odd with respect to the (110) mirror plane and even with respect to the (010) mirror plane.

IV. WAVE FUNCTIONS

In a crystal with cubic symmetry the Mn 3d states are split into the doubly degenerate e_g states and triply degenerate t_{2g} states. For an octahedral environment of anions, like in LSMO, the t_{2g} states have lower energies than the e_g states.²¹ When the symmetry is lower than cubic the e_g states will split into different energy levels. Early studies of LSMO indicate that the t_{2g} states are about 2 eV below E_F , while the low binding-energy states near E_F mainly originate from the e_g states.²²

In order to analyze the wave functions of the low binding-energy states, let us consider e_{g1} and e_{g2} as basis functions of the e_g states. The two basis functions are isomorphic to that of the cubic harmonics $3z^2 - r^2$ and $x^2 - y^2$, with the x, y , and z axes along the [100], [010], and [001] directions, respectively. Other equivalent pairs of the basis functions can be generated through linear combinations. The normal to the sample surface is [001]. e_{g1} possesses even symmetry with respect to both the (010) and (110) mirror planes, while e_{g2} is even with respect to (010) and odd to (110). The Bloch sum of e_{g1} can be constructed for a wave vector $\mathbf{k}$ as

$$E_{g1} = N^{-1/2} \sum \exp(i\mathbf{k} \cdot \mathbf{R}) e_{g1}(\mathbf{r} - \mathbf{R}),$$

where N is the total number of lattice points and the summation runs over all the lattice points $\mathbf{R}$. Similar linear combinations E_{g2} and O_{Pn} can be obtained from e_{g2} and oxygen 2p orbitals. In the tight-binding scheme, the wave functions ψ_1 and ψ_2 for the low-binding energy states can be written as

$$\psi_1 = A_1(\mathbf{k})E_{g1} + B_1(\mathbf{k})E_{g2} + \sum_n C_n(\mathbf{k})O_{Pn}, \quad (1)$$

$$\psi_2 = A_2(\mathbf{k})E_{g1} + B_2(\mathbf{k})E_{g2} + \sum_n D_n(\mathbf{k})O_{Pn}, \quad (2)$$

where A–D are $\mathbf{k}$ -dependent coefficients.

Let us consider ψ_1 and ψ_2 , the wave functions associated with the dispersions observed along the sample normal and along its surface, respectively. When ψ_2 has exclusively odd parity with respect to the reflection in the (110) mirror plane, the terms $A_2(\mathbf{k})E_{g1}$ and $\mathbf{P}_e \sum_n D_n(\mathbf{k})O_{Pn}$ will be projected out from Eq. (2). Here $\mathbf{P}_e$ is the even symmetry projection

operator with respect to the mirror plane. ψ_2 becomes

$$\psi_2 = B_2(\mathbf{k})E_{g2} + (1 - \mathbf{P}_e) \sum_n D_n(\mathbf{k})O_{Pn}. \quad (3)$$

As discussed above, the states associated with the dispersion observed in the mirror plane (110) have dominantly odd symmetry with respect to the reflection in this mirror plane. Therefore their wave functions can be described as Eq. (2) with

$$|B_2(\mathbf{k})| \gg |A_2(\mathbf{k})|, \quad (4)$$

$$|(1 - \mathbf{P}_e) \sum_n D_n(\mathbf{k})| \gg |\mathbf{P}_e \sum_n C_n(\mathbf{k})|. \quad (5)$$

One can conclude that Ψ_2 has mainly $x^2 - y^2$ character for those $\mathbf{k}$ points that can be observed in the (110) mirror plane in ARPES measurements.

Since ψ_1 is orthogonal to ψ_2 for any $\mathbf{k}$ point, if we neglect the overlap of the orbitals that belong to Mn atoms at different sites, ψ_1 becomes

$$\psi_1 \approx B_2(\mathbf{k})E_{g1} - A_2^*(\mathbf{k})E_{g2} + \sum_n C_n(\mathbf{k})O_{Pn} + \dots \quad (6)$$

According to Eq. (4), ψ_1 has mainly $3z^2 - r^2$ character and it is a linear combination of e_{g1} and O 2p orbitals.

The small residual intensity of the dispersive peak in Figs. 2(b) and 2(e) could originate from small random deviations of the Mn orbitals from $x^2 - y^2$ and/or of the O 2p orbitals from the crystal axes. Electron scattering may be another reason, i.e., some of the photoelectrons from the vicinity of the mirror plane are scattered into the mirror plane before they leave the sample surface.

Our ARPES results indicate that the symmetry of the studied system is lower than cubic. The $\text{Mn}^{3+/4+}$ ions are situated in an environment in which a large cubic field, which causes the splitting of the 3d states into e_g and t_{2g} , is supplemented by a tetragonal field. The reasons are the following:

(i) The electronic structure is anisotropic: we only found a nonvanishing intensity at E_F in the vicinity of $(0,0,0.4)\pi/a$, but not near $(0.4,0,0)\pi/a$ and $(0,0.4,0)\pi/a$, which should be equivalent to $(0,0,0.4)\pi/a$ if the system would have cubic symmetry.

(ii) For cubic symmetry, the two bands resulting from the e_g orbitals would be degenerate along the body diagonal $\Gamma-R$ of the Brillouin zone (BZ) [the dashed line in Fig. 2(d)] and their wave functions would have different parities with respect to the reflection in the (110) mirror plane. However, we only found one energy band with odd symmetry to the (110) mirror plane in the vicinity of the intersection between $\Gamma-R$ and the path along the spectra were taken (Fig. 2).

(iii) Because (110) and (010) remain mirror planes, the system has tetragonal symmetry with fourfold rotation axis along [001], which is the surface normal.

As a consequence of the lower symmetry, the doubly degeneracy of the e_g states is lifted. The splitting of the e_g levels is evident because no energy-band crossover was observed at any $\mathbf{k}$ point. This means that the energy band associated with the finite spectral weight at E_F [Fig. 1(c)] lies above the other band which always remains below E_F [e.g.,

Figs. 1(a) and 1(b)]. Thus the form for the wave functions we obtained from the ARPES data in the (110) mirror plane can be extended to general $\mathbf{k}$ points in the BZ.

This orbital assignment of the energy band agrees with the present experimental findings: the energy band associated with ψ_2 indicates a 2D-like character from its strong dispersion in the (k_x, k_y) plane, which is parallel to the sample surface.

The observed anisotropy in the low binding-energy electronic structure is different with respect to the earlier reported band-structure calculations²³ that, it is noted, assumed cubic symmetry. It is known that the LSMO films are under tensile stress on the STO substrate due to lattice mismatch.²⁴ The open question is whether the small ($\sim 0.5\%$) difference between the lattice constants of the LSMO bulk single crystal and STO substrate, respectively, is the origin of the observed anisotropy or other effects are also involved.

In summary, the two-band picture⁹ persists in the LSMO thin film with T_c close to the lowest transition temperature

from the PM to FM metallic state. We found a finite spectral weight at E_F . Through a detailed polarization-dependent ARPES analysis, we have determined the symmetry of the 2D-like character dispersive band. The initial states associated with this band are dominantly odd with respect to the (110) mirror plane and even with respect to the (010) mirror plane. Within the tight-binding scheme, we have derived the spatial part of the wave functions that describe these two bands.

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