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Photoemission line-shape study of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ ($\delta = 0$, 0.03, 0.06)

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We have studied the line shapes of ultraviolet photoemission spectra of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ ($\delta = 0$, 0.03, and 0.06) systems to test the extrinsic image charge screening effect on photoemission spectra recently suggested by R. Joynt [Science **284**, 777 (1999)], who argued that the photoemission spectrum near the Fermi energy, especially for poorly conducting system, can be very different from the intrinsic density of states because the outgoing electron has the probability of losing its kinetic energy due to the image force. We tested this argument in real materials experimentally by measuring the photoemission line shapes of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ systems, for which all the requirements of this theory are satisfied and sample resistivities change systematically. We found that experimental photoemission spectra do not show the change of line shapes expected from the extrinsic image force effect, and we conclude that the influence of this long-range interaction is not so large as suggested in the paper by Joynt.

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I. INTRODUCTION

Photoemission spectroscopy (PES) has been widely considered as the most powerful tool for probing the electronic structure of occupied states in condensed-matter systems. Conventionally the photoemission process is explained by a three-step model[1] which involves (1) the excitation of the photoelectron, (2) its travel to sample surface, and (3) the escape through the surface into the vacuum. This simple model, though it is a purely phenomenological approach and has some shortcomings due to its semiclassical nature, has proved to be quite successful in explaining many features in photoemission spectra.

Recently, Joynt[2] suggested that more careful consideration is needed in the third step, where the outgoing electron experiences an attractive interaction due to its image charge in the sample part during its travel from the sample to the analyzer, and so can lose its kinetic energy with some probability distribution. Moreover it was argued that this long-range interaction effect should appear most drastically when the sample resistivity is rather high (roughly $\rho_0 \gtrsim 0.1\ \mathrm{m}\Omega\,\mathrm{cm}$), which is based on Joynt's calculation results of energy-loss probability distribution and some fitting parameters taken from experiments. The argument of Ref. 2 is so timely that many photoemission spectroscopists paid attention to this assertion because currently much-studied materials such as high-T_c superconductors[3] and colossal magnetoresistance (CMR) materials[4] show so-called pseudogap features and this theory looks like a master key to interpret these phenomena, especially for the case of CMR manganites.

Though this argument certainly contains some elements that should be considered seriously, there are different opinions and opposing views. Dessau and co-workers[5] claimed that their angle-resolved photoemission of single-crystalline double-layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ showed a momentum-dependent pseudogap feature, which could not originate from the extrinsic loss in Ref. 2 because the extrinsic loss should not change much with momentum. Recently Chuang *et al.*[6] gave an explanation for the pseudogap of this double-layered manganite, namely, that it originates from a short-range charge/orbital density wave enhanced by Fermi surface nesting. Mills[7] followed up the approach of Ref. 2 with his own calculations to give different results using a sum rule which determined the total amount of energy loss probability, and he suggested that the extrinsic loss shifts the kinetic energy of all photoelectrons downward by roughly the same amount in the usual photoemission experiments. Schulte *et al.*[8] presented several arguments, both theoretical and experimental, that the zero-energy-loss probability P_0 is not so small as assumed in Ref. 2. They also obtained $P(\omega)$ from their electron-energy loss spectroscopy (EELS) spectra of the double-layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ to calculate PES spectra, and compared them with the photoemission spectra. From these comparisons they asserted that this extrinsic effect cannot make pseudogaplike feature in photoemission spectrum as long as P_0 is different from zero, and in most cases can be either neglected or treated as a weak structureless background. In the recent preprint,[9] Haslinger and Joynt gave a quantitative criterion when Ohmic losses are important and pointed out the layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ is not a good candidate for testing the theory of inelastic processes in PES because its resistivity is too high and its crystal structure is not cubic. The present responses to Ref. 2, both theoretical and experimental, are somewhat critical. However, more experimental results are needed. Since many strongly correlated materials lie close to a metal-insulator phase transition and possess a large resistivity, determining whether the argument of Ref. 2 is correct becomes important. Furthermore, as far as we know, though a few indirect proofs were reported, as described briefly above, there are no reports that gave a direct experimental comparison and analysis of the relation between the resistivity and line shape of PES. In addition, previously studied systems might be inadequate for this test, as claimed in Ref. 9. In this paper, we choose the most adequate system and provide such direct experimental evidence in order to test the hypothesis of Ref. 2, which is important for the reliability of the information extracted from PES experiment.

