Temperature-dependent photoemission spectral weight in $La_{0.6}Sr_{0.4}MnO_3$

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We report temperature-dependent redistribution of spectral weight in photoemission spectra of $La_{0.6}Sr_{0.4}MnO_3$ over a wide energy range of several eV. We attribute this to a change in the electron correlation strength induced by the changing degree of ferromagnetic order with temperature. We discuss the relationship between the temperature-dependent spectral weight close to the Fermi level and the unusual transport properties.

Following the discovery of high-T_c cuprates, metal-insulator transitions (MIT) induced by doping of charge carriers into a Mott insulator have been extensively studied. MIT can also be achieved in the absence of any doping by altering the interaction strengths, namely, the Coulomb interaction strength U, the charge-transfer energy Δ, and the hopping interaction strength t_{pd} between the transition metal d and oxygen p states.[1] This can arise from a change in temperature, pressure, or composition affecting the lattice parameters or distortion. For example, temperature-driven first order MIT in V_2O_3 (Ref. 2) or composition-driven MIT in LnNiO$_3$ (Ln = rare earth) (Ref. 3) are well known. In these cases, changes in crystal structure affect the magnitude of the band gap, $\sim U$ or $\sim\Delta$, or the effective d-band width, W.[4] Unusual spectral weight transfer has been observed by tuning U/W in a series of early transition metal oxides.[5,6]

With respect to the above discussion, the family of compounds $La_{1-x}Sr_xMnO_3$ exhibits very unusual properties and has attracted considerable attention in recent years.[7–12] $LaMnO_3$ is an A-type (layered-type) antiferromagnetic insulator. When it is doped with holes as in $La_{1-x}Sr_xMnO_3$, it exhibits a temperature induced paramagnetic to ferromagnetic transition with unusual transport properties. For example, the resistivity (ρ) shows an insulating behavior ($d\rho/dT < 0$) for $x \geqslant 0.2$ in the paramagnetic regime, but becomes metallic with a rapid decrease of resistivity in the ferromagnetic regime.[8,12] Magnetization in the ferromagnetic state is found to increase with decreasing T below T_c,[7,8] indicating an increasing extent of ferromagnetic order with a concomitant decrease in resistivity. Mn ions are in the high-spin state and are fully spin polarized at the lowest temperatures. The resistivity ratio between the room and low (20 K) temperatures is about $\sim 10^2$ for $x = 0.2$, about ~ 20 for $x = 0.3$, and about ~ 10 for $x = 0.4$.[13] These results suggest that the mobility of doped holes in these compounds is intimately connected with the development of a ferromagnetic correlation and indicates an unusually strong coupling between transport and magnetic properties. This is further evidenced by the observation of giant negative magnetoresistance in this family of compounds, $La_{1-x}M_xMnO_3$ (M = Ca, Sr, or Ba),[12] since the application of a magnetic field induces an increase in the ferromagnetic order. It is also to be noted that these unusual changes in the transport properties cannot be attributed to any changes in the bare electronic interaction energies, such as U, Δ and t_{pd}, since the structural parameters do not change significantly with temperature.

In this work, high-resolution temperature-dependent photoemission experiments probing the high-energy scale show an unusual redistribution of spectral weight with temperature which parallels the unusual low-energy properties of these systems. In particular, unique changes in the spectral weight close to the Fermi level (E_F) with T appears to be directly related to the temperature-dependent transport properties. We interpret our results with the help of spin-polarized band-structure calculations and the Anderson-Hasegawa theory[15] of Zener double-exchange mechanism[16] and argue that electron correlation strength, U/W, is a sensitive function of temperature arising from a simultaneous change of the effective d-band width (W), as well as the effective Coulomb interaction strength (U).

Polycrystalline samples of $La_{0.6}Sr_{0.4}MnO_3$ were prepared by solid-state reaction as described elsewhere.[9,10] The T_c of the sample was $\sim$ 350 K, so that the present measurements have been made below T_c. The total resolution of photoemission spectra was $\sim$35 meV for He I ($h\nu$ = 21.2 eV) spectra and $\sim$ 75 meV for He II ($h\nu$ = 40.8 eV) spectra.

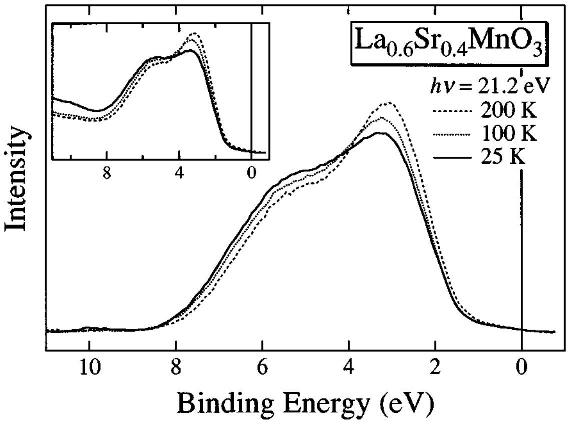

FIG. 1. Valence-band photoemission spectra of $La_{0.6}Sr_{0.4}MnO_3$. The inset shows raw data without background subtraction.

