Photoemission Line shape Study on La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Al$_3$O$_3$ ($\delta = 0, 0.03, 0.06$)

Han-Jin Noh

School of Physics & Center for Strongly Correlated Materials Research (CSCMR), Seoul National University, Seoul 151-742, South Korea

E.-J. Cho

Department of Physics, Chonnam National University, Kwangju, 500-757, South Korea

K.H. Kim†, H.-D. Kim‡, and S.-J. Oh†

School of Physics & CSCMR, Seoul National University, Seoul 151-742, South Korea (2001)

We have studied the line shapes of ultraviolet photoemission spectra of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Al$_3$O$_3$ ($\delta = 0, 0.03, 0.06$) 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, specially for poorly conducting system, can be very different from the intrinsic density of states because the outgoing electron has 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$_{1-x}$Al$_3$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 that paper.

I. INTRODUCTION

Photoemission Spectroscopy (PES) has been widely considered as the most powerful tool for probing the electronic structure of the occupied states in condensed matter systems. Conventionally photoemission process is explained by a three-step model 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 short-comings due to its semi-classical nature, has proved to be quite successful in explaining many features in photoemission spectra.

Recently, R. Joynt has 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, 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 $\rho_0 \gtrsim 0.1 m\Omega cm$), which is based on his 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 spectroscists pay attention to this assertion because the currently much-studied materials such as high-T$_c$ superconductors and colossal magnetoresistance (CMR) materials 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. D. S. Dessau et al. gave a technical comment that their angle-resolved photoemission (ARPES) of single crystalline double layered manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ shows the 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 Y.-D. Chuang et al. gave a new explanation about the pseudogap of this double layered manganite that it originates from a short range charge/orbital density wave enhanced by Fermi surface nesting. D. L. Mills followed up the approach of Ref. 2 with his own calculations to give different results using the sum rule which determines the total amount of energy loss probability, and suggested that the extrinsic loss just shifts the kinetic energy of all photoelectrons downward by roughly the same amount in the usual photoemission experiments. Schulte et al. presented several arguments, both theoretical and experimental, that the zero energy loss probability $P_0$ is not so small as was assumed in Ref. 2. They also obtained $P(\omega)$ from their electron energy loss spectroscopy (EELS) spectra of double layered manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ to calculate PES spectra and compare them with the photoemission spectra. From these comparisons they asserted this extrinsic effect cannot make pseudogap-like
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 [3], R. Haslinger et al. gave quantitative criterion when ohmic losses are important and pointed out the layered manganite \( \text{La}_{1-x}\text{Sr}_x\text{Mn}_2\text{O}_7 \) 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 theory and experiment, 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 evidences were reported as briefly described above, there are no reports that give the direct experimental comparison and analysis about 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 \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_1-x\text{Al}_x\text{O}_3 \) (\( \delta = 0, 0.03, \) and 0.06) systems. The transport properties of \( \text{Al} \)-doped \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) were well studied by Y. Sawaki et al. [10]. According to their reports, when a small amount of aluminum is doped in \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) it substitutes \( \text{B} \) site (\( \text{Mn} \) element) without any structural transition. Aluminum ion has the 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 the increase of random electrical potential, and the other is the local cutoff of magnetic interaction between the spins of \( t_{2g} \) electrons, i.e. it increases magnetic randomness. These changes are enough to cause a resistivity change of two orders of magnitude from \( \delta = 0 \) to \( \delta = 0.06 \). 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 \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \). Thus the increase of 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 affects 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 the changes of the carrier concentration or the electronic structure originating from phase transition [3]. (Recall in Drude model the DC conductivity is given by \( \sigma_0 = ne^2\tau/m^* \), where \( n \) is carrier concentration, and \( \tau \) relaxation time, \( m^* \) effective mass.) But in our case, all the parameters are fixed except for the scattering rate of carriers (or inversely relaxation time \( \tau \)).