To study more thoroughly how the sample resistivity affects the line shapes of photoemission spectra, we chose cubic perovskite $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ ($\delta=0$, 0.03, and 0.06) systems. The transport properties of Al-doped $La_{0.7}Sr_{0.3}MnO_3$ were well studied by Sawaki *et al.*[10] According to their reports, when a small amount of aluminum is doped in $La_{0.7}Sr_{0.3}MnO_3$ it substitutes a *B*-site (Mn) element without any structural transition. The aluminum ion has a closed-shell configuration with no *d* electrons, so it gives the same valence as the host manganese (+3) and no magnetic moments. Hence aluminum doping induces only two kinds of changes: one is an increase of the random electrical potential, and the other is the local cutoff of magnetic interaction between the spins of t_{2g} electrons, i.e., an increase in the magnetic randomness. These changes are enough to cause a resistivity change of two orders of magnitude from $\delta=0$ to 0.06. The useful property most relevant to our study is the first one. Because the dopant aluminum gives three electrons it does not change the hole concentration of $La_{0.7}Sr_{0.3}MnO_3$. Thus the increase of the resistivity with increasing dopants is solely due to the increase of the carrier scattering rates as a result of the increased randomness in potential. This simplifies the analysis of the data in the model of Ref. 2 dramatically. In most cases, there are too many parameters to consider when a systematic study is undertaken to understand how the sample resistivities affect the line shapes of the photoemission spectra. For example, the temperature-dependent resistivity variation can come about not only from the change of the scattering rate but also from changes of the carrier concentration or the electronic structure originating from phase transition.[8] (Recall that in the Drude model the dc conductivity is given by $\sigma_0=ne^2\tau/m^*$, where *n* is the carrier concentration, τ is the relaxation time, and m^* is the effective mass.) But in our case, all the parameters are fixed except for the scattering rate of carriers (or inversely relaxation time τ).

According to the calculations in Ref. 2, photocurrent intensity $I(\omega,T)$ is given by

$$I(\omega,T)=P_0(T)N(\omega)f(\omega) + \int_0^{\infty} P(\omega'-\omega,T)N(\omega')f(\omega')d\omega', \qquad (1)$$

where[11]

$$P(\omega)=\frac{4\pi e^2}{\hbar v\omega^2}\frac{\mathrm{Re}\{\sigma(\omega)\}}{|1+\epsilon(\omega)|^2}, \qquad (2)$$

with the normalization condition

$$1=P_0+\int_0^{\infty} P(\omega)d\omega. \qquad (3)$$

Here, P_0 is the zero-energy-loss probability, $P(\omega)$ the probability of losing the kinetic energy $\hbar\omega$, $N(\omega)$ the temperature-independent density of states (DOS), $f(\omega)$ the Fermi-Dirac distribution function, $\sigma(\omega)$ the conductivity, and $\epsilon(\omega)$ the dielectric function. To apply these formulas to the manganites, the Drude model was used with additional parameter *r* following the approach of Ref. 2,

$$\epsilon(\omega)=\frac{4\pi i}{\omega}\sigma(\omega)=\frac{4\pi i}{\omega}\left(r+\frac{1}{1-i\omega\tau}\right)\sigma_0, \qquad (4)$$

for the dielectric function. Here *r* represents the relative strength of the frequency-independent part compared with Drude part in the conductivity. This parameter *r* is somewhat artificial and its physical origin is not yet well understood, but the inclusion of this parameter makes a sloping line shape often observed in PES. In this paper we will assume that the above scheme is suitable for describing the line shapes of PES for manganites, and test if it describes the experimental line shapes of samples with different resistivities consistently.