Spectra were recorded after cleaning the sample surface by *in situ* scraping with a diamond file. At each temperature, the scraping was repeated until no feature about 10 eV below E_F, which is well known due to contamination or surface degradation of oxide samples, was seen. Further, time dependence of the spectra was monitored after each scraping and collected only data taken within 0.5–2 h of scraping depending on the temperature. The temperature dependence of the spectra were fully reproducible for several temperature cycling (lowering and raising) and for different samples (Tsu-Kyoto and Bangalore) and different instruments (Tokyo and Berlin). The Fermi level has been calibrated by evaporating Au onto the sample and measuring at each temperature.

We show He I spectra recorded at different temperatures in Fig. 1. The spectra have been normalized to the same integrated area after removing an integral background, which slightly changed with scraping, temperature and/or sample positioning, but the temperature dependence of the spectra shown here is so substantial that it is free from such background subtraction procedure. This is clearly evidenced in the raw data shown in the inset of Fig. 1. From these figures, it is evident that there is a transfer of spectral weight from higher ($>$ 4 eV) to lower binding energies (between 1 and 4 eV) with increasing temperature. This temperature dependence is indeed opposite to what would be expected for surface degradation; surface degradation increases O $2p$ features at higher binding energies ($\sim$6 eV) at higher temperature as has been observed in high-T_c cuprates. Therefore, we believe that the observed changes reflect intrinsic bulk properties. Such spectral weight transfer as a function of temperature over such a wide energy range has never been observed in any other system and suggests an unusual temperature dependence of the electronic structure. The spectral intensity close to E_F in Fig. 1 appears to be very low in every case. He II spectra exhibit nearly the same behaviors, in spite of the greater Mn $3d$ contribution, because of the strong Mn $3d$-O $2p$ mixing. Our recent experiment on $La_{0.8}Sr_{0.2}MnO_3$ also shows similar redistribution of spectral weight over the same range of energies with changing T, while $La_{1-x}Sr_xCoO_3$ spectra do not.[17] This strongly suggests that this unusual redistribution of spectral weight is indeed an intrinsic property unique to $La_{1-x}Sr_xMnO_3$. Although the origin of this effect is not clear at the moment and further theoretical input will be important, it is tempting to associate the effect with the changing ferromagnetic order as described below.

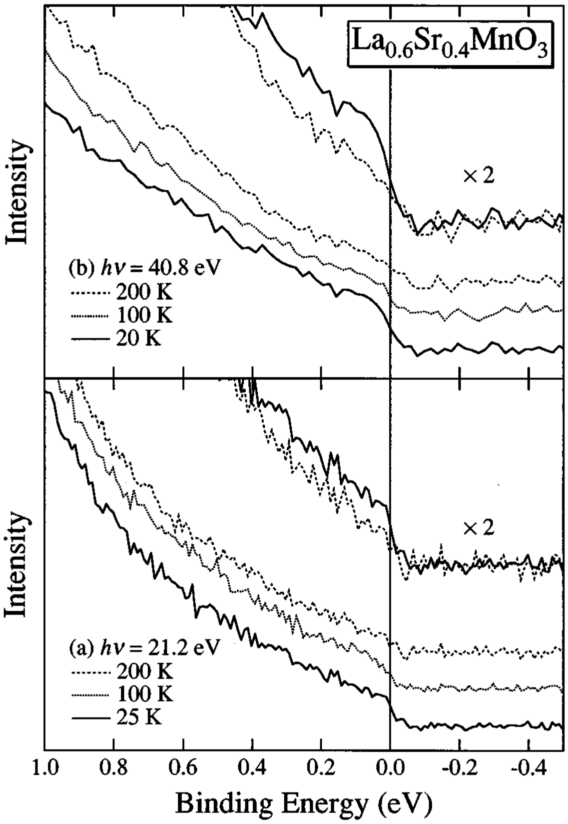

FIG. 2. Photoemission spectra of $La_{0.6}Sr_{0.4}MnO_3$ near E_F.