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

\[
I(\omega, T) = P_0(T)N(\omega)f(\omega) + \int_0^\infty P(\omega' - \omega, T)N(\omega')f(\omega')d\omega'
\]

, where \([11]\)

\[
P(\omega) = 4\pi e^2 \frac{\text{Re}\{\sigma(\omega)\}}{\hbar \omega^2 (1 + \epsilon(\omega))^2}
\]

with the normalization condition

\[
1 = P_0 + \int_0^\infty P(\omega)d\omega.
\]

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, \( \epsilon(\omega) \) the dielectric function. To apply these formulae to the manganites, the Drude model was used with additional parameter \( r \) following the approach of Ref. 2:

\[
\epsilon(\omega) = \frac{4\pi i}{\omega} \sigma(\omega) = \frac{4\pi i}{\omega} (r + \frac{1}{1 - i\omega\tau})\sigma_0
\]

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 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 \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3 \) (\( \delta = 0, 0.03, 0.06 \)) were made by the standard solid state reaction method. Stoichiometric amounts of high purity (\( \geq 99.99 \% \)) \( \text{La}_2\text{O}_3, \text{SrCO}_3, \text{Al}_2\text{O}_3, \) and \( \text{MnO}_2 \) powders were weighed and mixed with a pestle and a mortar. After calcining and grinding repeatedly, resulting powders were pressed into a pellet. Three pellets of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3 \) (\( \delta = 0, 0.03, 0.06 \)) were prepared together. And, they were finally sintered
at 1440°C for 24 hrs 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 multi-channeltron electron energy analyzer with the energy resolution of 40 meV full width at half maximum (FWHM) at Seoul National University under the base pressure of $1.0 \times 10^{-10}$ torr. Photon source was unmonochromatized He 1 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.

### 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$_3$O$_7$ for three doping cases $\delta = 0$, 0.03, 0.06. Several prominent features can be seen in the spectra and are labeled as 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 2$p$ states. Peak C is usually assigned to O 2$p$ nonbonding states and peak E to Mn 3$d$-O 2$p$ bonding states [14][13]. Peak D around 4.5 eV in $\delta=0.03$ and 0.06 cases is thought to originate from Al 3$s$-$p$ 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$_3$ [14] and La$_{0.67}$Ca$_{0.33}$MnO$_3$ [15]. But small doping effects are clearly seen in several points. The position of peak E is slightly shifted to higher binding energy side and a small peak D appears around 4.5 eV as Al is doped. 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 Al$^{3+}$ ion replaces 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 2$p$ nonbonding states (peak C) show almost no change, as expected. 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 Fermi level and seem to be identical to undoped case [10]. From these spectra we infer that the overall electronic structures do not change much with doping and consistent with the results of structural and transport study by Y. Sawaki et al. [10]. This is a strong evidence that the increase of resistivity is not due to the change of electronic structure or phase transition, but due to the increase of scattering rates of carriers. We note that for the doped samples, specially $\delta = 0.06$, 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, resistivity curve and PES data show doped samples are still metallic. This behavior is similar to the cases of $\mathrm{La}_3\mathrm{Ca}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_6$ ($\Lambda = \mathrm{K, Rb}$), La$_{1.95}$Sr$_{0.05}$CuO$_4$, and Sr$_2$RuO$_4$ [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 ”Mn $e_g$ band” as Al is doped, which is as expected. Because the atomic cross section of O 2$p$ is about one order of magnitude larger than that of Mn 3$d$ at $h\nu=21.2$ eV [20], most of the spectral weight change near $E_F$ reflects the O 2$p$ 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 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 [3] there are two inequalities that should be satisfied by samples for the extrinsic effect to be important in PES. For our experiments with the values of the analyzer resolution $R = 40$ meV, band structure width of interest $B = 1$ eV, carrier concentration $n = 1.5 \times 10^{22} \text{cm}^{-3}$ under the assumption that the ratio of effective mass to bare mass of electron is order of 1, resistivity $\rho$ must lie in the region from 1 to 100 $\text{mOhm cm}$ for ”insulator regime” and $\sigma_0/\tau$ from $5 \times 10^{26}$ to $5 \times 10^{29} \text{sec}^{-2}$ for ”metallic regime” to meet this criterion. Clearly, our samples pass through these regions (see table 1). So the fact that we observe nearly no change of PES line shape in our spectra is quite surprising if 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 undoped sample with the 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 on how reasonable the model calculation is. From this fit, we determine the values of parameters $P_0$ and $r$ as well as $\sigma_0/\tau$. Since $\sigma_0/\tau = ne^2/m^* r$ 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 [22]. 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 $\sigma_0/\tau$, 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 FWHM and the height of spectra are adjusted to coincide with the experiment around 0.6 eV below the Fermi level.

