FAST TRACK COMMUNICATION

The electronic structure of La$_{1-x}$Sr$_x$MnO$_3$ thin films and its $T_c$ dependence as studied using angle-resolved photoemission

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Abstract

We present angle-resolved photoemission spectroscopy (ARPES) results for thin films of the three-dimensional manganese perovskite La$_{1-x}$Sr$_x$MnO$_3$. We show that the temperature of the transition ($T_c$) from the paramagnetic insulating to the ferromagnetic metallic state is closely related to details of the electronic structure, particularly to the spectral weight at the $k$-point, where the sharpest step at the Fermi level was observed. We found that this $k$-point is the same for all the samples, despite their different values of $T_c$. The change of $T_c$ is discussed in terms of kinetic energy optimization. Our ARPES results suggest that the change of the electronic structure for the samples having different transition temperatures is different from the rigid band shift.

(Some figures in this article are in colour only in the electronic version)
One major obstacle in understanding the physics of the three-dimensional manganites has been a lack of detailed knowledge of the electronic structure of the low binding energy electronic states. So far, only very limited experimental results on k-resolved electronic structures of La$_{1-x}$Sr$_x$MnO$_3$ have been reported [9-11]. In this work we apply angle-resolved photoemission spectroscopy (ARPES) to probe the electronic structure of metallic single crystalline films of La$_{1-x}$Sr$_x$MnO$_3$ with different $T_c$. We observe that the finite spectral weight at the Fermi level ($E_F$) is closely associated with a broad peak which disperses at higher binding energies. The difference in $T_c$ is directly reflected by a change in the electronic structure of the lowest binding energy states.

1300 Å-thick single crystalline thin films of LSMO were prepared by in situ heteroepitaxial growth on SrTiO$_3$ (001) substrates by a novel adaptation of pulsed laser deposition [12, 13]. In situ reflection high-energy electron-diffraction patterns and Kiessig fringes in ex situ x-ray reflectivity curves demonstrate that the films have a surface roughness of less than one monolayer. Low-energy electron-diffraction analysis shows a clear (1 × 1) pattern with no sign of surface reconstruction. Three LSMO samples with ascending Sr/La ratios (0.44, 0.48, 0.52) were prepared. Because the hole-doping level could be changed by the small variation of the oxygen stoichiometry, which can result in a change of $T_c$, we further characterize the bulk properties of the samples by transport measurements. Figure 1(a) shows the resistance–temperature curves [R(T)] obtained from four-probe measurements. The transition temperatures determined from these data are 241 K, 342 K and 313 K, respectively. In the rest of the paper we will label the samples by their $T_c$ as S241, S342 and S313, respectively. The transition temperatures were confirmed by DC magnetization measurements. Figure 1(b) shows the magnetic momentum [4π M(T)] of S313, together with R(T), as a function of temperature. The stoichiometry of S313, as determined by ex situ using Rutherford backscattering spectrometry, was La$_{0.46}$Sr$_{0.54}$MnO$_3$.

ARPES measurements were performed at the surface and interface spectroscopy (SIS) beamline at the Swiss light source (SLS). During measurements, the pressure always remained less than 1 × 10$^{-10}$ mbar. The spectra were recorded with a Scienta 2002 analyzer with an angular resolution of better than 0.2°. The energy resolution was relaxed to 40 meV to obtain a high intensity. All measurements were performed at temperature below 30 K. The reduced zone scheme is used to indicate the wavevectors (k) in reciprocal space. The free-electron final state approximation with ($V_0-\phi$) = 10.16 eV [9] is applied to determine paths or k-points, where $V_0$ is the inner potential and $\phi$ is the work function. Photon energies ($E_{ph}$) are indicated in the figure captions. In our ARPES measurements the polar angles (between the surface normal and the direction of the outgoing photoelectrons) were in the range of $-5^\circ < \theta < 18^\circ$.