We have recorded spectra with better signal-to-noise ratio over a narrow energy range close to E_F, as shown in Fig. 2. At the lowest temperature, both He I and He II spectra exhibit clear evidence of a Fermi cutoff. With increasing T, the intensity between E_F and 0.8 eV below decreases systematically. This can be seen clearly in the figure where we have superimposed the spectra at two extreme temperatures for comparison. In this comparison, we have normalized the entire spectral intensity of each spectrum shown in Fig. 1. It is to be noted that if we adopt an alternate approach and normalize the peak heights to be the same in Fig. 1, the changing intensity near E_F will be further enhanced. Thus, the decreasing intensity at E_F with increasing T appears to be a clearly intrinsic effect independent of the normalization procedure. This interesting temperature dependence has not been observed in any other metallic substance, where apart from a broadening in the Fermi-Dirac distribution, the Fermi edge is not influenced by temperature. Since the Mn $3d$-to-O $2p$ relative cross section increases with photon energy, the higher Fermi edge intensity in the He II spectra indicates that Mn $3d$ contribution to the states at E_F is larger. From the present results, it is natural to assume that the temperature-dependent spectral weight at E_F is intimately related to the temperature-dependent magnetic and transport properties.

To understand the interdependence between magnetic

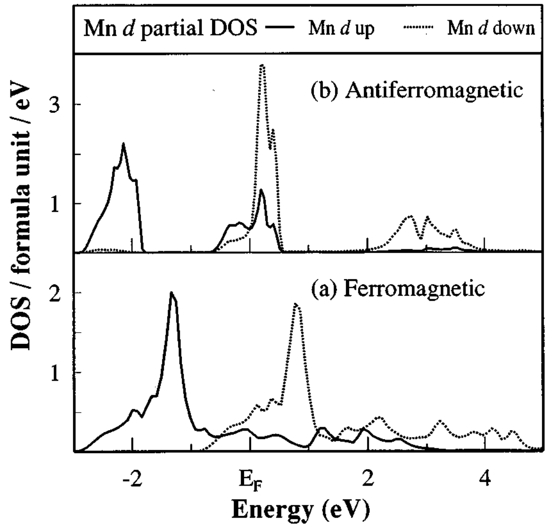

FIG. 3. Mn $3d$ partial DOS of cubic $LaMnO_3$ calculated using the LSDA for (a) ferromagnetic and (b) antiferromagnetic states.

properties and electronic structure, we determined the Mn d partial density of states (DOS) in cubic $LaMnO_3$ by *ab initio* local-spin-density approximation (LSDA) band-structure calculations employing the linearized muffin-tin orbital method for ferromagnetic and (G-type) antiferromagnetic states, as shown in Fig. 3. We believe that band-structure results for the antiferromagnetic state, rather than that for the paramagnetic state, is more relevant for the spectral features above the transition temperature, due to the existence of local short range antiferromagnetic correlations in the paramagnetic state. This may be suggested by the fact that the *ab initio* antiferromagnetic band structure provides a good description for the spectroscopic features.[14] Figure 3 shows that Mn d states are split into low-lying narrower t_{2g} and high-lying broader e_g subbands, due to the cubic crystal field; each of these subbands is further split into up- and down-spin bands, due to exchange splitting. The bandwidths of the t_{2g} and e_g bands are found to be 2 and 4 eV, respectively, in the ferromagnetic case [Fig. 3(a)], while they are severely reduced in the antiferromagnetic case (by about a factor of 2). This demonstrates that, while the crystal structure governing the electronic interaction strengths remain unchanged, magnetic structure has a pronounced effect on the d band width. This evidently arises from a variation of the effective charge-transfer energy between the nearest neighbor Mn sites in the antiferromagnetic case, in presence of a large exchange interaction strength, J; this effect is absent in the ferromagnetic state, with all Mn sites being equivalent.

The above result is closely related to the works of Zener,[16] as well as Anderson and Hasegawa[15] who addressed the question of ferromagnetism in doped $LaMnO_3$ system many years ago. First, we note that the band-structure results in Fig. 3 suggest a J value of more than 2 eV ($\sim 3j$, where j is the e_g- t_{2g} exchange integral), as well as an effective d-d hopping strength (t) of less than 0.2 eV and about 0.3 eV for the t_{2g} and e_g subbands, respectively, in the ferromagnetic case, implying $j > t$. While Zener had assumed an infinitely large j, Anderson and Hasegawa worked out the details of the model with finite j and in two different limits of $j >> t$ and $j << t$. Our estimates here establish the former as the more realistic limit. In this limit, W was shown[15] to vary as $\cos(\theta/2)$, where θ is the angle between the spin moments at the two adjacent sites. Thus, when the system becomes ferromagnetic from the antiferromagnetic state, θ approaches zero with a consequent increase in W. This result is clearly reflected in the band-structure results shown in Fig. 3. These authors also pointed out that in presence of disordered spin moments, the bandwidth will again be narrowed in analogy to the electron motion in a disordered alloy system. It is to be noted here that the magnetization continuously increases with lowering of temperature within the ferromagnetic state in $La_{1-x}Sr_xMnO_3$,[8] indicating an increasing order of the spin moments with decreasing T. This is then expected to increase the effective bandwidth W with decreasing T, even within the ferromagnetic state that we have probed experimentally in this present work.

