Effect of strong localization of doped holes in angle-resolved photoemission spectra of La$_{1-x}$Sr$_x$FeO$_3$

H. Wadati, 1 A. Chikamatsu, 2 M. Takizawa, 1 R. Hashimoto, 2 H. Kumigashira, 2 T. Yoshida, 1 T. Mizokawa, 1 A. Fujimori, 1 M. Oshima, 2 M. Lippmaa, 3 M. Kawasaki, 4 and H. Koinuma 5

1 Department of Physics and Department of Complexity Science and Engineering, University of Tokyo, Kashiwa, Chiba 277-8561, Japan
2 Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
3 Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
4 Institute for Materials Research, Tohoku University, Aoba, Sendai 980-8577, Japan
5 National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

(Dated: March 23, 2002)

We have performed an angle-resolved photoemission spectroscopy study of La$_{0.6}$Sr$_{0.4}$FeO$_3$ using in situ prepared thin films and determined its band structure. The experimental band dispersions could be well explained by an empirical tight-binding band structure assuming the G-type antiferromagnetic state. However, the Fe 3d bands were found to be shifted downward relative to the Fermi level ($E_F$) by $\sim 1$ eV compared with the calculation and to form a (pseudo)gap of $\sim 1$ eV at $E_F$. We attribute this observation to a strong localization effect of doped holes due to polaron formation.

PACS numbers: 71.28.+d, 71.30.+h, 79.60.Dp, 73.61.-r

Metal-insulator (MI) transitions in strongly-correlated electron systems have been generally understood in terms of band-width control and filling control [1]. However, the actual situation is more complicated because of the effect of disorder, electron-phonon interaction, charge and orbital ordering, etc [2,3,4,5]. Electron-phonon interaction causes a polaronic effect on charge carriers and increases their effective masses. In some filling-controlled systems, carriers doped into the Mott insulator remain localized as self-trapped small polarons and the system remains insulating. The problem of how an MI transition occurs when strong electron-phonon interaction is present remains highly controversial. A striking example is a hole-doped Mott insulator (charge-transfer type insulator) La$_{1-x}$Sr$_x$FeO$_3$ (LSFO), where the insulating phase is unusually wide in the phase diagram ($0 < x < 0.5$ at room temperature and $0 < x < 0.7$ at low temperatures) [3]. In a previous photoemission study, the gap at the Fermi level ($E_F$) was seen for all compositions in the range $0 \leq x \leq 0.67$ [3], consistent with the wide insulating region.

The effect of electron-phonon interaction is clearly reflected on the spectral function [4], and recent photoemission results have been discussed in this context for high-$T_c$ superconductors [4,5]. Mn oxides [6], VO$_2$ [7], and Fe$_3$O$_4$ [7]. Angle-resolved photoemission spectroscopy (ARPES) is a particularly powerful technique by which one can directly study the band structure of a material. However, there have been few studies on transition metal oxides (TMOs) with the cubic perovskite structures like LSFO because many of them do not have a cleavage plane. Recently, the band structure of the three-dimensional perovskite La$_{1-x}$Sr$_x$MnO$_3$ has been studied by ARPES using well-defined surfaces of in situ prepared epitaxial thin films [8,9], demonstrating that such an approach on TMO films is one of the best methods for such a purpose. In this paper, we report on in-situ ARPES results of single-crystal LSFO ($x = 0.4$) thin films grown on SrTiO$_3$ (001) substrates. We observed several dispersive bands which can be assigned to the Fe 3d $e_g$, $t_{2g}$, and O 2p bands. The experimental band structure was interpreted based on an empirical tight-binding band structure assuming the G-type antiferromagnetic (AF) state. In spite of the overall agreement between experiment and theory, fundamental discrepancies were found for the overall shift of the Fe 3d bands away from $E_F$ and the suppression of spectral weight around $E_F$. We shall discuss these discrepancies in terms of strong polaronic effect.

Experiment was carried out using a photoemission spectroscopy (PES) system combined with a laser molecular beam epitaxy (MBE) chamber at beamline BL-1C of the Photon Factory, KEK [10]. The LSFO ($x = 0.4$) thin films were grown epitaxially on Nb-doped SrTiO$_3$ substrates by the pulsed laser deposition method. Details are described in Ref. [9]. The lattice constants were determined to be $a = b = 3.905$ Å and $c = 3.883$ Å. In this paper, $k_\parallel$ denotes the in-plane electron momentum, and $k_z$ the out-of-plane one, expressed in units of $\pi/a$ or $\pi/c$. By low energy electron diffraction, sharp 1 1 spots were observed with no sign of surface reconstruction. ARPES measurements were performed under ultrahigh vacuum of $\sim 10^{-10}$ Torr at 150 K, below the Neél temperature ($T_N = 320$ K) of LSFO with $x = 0.4$ [7], using a Scienta SES-100 electron energy analyzer. The total energy resolution was set to about 150 meV. The $E_F$ position was determined by measuring gold spectra.