II. EXPERIMENT

High quality polycrystalline specimens of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ ($\delta=0$, 0.03, and 0.06) were made by a standard solid-state reaction method. Stoichiometric amounts of high-purity ($\geqslant$99.99%) La_2O_3, $SrCO_3$, Al_2O_3, and MnO_2 powders were weighed and mixed with a pestle and a mortar. After calcining and grinding repeatedly, the resulting powders were pressed into a pellet. Three pellets of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ ($\delta=0$, 0.03, and 0.06) were prepared together. They were finally sintered at 1440 °C for 24 h and slowly cooled in air. We applied the identical synthesis condition for all the samples investigated. We cut each sintered pellet into two pieces, one for transport measurement and the other for photoemission spectroscopy. The resistivities were measured by the conventional four probe method. The photoemission spectra were taken with VG Microtech CLAM-4 multichanneltron electron energy analyzer with an energy resolution of 40 meV full width at half maximum (FWHM) at Seoul National University under a base pressure of 1.0×10^{-10} torr. Photon source was unmonochromatized He I line ($h\nu=21.2$ eV). The samples were cooled down to 95 K with liquid nitrogen, and were fractured *in situ* to obtain a clean surface at that temperature by means of a top post. We obtained the spectra within one hour after the cleave, and checked the surface contamination by taking the valence band spectra.

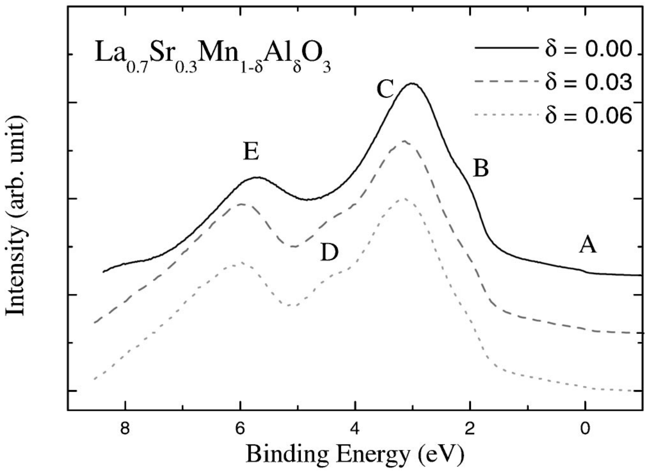

FIG. 1. Valence-band photoemission spectra of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$. Solid, dashed, and dotted lines are for $\delta=0$, 0.03, and 0.06 samples, respectively. All the spectra are taken using the He I line ($h\nu=21.22$ eV) at a temperature 95 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the angle integrated photoemission spectra up to 9-eV binding energy of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ for three doping cases $\delta=0$, 0.03, and 0.06. Several prominent features can be seen in the spectra and are labeled *A*, *B*, *C*, *D*, and *E* as shown in the figure. Two peaks *A* and *B* are strongly hybridized Mn t_{2g} and e_g states with O $2p$ states. Peak *C* is usually assigned to O $2p$ nonbonding states and peak *E* to Mn $3d$–O $2p$ bonding states[1213]. Peak *D*, around 4.5 eV in $\delta=0.03$ and 0.06 cases, is thought to originate from Al $3sp$ impurities. The overall shapes are very similar to one another and to those of previously published spectra for $La_{0.7}Sr_{0.3}MnO_3$ (Ref. 14) and $La_{0.67}Ca_{0.33}MnO_3$.[15] But small doping effects are clearly seen at several points. The position of peak *E* is slightly shifted to the higher-binding-energy side and a small peak *D* appears around 4.5 eV as Al is doped.