We show representative ARPES spectra taken from S313 in figure 2. Similar ARPES spectra were also obtained for S241 and S342. The spectra were collected along paths parallel to the sample surface in the (010) mirror plane (figure 2(a)) and (110) mirror plane (figure 2(b)), with linearly horizontally polarized light and with circularly polarized light, respectively. The common features in figures 2(a) and (b) are: close to the (001) axis a broad peak (peak A) sits on the sloped background and shows nearly no dispersion along $k_{\parallel}$ (the component of k parallel to sample surface). Away from the (001) axis at about $k_{\parallel} \approx 0.3\pi/a$, another peak (peak B) appears at higher binding energy and disperses towards $E_F$ as $k_{\perp}$ increases. Further increasing $k_{\perp}$ does not change the peak position of peak B in the (010) mirror plane, while it folds back to high binding energy in (110) mirror plane (not shown). The bandwidth of peak B in the (110) mirror plane is larger than that in the (010) mirror plane. In contrast to its non-dispersive behavior with respect to $k_{\perp}$ in the vicinity of the (001) axis, peak A does show a dispersion with respect to $k_{\perp}$ (along the surface

**Figure 1.** (a) Resistance versus temperature for samples S241, S342 and S313. The resistance was normalized to the peak value. (b) Resistance and DC magnetization of S313 versus temperature. Inset: magnetic hysteresis curves of S313 measured at temperatures 100 K (1) and 250 K (2).
Figure 2. ARPES spectra for S313 at 30 K. (100) and (110) are along the sample surface, while (001) is the surface normal. Peak A and peak B are used to facilitate the discussion in the text. (a) and (b) EDCs taken by using \( E_{hv} = 44 \) eV with linearly horizontally polarized light and with circularly polarized light, respectively. The paths in the BZ are indicated with arrowed lines in the middle and bottom-right of the figure. Circles indicate the peak positions of broad peaks. (c) EDCs taken with circularly polarized light with \( E_{hv} = 34 \) eV (lower), 38 eV (middle) and 46 eV (upper) in the normal emission. The \( k \)-points are indicated in the bottom-right of the figure with filled circles for \( E_{hv} = 34 \) eV (lower), 38 eV (middle) and 46 eV (upper), respectively. The vertical line indicates the energy where the slopes of the EDCs change, circles indicate the peak positions of broad peaks.

It can be seen that there is a close correlation between the peak position and the spectral weight at \( E_F \). Specifically, when peak A approaches \( E_F \), the spectral weight at \( E_F \) increases and the step at \( E_F \) sharpens. It should be noted that a finite spectral weight at \( E_F \) has only been observed in the vicinity of the (001) axis in the Brillouin zone (BZ) with \( k_1 < 0.4\pi/a \). The highest spectral weight and the sharpest step at \( E_F \) have been found when \( E_{hv} = 38 \) or 67 eV is used. This applies for all the investigated samples, despite their different \( T_c \). Peak B also disperses along a path parallel to the (001) axis [9]. This is strong circumstantial evidence that the dispersion of peak B derives from the bulk electronic structure. However, the dispersive feature is much weaker than that in the planes perpendicular to the (001) axis. It is important to mention that we have traced the peak B in different mirror planes, as well as many general \( k \)-points in the BZ by using various photon energies and photon polarizations. We found that there is a correspondence between the positions of peak B and the \( T_c \) of the samples (figure 3(c)): the higher \( T_c \) is, the closer becomes peak B to \( E_F \). However, for all three samples, the centroids of peak B never approach closer than 0.6 eV to \( E_F \), and there is never more than a vanishingly small spectral weight at \( E_F \).

Besides the many similarities, there are some quantitative differences in the ARPES spectra of S241, S342 and S313. Figures 3(a) and (b) show the EDCs taken with \( E_{hv} = 38 \) eV, corresponding to \( k \approx (0, 0, 0.4)\pi/a \), where the highest spectral weight at \( E_F \) was observed for all three samples. The spectra were normalized to the total areas under the EDCs. An important observation is that the spectral weight at \( E_F \) is closely related to the transition temperatures, namely, the spectral weight at \( E_F \) is higher when \( T_c \) increases (figure 3(a)). In order to remove any ambiguity when comparing the spectral weight at \( E_F \), two additional normalization methods were employed. First, to minimize the contribution of the sloped background, we normalized the EDCs to the intensity at \( E_B = 200 \) meV below \( E_F \) (the inset of figure 3(a)). Second, for normalization we used the ‘shoulder’ of the Mn t_{2g} states of Mn (figure 3(b)). In both cases the spectral weights at \( E_F \) for different samples have the same trend as the \( T_c \)'s of the samples. Figure 3(a) also shows that the line shape of peak A changes dramatically for the samples with different \( T_c \). For S241, it has the lowest \( T_c \) among the three samples, and peak A is well defined. As \( T_c \) increases some spectral weight is transferred from high binding energies to that close to \( E_F \), and at the same time peak A becomes broader and less pronounced. On the other hand, the line shape of peak B is rigid with respect to the change of \( T_c \). Figure 3(c) shows the EDCs for S241 and S313 taken at the same \( k \approx (0.6, 0.7)\pi/a \) where a single e_g band is expected [14, 15]. The peak position of the EDC of S313 is shifted about 170 meV towards \( E_F \) with respect to that of S241. After offsetting the EDC of S313 by –170 meV the two EDCs overlap over nearly the entire energy range, except at the very
where quasiparticles were observed in the layered manganite.