Figure 1 shows ARPES spectra of an LSFO ($x = 0.4$) thin film taken with a photon energy of 74 eV. The inset shows a trace in $k$-space for $h\nu = 74$ eV with changing polar emission angle $\theta$. Here, we have assumed the work function of the sample $\phi = 4.5$ eV, and the inner potential $V_0 = 10.5$ eV so that the periodicity of the band dispersion is correctly given in normal emission (not shown).
The shoulder structure at $\sim -1.3$ eV shows a significant dispersion, and is assigned to the Fe 3$d$ majority-spin $e_g$ bands. The peak structure at $\sim -2.4$ eV shows a weaker dispersion, and is assigned to the Fe 3$d$ $t_{2g}$ majority-spin bands. The structures at $-(4-7)$ eV show strong angular dependence and are assigned to O 2$p$ bands. The $e_g$ bands do not cross $E_F$, consistent with the insulating behavior and the persistence of the gap observed in the angle-integrated PES (AIPES) spectra.

The band dispersions are more clearly seen in the grayscale plot in the left panel of Fig. 2 (a). Here, the second derivatives of the energy distribution curves (EDCs) are plotted on the gray scale with dark parts corresponding to energy bands. The same plot for $h\nu = 88$ eV [corresponding to the upper trace in Fig. 2 (c)] is shown in the left panel of Fig. 2 (b). In Fig. 2 (c), hole pockets obtained by the tight-binding calculation (described below) are also shown. The trace for 74 eV crosses the calculated hole pocket at $k_\parallel \sim 1.5\pi/\alpha$, while that for 88 eV does not in the same $k_\parallel$ region. Figure 3 shows enlarged grayscale plots near $E_F$ in $E-k$ space. Panel (a) is a direct intensity plot of the EDCs in Fig. 1. Angle-independent part has been subtracted as a background. Second derivatives of the EDCs are produced in panel (b) and those of momentum distribution curves (MDCs) in panel (c). In all the plots, the band has a minimum at $k_\parallel \sim 2.0\pi/\alpha$, and disperses upward toward both sides and disappears at $k_\parallel \sim 1.5\pi/\alpha$ and $k_\parallel \sim 2.5\pi/\alpha$, not at $E_F$, but $\sim 1$ eV below it.

In order to interpret the experimental band dispersions more quantitatively, we performed a tight-binding band-structure calculation with empirical parameters, following the scheme in Refs. 13, 14, 15. We performed the calculation, however, assuming the G-type AF state co-
responding to the magnetic ordering in LSFO. Here, the effect of G-type antiferromagnetism was taken into account phenomenologically by imposing an energy difference $\Delta E$ between the spin-up and spin-down Fe sites. Parameters to be fitted were therefore $\Delta E$, the energy difference between the Fe 3d level and the O 2p level, $\epsilon_p - \epsilon_d$, and a Slater-Koster parameter, $(pd\sigma)$ [10]. For the other Slater-Koster parameters, we assumed $(pd\sigma)/(pd\sigma) = -2.2$, and $(pp\sigma)$ and $(pp\pi)$ were taken to be 0.60 eV and $-0.15$ eV, respectively [11]. $(pd\sigma)$ is expected in the range of $-1.4$ to $-1.9$ eV from a configuration-interaction (CI) cluster-model calculation [10]. Crystal-field splitting $10Dq$ of 0.41 eV was taken from Ref. [8]. It should be noted that $\epsilon_p - \epsilon_d$, $(pd\sigma)$ and $\Delta E$ primarily determine the Fe 3d – O 2p band positions, their dispersions, and the optical band gap, respectively, and therefore can be rather uniquely determined.

The best fit to the observed band dispersions of LSFO and the optical gap 2.1 eV of LaFeO$_3$ (LFO) [21] as shown in the right panels of Fig. 2 (a) and (b) has been obtained for reasonable parameter values $\epsilon_p - \epsilon_d = 0$ eV, $(pd\sigma) = -1.5$ eV, and $\Delta E = 5.3$ eV. For these plots, we have considered the effect of $k_z$ broadening ($\Delta k_z$) caused by a finite escape depth $\lambda$ of photoelectrons [21] $\Delta k_z \sim 1/\lambda$ ($\sim 0.2$ Å$^{-1}$) is approximately 10% of the Brillouin zone ($2\pi / c$]). The dispersions of the $e_g$ bands were thus successfully reproduced. The weak dispersions of the $t_{2g}$ bands and the width of the O 2p bands were also well reproduced by these parameters. According to the band-structure calculation, spectral weight should be cut off above the calculated $E_F$, which is determined by the band filling for $x = 0.4$, while in experiment it gradually decreases from the calculated $E_F$ toward the experimental $E_F$. This discrepancy inevitably arises from the fact that this material is insulating up to 70% hole doping while the rigid-band model based on the present band structure gives the metallic state.