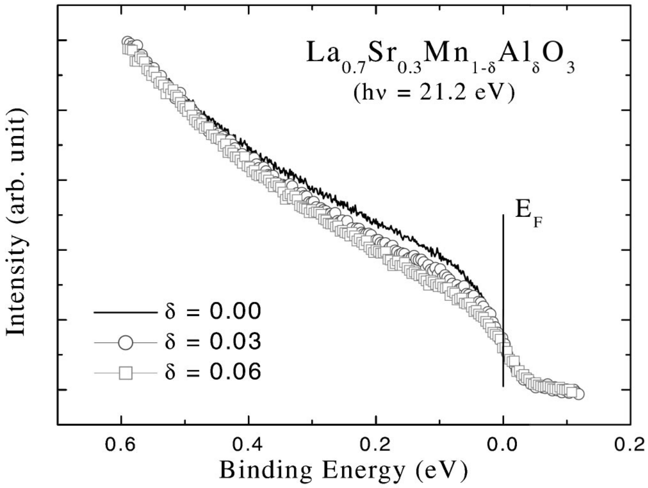

FIG. 2. Near E_F photoemission spectra of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$. The solid line is for $\delta=0$, the solid circles are for $\delta=0.03$, and the solid squares are for $\delta=0.06$. The vertical line is the Fermi level determined by the reference Au sample.

TABLE I. Parameter values in the analyses. The resistivities of each sample are taken at 95 K. σ_0/τ should be the same for all samples in the Drude model, since it is equal to ne^2/m^*. r and P_0 values in fitting 1 are fixed for all samples as those obtained from the fitting of undoped sample spectrum, while in fitting 2 P_0 is allowed to vary depending on the sample.

δ	ρ (mΩ cm)	σ_0/τ (1/sec^2)	r	P_0 (fit 1)	P_0 (fit 2)	P_0 (sloping DOS)
0.00	0.29	6.08×10^{28}	0.25	0.05	0.05	0.5
0.03	4.8	”	”	”	0.12	0.03
0.06	13.0	”	”	”	0.10	0.03

The apparent position change of peak *E* is thought to come from the change of relative concentration of Mn^{3+} and Mn^{4+} ions. Since the Al^{3+} ion replaces the Mn^{3+} site, the spectral weight due to Mn^{3+} sites will be reduced upon Al doping, which should lie at lower binding energy than Mn^{4+} because of correlation energy. The O $2p$ nonbonding states (peak *C*) show almost no change, as expected. The Mn t_{2g} (peak *B*) and e_g states (peak *A*), which are more intimately involved in the transport properties of manganites, are also clearly seen around 2 eV and the Fermi level, and seem to be identical to the undoped case.[16] From these spectra we infer that the overall electronic structures do not change much with doping, and are consistent with the results of structural and transport study by Sawaki *et al.*[10] This is strong evidence that the increase of resistivity is not due to the change of

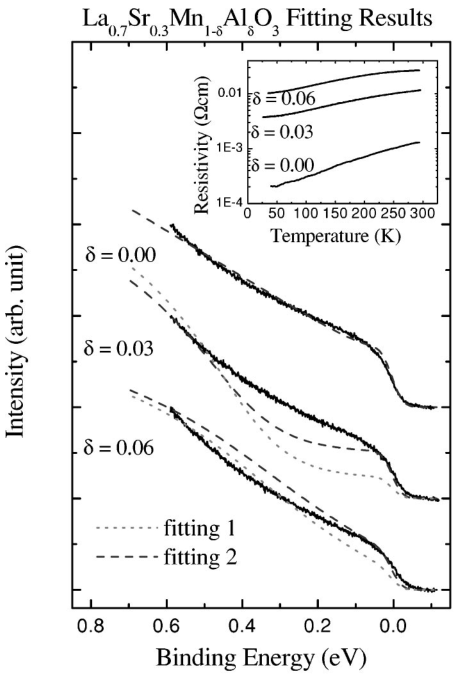

FIG. 3. Experimental vs calculated fitting spectra. The parameter values used in the fitting are listed in Table I. In fittings 1 and 2, all the parameter values are the same except for the zero-energy-loss probability P_0 (see Table I). Inset: Resistivity vs temperature curve of $La_{0.7}Sr_{0.3}Mn_{1-\delta}Al_{\delta}O_3$ samples used in our PES experiments.