For \( \delta = 0 \) case, we are able to fit the experimental spectrum quite well with the line shape calculated from eq. (1) by proper choice 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 \((P_0 \leq 0.0025)\), it is still too small in comparison with the estimated value from the sum rule derived by D. L. Mills \([7]\) \((P_0 = 0.35)\) or electron energy loss spectra (EELS) taken by K. 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 m\( \Omega \)cm is expected to make large effect on the line shape. Other parameters give relatively weak dependence. This strong resistivity dependence of PES line shape in eq (1) suggests the possibility that the PES can give severely distorted information about the density of states near Fermi level when the material under investigation is a poor conductor like manganites, 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 \( \delta \)-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 free parameter for each \( \delta \). 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 sloping DOS and \( r \) makes 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 big difference between the values of \( P_0 \) in doped sample and undoped ones. If we use a small value of \( P_0 \) for undoped sample, the calculated spectrum always shows the step-like feature around 400 meV binding energy. This is the effect of surface plasmon \([9]\). To remove this step-like 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 alloy semiconductor Al\(_x\)Ga\(_{1-x}\)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 the 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 was 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 Fermi energy as the replica of the density of states in condensed matter whether its conductivity is good or not.

### IV. CONCLUSION

In summary, we presented an 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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The resistivity of polycrystalline manganites is always higher than that of single crystals due to the intergrain tunneling effect.\cite{17}\[19\]. To estimate the mean free path, intragrain conductivity must be used, which can be obtained from single crystal sample\cite{10}. Under the assumption of a spherical Fermi surface, the mean free path $l$ is given by $l = \hbar / \omega_{F \sigma_{tra}} e^2$ if the Drude formula is used. Taking $n = 1.5 \times 10^{22} \text{cm}^{-3}$\cite{21}, we obtain $l = 2.25/\rho_{polycr}$. Here, $\rho_{polycr}$ means the resistivity in $m \Omega \text{cm}$ unit. If we take $\rho_{polycr} = 0.3$ for $\delta = 0.06$ sample, $l = 7.5$ Å, which is close to the unit cell spacing $a \sim 8$ Å.

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\[23\] If we consider multiple scattering process, the sum rule\cite{8} does not hold, and $P_0$ can change with Al doping because the dopant Al cause the change of dielectric constant in our system through the change of relaxation time. However, its dependency cannot be strong under the condition of no structural transition and constant carrier concentration, which is consistent with EELS experiments on Al$_x$Ga$_{1-x}$As\cite{22}. In the case of $r$ value, it represents the incoherent part of optical conductivity, which is almost constant below 0.1 eV in infrared spectroscopy data. There is no clear reason why this incoherent part must be affected by the increase of scattering rates of carriers. Furthermore, many results of optical conductivity of manganites\cite{22} indicate that the incoherent part will remain almost the same with small Al doping since the electronic structure does not change and the carrier concentration and temperature are fixed in this study.

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FIG. 1. Valence band photoemission spectra of La$_{0.7}$Sr$_{0.3}$Mn$_{1-\delta}$Al$_{\delta}$O$_3$. Solid, dashed, dotted lines are for $\delta = 0, 0.03, 0.06$ samples respectively. All the spectra are taken using He I line (h$\nu$ = 21.22 eV) at the temperature 95 K.

FIG. 2. Near E$_F$ photoemission spectra of La$_{0.7}$Sr$_{0.3}$Mn$_{1-\delta}$Al$_{\delta}$O$_3$. Solid line is for $\delta = 0$, solid circles for $\delta = 0.03$, solid squares for $\delta = 0.06$. Vertical line is the Fermi level determined by the reference Au sample.

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 sloping DOS. For each experimental spectrum, the same sloping DOS is used as shown with the dashed line in $\delta = 0$ case.

TABLE I. Parameter values in the analyses. The resistivities of each sample are taken at 95 K. $\sigma_0/\tau$ should be the same for all samples in the Drude model, since it is equal to $n e^2/m^*$. $r$ 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.

| $\delta$ | $\rho$ (m$\Omega$cm) | $\sigma_0/\tau$ (1/sec) | r | $P_0$ (fit 1) | $P_0$ (fit 2) | $P_0$ (sloping DOS) |
|----------|----------------------|-------------------------|---|----------------|--------------|---------------------|
| 0.00     | 0.29                 | $6.08 \times 10^{28}$   | 0.25 | 0.05          | 0.05         | 0.5                 |
| 0.03     | 4.8                  | "                       | "  | "             | 0.12         | 0.03                |
| 0.06     | 13.0                 | "                       | "  | "             | 0.10         | 0.03                |