Figure 3 (a) shows the density of states (DOS) of the G-type AF state calculated using the same parameter set. The partial DOS’s for the majority-spin Fe $e_g$, the majority-spin $t_{2g}$, the minority-spin $e_g$, and the minority-spin $t_{2g}$ orbitals are shown in the lower panels. A large band gap opens between the occupied majority-spin $e_g$ bands and the unoccupied minority-spin $t_{2g}$ bands for the present $\Delta E$ value. These characteristic features were already reported by the previous Hartree-Fock calculation [22] and the local spin-density-approximation calculation [23]. In Figs. 2 and 4 $E_F$ for $x = 0.4$ has been determined from the filling of electrons when holes are doped into the AF insulator. In Figs. 3 (b) and (c) the calculated results are compared with the combined AIPES and O 1s x-ray absorption (XAS) spectra of LFO and LSFO ($x = 0.4$), respectively [8]. For LFO, the three main structures of the valence band, A, B, and C are successfully reproduced by the calculation, while the satellite structure in the valence-band photoemission spectrum could not be reproduced. The crystal-field splitting into D and E above $E_F$ is also well reproduced. For LFO, although the calculated band gap has been adjusted to the experimental value, the peak positions of structures A and E are still shifted away from $E_F$ in the experiment compared to the calculation [as denoted by broken lines in Fig. 4 (b)]. As for $x = 0.4$ [Fig. 3 (c)], structure A is shifted away from $E_F$ compared to the calculation even more.

Generally speaking, doped holes may be localized due to disorder or through coupling to lattice distortion. The latter effect, namely, polaronic effect was recently observed in the photoemission spectra of a number of TMOs [2, 4, 5, 6]. Note that for $x = 0.4$ a hole-induced peak $P$ appears within the band gap of LFO and accommodates doped holes. These observations cannot be explained by the rigid-band model in which $E_F$ has been shifted according to the band filling. The breakdown of the rigid-band model means that doped holes do not enter the top of the $e_g$ majority-spin band but enter localized states split off from the top of the $e_g$ band, causing the insulating behavior of this material.

Finally, we further discuss the discrepancy between the band-structure calculation and the experimental results near $E_F$ and the origin of the insulating behavior of LSFO. Figure 5 schematically shows the calculated and experimental band structure and DOS of LSFO. Our tight-binding calculation is similar to local-density approximation (LDA) +U in the sense that the effect of electron-electron interaction and hence the value of the band gap is adjusted via $\Delta E$ in the tight-binding calculation and via $U$ in the LDA +U calculation. Broken lines indicate the tight-binding or LDA +U band structure, where the value of the band gap of the parent insulator has been adjusted to $\sim 2$ eV in order to reproduce the optical gap [20]. When holes are doped into this system, $E_F$ moves downward and crosses the $e_g$ band, making the system metallic if the rigid-band model can be applied. However, from the comparison of calculation and experiment in Figs. 2 and 4 the $e_g$ structures are shifted away from $E_F$, and hole-induced states appear above $E_F$. The existence of these hole-induced states means that the rigid-band model is no more valid, and doped holes enter split-off localized states formed by
hole doping. There is also a spectral line-shape broadening compared to the band-structure calculation. Such a modification of the structures and line-shape broadening have been attributed to a polaronic effect recently observed in a number of TMOs [2, 3, 4]. For example, in the case of Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$, the spectral weight of quasiparticle peak $Z$ becomes extremely small due to a strong coupling to phonons [2]. In the case of VO$_2$ [5] and Fe$_3$O$_4$ [6], spectral changes with temperature were interpreted by considering strong coupling of electrons to phonons. In the case of LSFO, we consider that electron-phonon coupling is very strong for the $e_g$ orbitals compared to the $t_{2g}$ orbitals, the effect can be dramatic as observed in LSFO, where doped holes have $e_g$ character. Moreover, according to the temperature-dependent PES and XAS studies, short-range (local) charge order may exist in the wide composition range [24]. The polaronic effect probably enhances the tendency toward local charge ordering and explains the unusually wide insulating phase in LSFO.