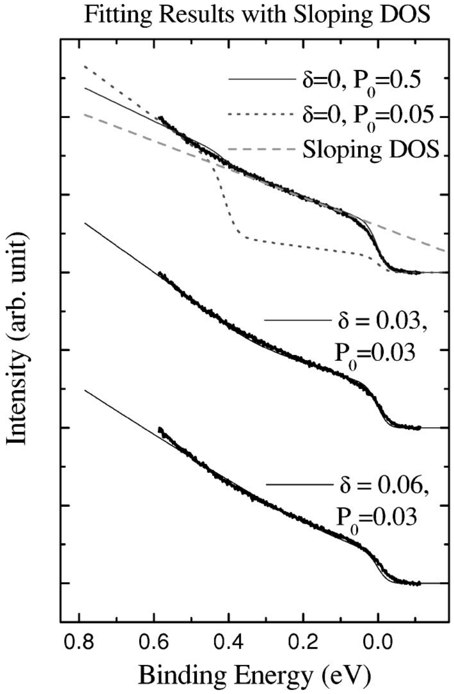

FIG. 4. Experimental vs calculated fitting spectra with a sloping DOS. For each experimental spectrum, the same sloping DOS is used, as shown by the dashed line in the $\delta=0$ case.

electronic structure or phase transition, but due to the increase of scattering rates of carriers.[17] We note that for the doped samples, especially $\delta=0.06$, the resistivity is fairly high (see the inset of Fig. 3) and the estimated electron mean free path is comparable to the unit cell spacing.[18] In spite of this fact, the resistivity curve and PES data show doped samples are still metallic. This behavior is similar to the cases of A_3C_{60} (A = K, Rb), $La_{1.85}Sr_{0.15}CuO_4$, and Sr_2RuO_4,[19] where its physical origin is currently under active debate.

To study the relation between the line shape of PES near the Fermi energy (E_F) and the sample resistivity, we obtained the photoemission spectra near the Fermi level in detail. These spectra are shown in Fig. 2. Each spectrum is normalized to the height at 0.6 eV below the Fermi level. We can see clearly the slight decrease of the spectral weight of the "Mn e_g band" as Al is doped, which is as expected. Because the atomic cross section of O $2p$ is about one order of magnitude larger than that of Mn $3d$ at $h\nu=21.2$ eV,[20] most of the spectral weight change near E_F reflects the O $2p$ characters mixed in the Mn e_g bands. Even though the sample resistivity changes by about two orders of magnitude, the whole line shapes remain very similar to one another, and only a small change of PES spectra is detected. This result seems to be quite different from the expectation of the argument of Ref. 2, as discussed below in more detail.

First of all, we must check whether the resistivity of our samples covers the valid region for the test of this theory. According to a recent report,[9] there are two inequalities that should be satisfied by samples for the extrinsic effect to be important in PES. For our experiments using values of the analyzer resolution ($R=40$ meV), the band-structure width of interest ($B=1$ eV), and the carrier concentration[21] $n=1.5\times10^{22}$ cm^{-3}, under the assumption that the ratio of the effective mass to the bare mass of the electron is on the order of 1, the resistivity ρ must lie in a region from 1 to 100 mΩ cm for the "insulator regime" and σ_0/τ must stretch from 5×10^{26} to 5×10^{29} sec^{-2} for the "metallic regime" to meet this criterion. Clearly, our samples pass through these regions (see Table I). Thus the fact that we observe nearly no change of the PES line shape in our spectra is quite surprising if a significant extrinsic effect does exist.