Interestingly, the effective Coulomb interaction strength U in the present system is also dependent on the degree of ferromagnetic order and hence on T. This can be easily understood by considering once again the limiting cases of ferromagnetic and antiferromagnetic arrangement of the magnetic moments. The energy associated with the nearest neighbor Mn-Mn charge fluctuation in the ferromagnetic state is U-J, due to the exchange stabilization of parallel spins, while the same fluctuation in the antiferromagnetic state costs an energy U. Thus, we expect the energy U_{eff} associated with the nearest neighbor charge fluctuation to decrease continuously from U to U-J with increasing ferromagnetic order in the system. Since the transfer of spectral weight from the coherent to the incoherent part is controlled by U_{eff}/W,[5,6] the decrease of the intensity at E_F with temperature (Fig. 2) is a direct consequence of decreasing W, as well as of effectively increasing U arising from the decrease in the degree of ferromagnetic order. While it would be most desirable to have direct evidence of changing U and W from the spectroscopic data, the intrinsic low intensity of the coherent feature near E_F with overlapping spectral intensities of other features at higher binding energies (see Fig. 1) makes it impossible to obtain an estimate of these parameters. Thus, we can only infer about the changing strength of U/W based on the transfer of spectral weight from the coherent features near E_F to higher binding energies and theoretical considerations presented here.

In view of the above discussions, this class of compounds provides a unique opportunity to study MI transitions by a continuous tuning of U/W with variation in temperature. Normally, a change of U/W is introduced by changing samples or crystal chemistry, which makes it difficult to vary U/W continuously. The unambiguous description that emerges from our results is that the single-particle spectral weight at the Fermi energy decreases smoothly with increasing U/W. This means that the k mass, m_k, which represents the momentum dependence of the electron self-energy $\Sigma(\mathbf{k},\omega)$ $(m_k/m_b \equiv [1+(m_b/k)\partial\,\mathrm{Re}\Sigma(\mathbf{k},\omega)/\partial k]^{-1}|_{k=k_F}$, where m_b is the bare band mass), decreases since the intensity at E_F is given by $A(0) = (m_k/m_b)N_b(0)$,[6,18] where $N_b(0)$ is the DOS at E_F given by LSDA band-structure calculations. The decrease in $A(0)$ cannot be due to a decrease in $N_b(0)$ with changing magnetic correlation, because the exchange splitting of the d band would reduce $N_b(0)$ in the ferromagnetic state compared to the paramagnetic state. On the other hand, narrowing of the conduction bandwidth ($\propto 1/m^*$) with temperature has been suggested from a decrease of the Drude weight in the optical spectra of $La_{0.825}Sr_{0.175}MnO_3$.[11] In photoemission spectra, the coherent-to-incoherent spectral weight ratio is given by $1/(m_\omega/m_b - 1)$, where $m_\omega/m_b \equiv 1 - \partial\, \mathrm{Re}\Sigma(\mathbf{k},\omega)/\partial\omega|_{\omega=0}$. Since $m_\omega = (m^*/m_k)m_b$, $m^* \to \infty$ and $m_k \to 0$ means that spectral weight transfer from the coherent part near E_F to the incoherent part [apparently located 1–2 eV below E_F (Ref. 10)] is very dramatic. Since the ω mass, m_ω, represents the dynamical contribution to the mass enhancement, $m_\omega/m_b >> 1$ already at the lowest temperature means that the conduction electrons are strongly correlated in the ferromagnetic metallic state.

At present, there are no available theoretical results that can be directly compared with the present results. Calculations of single-particle spectral weight within the doped two-dimensional Hubbard model do not exhibit any comparable temperature effects.[19] Infinite-dimension calculations for the Hubbard model with integer filling suggest that the transfer of spectral weight from the coherent to the incoherent part is entirely due to the narrowing of the coherent part with increasing U/W and not due to the decrease in the spectral weight at E_F, that is, m_k/m_b remains unity for all U/W.[20] While experimental observations on a large number of systems do not provide any conclusive support for this theoretical prediction, there is always the possibility that the right regime of U/W has not been reached in the experiment. The present type of experiment circumvents that problem by providing a continuous tuning of U/W by changing temperature.

So far, we have considered that changing temperature in the present system is equivalent to changing U/W. Within the U/W-δ plane, where δ is the doped hole concentration, one moves along the $\delta = 0.4$ line parallel to the U/W axis in the present experiment. In the ''bandwidth-control'' system $Sr_{1-x}Ca_xVO_3$ with $\delta = 0$, as U/W increases ($U/W \to 1$), m_k and m_ω steeply decreases and increases, respectively, while m^* inceases only slowly.[6] Comparison between different routes to a MI transition in the U/W-δ parameter space would require further systematic studies.

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