In summary, we have performed an in-situ ARPES study on single-crystal LSFO ($x = 0.4$) thin films and determined its band structure. The observed dispersive bands were assigned to Fe 3$d$ $e_g$, $t_{2g}$ and O 2$p$ bands. The experimental band dispersions were interpreted using a tight-binding band-structure calculation by assuming the G-type antiferromagnetic state. From the discrepancy near $E_F$ between experiment and theory in spite of the overall agreement, the insulating behavior of this material is proposed to be caused by the localization of hole-induced states due to polaronic effect and/or short-range charge order.

The authors would like to thank N. Hamada and T. Saha Dasgupta for informative discussion and D. Kobayashi for sample preparation. We are also grateful to K. Ono for their support at KEK-PF. This work was supported by a Grant-in-Aid for Scientific Research (A16204024) from the Japan Society for the Promotion of Science (JSPS). This work was done under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2002S2-002). H. W. acknowledges financial support from JSPS.

---

FIG. 5: Schematic picture of polaronic effects and hole-induced states in LSFO. (a) Band dispersions, (b) DOS.

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[2] K. M. Shen, F. Ronning, D. H. Lu, W. S. Lee, N. J. C. Ingle, W. Meevasana, F. Baumberger, A. Damascelli, N. P. Armitage, L. L. Miller, Y. Kohsaka, M. Azuma, M. Takano, H. Takagi, and Z.-X. Shen, Phys. Rev. Lett. 93, 267002 (2004).
[3] O. Rösch, O. Gunnarsson, X. J. Zhou, T. Yoshida, T. Sasagawa, A. Fujimori, Z. Hussain, Z.-X. Shen, and S. Uchida, Phys. Rev. Lett. 95, 227002 (2005).
[4] O. Mannella, W. Yang, X. J. Zhou, H. Zheng, J. F. Mitchell, J. Zaanen, T. P. Devereaux, N. Nagaosa, Z. Hussain, and Z.-X. Shen, Nature (London) 438, 474 (2005).
[5] K. Okazaki, H. Wadati, A. Fujimori, M. Onoda, Y. Murakawa, and Z. Hiroi, Phys. Rev. B 69, 165104 (2004).
[6] D. Schrupp, M. Sing, M. Tsunekawa, H. Fujiwara, S. Kasai, A. Sekiyama, S. Suga, T. Muro, V. A. M. Brabers, and R. Claessen, Europhys. Lett. 70 (6), 789 (2005).
[7] J. Matsumo, T. Mizokawa, A. Fujimori, K. Mamiya, Y. Takeda, S. Kawasaki, and M. Takano, Phys. Rev. B 60, 4605 (1999).
[8] H. Wadati, D. Kobayashi, H. Kumigashira, K. Okazaki, T. Mizokawa, A. Fujimori, K. Horiba, M. Oshima, N. Hamada, M. Lippmaa, M. Kawasaki, and H. Koinuma, Phys. Rev. B 71, 035108 (2005).
[9] G. D. Mahan, Many-Particle Physics (Plenum, New York, 2003).
[10] M. Shi, M. C. Falub, P. R. Willmott, J. Krempasky, R. Herger, K. Hricovini, and L. Patthey, Phys. Rev. B 70, 140407(R) (2004).
[11] A. Chikamatsu, H. Wadati, H. Kumigashira, M. Oshima, A. Fujimori, N. Hamada, T. Ohnishi, M. Lippmaa, K. Ono, M. Kawasaki, and H. Koinuma, cond-mat/0503373 Phys. Rev. B in press.
[12] K. Horiba, H. Oguchi, H. Kumigashira, M. Oshima, K. Ono, N. Nakagawa, M. Lippmaa, M. Kawasaki, and H. Koinuma, Rev. Sci. Instr. 74, 3406 (2003).
[13] A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).
[14] L. F. Mattheiss, Phys. Rev. 181, 987 (1969).
[15] L. F. Mattheiss, Phys. Rev. B 6, 4718 (1972).
[16] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
[17] W. A. Harrison, Electronic Structure and the Properties of Solids (Dover, New York, 1989).
[18] L. F. Mattheiss, Phys. Rev. B 5, 290 (1972).
[19] A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B 45, 1561 (1992).
[20] T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B 48, 17006 (1993).
[21] The effect of $k_z$ broadening is given by the following Lorentzian function, $L(k_z) = 1/((k_z - k_{z0})^2 + (1/2\lambda)^2)$, where $\lambda$ denotes an escape depth of photoelectrons. Here we used the value $\lambda = 5 \, \text{Å}$.
[22] T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).
[23] D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. 75, 1126 (1995).
[24] H. Wadati, A. Chikamatsu, R. Hashimoto, M. Takizawa, H. Kumigashira, A. Fujimori, M. Oshima, M. Lippmaa, M. Kawasaki, and H. Koinuma, cond-mat/0410202 J. Phys. Soc. Jpn. in press.