The quasiparticle peaks are followed by incoherent excitations, and the single particle spectral function of the electron-pocket has a cubic-like shape [14, 15], the nesting of the Fermi surface between the parallel faces of the cube may introduce an instability and result in a gap opening in the electronic excitation spectra. The consequence of this will be that the spectral weight at $E_F$ diminishes and the relevant energy band folds back from $E_F$. In our previous ARPES studies on LSMO we observed the folding back of an energy band which is supposed to cross the calculated Fermi surface of the hole-pocket (see figures 1(a) and 2(a) in [10]).

Another possibility to explain the absence of the hole-pocket is heteroepitaxial strain in the samples. The common point in our ARPES studies and others is that single crystalline LSMO films grown on SrTiO$_3$ substrates were used in the experiments. The tensile stress due to the lattice mismatch between the LSMO and the substrate results in the ratio between the lattice constant in the [001] direction and those in the equivalent [100] directions is less than unity. Further studies are needed to understand the discrepancy between the experimental and calculated results, namely, is it due to the nesting, the change of lattice constant, a combination of these, or other effects? To clarify the role played by the strain induced by any lattice mismatch, it will be very useful to perform ARPES measurements on single crystals grown on different substrates, e.g. NdGaO$_3$. In this case the compressive stress results in the lattice constant in [001] direction being larger than that in [100] direction. Comparison of the ARPES results on LSMO crystals under different stress will be very important in understanding how the electronic structure responds to small changes of the lattice constants.

Our ARPES results also indicate that the change of the electronic structure for the samples with different $T_c$ is different than the rigid band shift, as suggested in the angle integrated photoemission on the LSMO films [19]. This is manifested by the facts that (a) for all the samples, the highest spectral weight was found at the same $k$-point $(0, 0, 0.4)\pi/a$ when $E_{F0} = 38$ eV is used in the measurements; (b) the centroid of peak A of S313 is closer to $E_F$ than that of S342 at this $k$-point, but S313 has a lower spectral weight at $E_F$ than S342 (figure 3(a)), which is opposite to what one would expect from the rigid band picture [20]; and (c) for S241 the peak position of peak A at $k = (0, 0, 0.4)\pi/a$ is about the same as that of peak B at $k = (0.6, 0, 0.7)\pi/a$ (figures 3(a) and (c)). When going to S313, the shift of the peak position of peak B ($170$ meV) is much smaller than that of peak A, $\sim 500$ meV, and compared to the small change in the line shape of the peak B at the low binding energy tail (the marked box in the figure 3(d)) the spectral weight of peak A undergoes a large redistribution (figure 3(a)).

The relationship between $T_c$ and the spectral weight at $E_F$, namely that a higher $T_c$ is associated with more spectral weight

![Figure 3](image-url)
at $E_F$, can be qualitatively explained by the double-exchange model [21–23]. The essential quantity for the transition from PM to FM is the metallic density of charge carriers, which are subject to Hund’s rule and other interactions. The scale of the transition temperature is set by the kinetic energy of the mobile charge carriers, which is proportional to the expectation value of the hopping Hamiltonian. The highest $T_c$ is obtained when the kinetic energy is maximized in the system. As the Fermi level divides the occupied states and unoccupied states of electrons, the spectral weight in electronic excitation spectra is directly related to the hopping probability given by the number of electrons that are free to move from site to site and the number of available empty states that the electrons can hop into.

In summary, our ARPES measurements on LSMO thin films with different $T_c$ reveal both common features and quantitative differences in their electronic structures in the FM phase. It was found that $T_c$ is closely related to the spectral weight at $E_F$ at $k \approx (0, 0, 0.4)\pi/a$, where the sharpest step at $E_F$ was observed for all investigated samples. We also provide evidence that the rigid band picture cannot account for the change of the electronic structure for the samples having different $T_c$ resulting from the change of dopings.

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