To compare the experimental results and the theoretical expectation based on the argument of Ref. 2, we try to fit the spectrum of the undoped sample with theoretical formula (1) by adjusting parameters P_0 and r under the assumption of a constant DOS as in Ref. 2. This comparison is thought to be a good estimation of how reasonable the model calculation is. From this fit, we determine the values of parameters P_0 and r as well as σ_0/τ. Since $\sigma_0/\tau=ne^2/m^*$ in the Drude model, we expect its value to remain the same for Al-doped samples as well. In addition, there are no physical reasons for P_0 and r values to change significantly with small Al doping.[23] Hence we calculate the line shape of PES for the other two doped samples using formula (1) with the same values for P_0, r, and σ_0/τ, and compared with the experimental spectra. The results are displayed in Fig. 3 with the label of fitting 1. Here the calculated lines are convoluted with the experimental resolution of 40 meV in the FWHM, and the height of the spectra are adjusted to coincide with the experiment around 0.6 eV below the Fermi level.

For the $\delta=0$ case, we are able to fit the experimental spectrum quite well with the line shape calculated from Eq. (1) by proper choices of P_0 and r values. The resulting fitting values are similar to those in Ref. 2 except the zero-energy-loss probability P_0. Though P_0 in our fitting ($P_0=0.05$) is much larger than that of Ref. 2 ($P_0\leqslant0.0025$), it is still too small in comparison with the estimated value from the sum rule derived by Mills[7] ($P_0=0.35$) or with electron-energy-loss spectra taken by Schulte *et al.*[8] ($P_0=0.82$). For $\delta=0.03$ and 0.06 cases, we can see that the photoemission line shapes calculated from Eq. (1) with the same parameter values show severe discrepancies from those of experimental spectra. Note the behavior of resistivity dependence of calculated PES line shape. Even the small change of resistivity around 1 mΩ cm is expected to have a large effect on the line shape. Other parameters give a relatively weak dependence. This strong resistivity dependence of the PES line shape in Eq. (1) suggests the possibility that the PES can give severely distorted information about the density of states near the Fermi level when the material under investigation is a poor conductor like manganite, if the extrinsic Ohmic loss effect is indeed important.

The zero-energy-loss probability P_0 is assumed the same for all samples in fitting 1. In fitting 2, P_0 is also allowed to vary depending on the δ value to see if this gives better agreement with experiment, although we do not think P_0 should be so much dependent on sample resistivity. However, we see that the results of fitting 2 do not give significantly better agreement between theory and experiment than the case of fitting 1, even though we take P_0 as a free parameter for each δ. All the parameter values used in the above analyses are tabulated in Table I.

Next we try to fit our data with the sloping DOS near E_F. In this fit, we do not use the additional parameter r because using both the sloping DOS and r make the analysis too arbitrary. Figure 4 shows the results in detail. In this case, we can fit all the experimental spectra quite well, but the obtained parameter values seem to give another question. There is a large difference between the values of P_0 in the doped sample and in undoped samples. If we use a small value of P_0 for an undoped sample, the calculated spectrum always shows a steplike feature around 400-meV binding energy. This is the effect of a surface plasmon.[2] To remove this steplike feature in the calculated spectrum, P_0 value must be larger than 0.5 at least, as seen in Fig. 4. This abrupt change of P_0 value by more than one order of magnitude with small Al doping is not expected judging from the EELS study of the alloy semiconductor $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$,[24] and cannot be explained even if we include the multiple-scattering process.

From our experimental results and fittings, as stated above, we conclude that the experimental spectra do not show any symptom of significant Ohmic loss effect, and that theoretical line shapes cannot reproduce experimental spectra for our series of manganite samples in a reasonable way without much conflict. Hence it seems clear that the long-range Coulomb interaction between the outgoing photoelectrons and the sample left behind is not so large as suggested in Ref. 2. Our fitting results show that the only way to explain the experimental spectra consistently is to increase the P_0 value rather large, and this means that we can regard the PES spectra near the Fermi energy as a replica of the density of states in condensed matter whether its conductivity is good or not.

IV. CONCLUSION

In summary, we presented experimental evidence that the theory suggested in Ref. 2 cannot explain consistently the behaviors of photoemission spectra for a series of systems in which resistivities vary systematically. Hence we conclude that the influence of this long-range Coulomb interaction is not so large as can distort the photoemission line shape significantly.

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