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Temperature dependence of the electronic structure of the charge-ordering manganite $Pr_{0.5}Sr_{0.5}MnO_3$

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We study the changes in the occupied density of states of $Pr_{0.5}Sr_{0.5}MnO_3$ as a function of temperature (25–300 K) using photoemission spectroscopy. The spectral weight transfer across the metal-insulator/charge-ordering/ferromagnetic-antiferromagnetic transition is abrupt and over very large energy scales (up to 1.2 eV from the Fermi level E_F) compared to the transition temperature $T_{mi}=140$ K (~12 meV) and the gap value in the insulating phase (~100 meV). Negligible changes observed at E_F in the ferromagnetic-metallic phase above T_{mi} and a weak spectral weight transfer across the ferromagnetic-paramagnetic transition at $T_{fp}=270$ K are consistent with negligible change in carrier density above T_{mi}. [S0163-1829(97)50948-9]

In the last ten years there has been tremendous interest in the study of transition-metal oxides due to the discovery of a variety of electronic, magnetic, and structural transitions. Preeminent among them are high-temperature superconductivity in layered cuprates[1] and colossal magnetoresistance (CMR) in the three-dimensional manganese perovskite oxides $A_{1-x}B_xMnO_3$ (A: La, Pr, Nd, Bi, etc., B: Ca, Sr, Ba, etc.).[2] The earliest work by Jonker and Van Santen on the manganese perovskites $La_{1-x}Sr_xMnO_3$ showed that hole doping (obtained by substituting Sr^{2+} for La^{3+}) of the parent insulating antiferromagnetic compound resulted in a ferromagnetic-metallic phase at low temperatures beyond a critical doping concentration x_c.[3] The tremendous interest in CMR of these systems is relatively recent[4,5] but has attracted enormous attention due to its intriguing behavior. The properties of the antiferromagnetic insulating parent and the transition to a ferromagnetic metal with CMR on doping is not easily understood in the framework of a simple one-electron band theory alone. While recent local spin-density approximation (LSDA) (without and with on-site Coulomb correction, LSDA/LDA+U) band-structure calculations[6] do give an insulating ground state for $LaMnO_3$ (Mn^{3+} in $LaMnO_3$ has the $t_{2g}^3e_g^1$ configuration), the most suitable picture for explaining the thermodynamic properties of the hole doped e_g band requires a strong electron-phonon coupling due to polaronic transport, a Jahn-Teller distortion, and a Zener-type double-exchange mechanism with a strong Hund coupling, as is borne out by recent theoretical and experimental results.[4,5] In the Zaanen-Sawatsky-Allen (ZSA) scheme,[7] these systems are characterized by the relative strengths of the on-site Coulomb correlation energy (U), the charge-transfer energy (Δ), and the hybridization strength between the Mn $3d$ and O $2p$ states (t_{pd}). The actual ground state requires additional considerations of the exchange splitting, the crystal-field splitting, spin and orbital ordering, to explain various properties. Estimates exist for the above energies in the literature from electron spectroscopy[8,9] as well as band calculations.[6] The estimates are not uniquely determined but in every case they are a few eV in magnitude—e.g., for $LaMnO_3$, on-site U has been estimated to be about 4–8 eV, Δ~4–5 eV, and t_{pd}~1.8–2.2 eV (Refs. 6, 8, and 9) and indicate a fairly mixed character ground state in the ZSA picture. More recently, the metal-insulator/charge-ordering first-order transitions observed in single crystal manganites near or at a 1:1 ratio for Mn^{3+} and Mn^{4+}, e.g., $La_{0.5}Ca_{0.5}MnO_3$ ($T_{mi}=135$ K),[5,10] $Pr_{0.5}Sr_{0.5}MnO_3$ ($T_{mi}=140$ K),[11,12] $Nd_{0.5}Sr_{0.5}MnO_3$ ($T_{mi}=158$ K),[13] $Pr_{1-x}Ca_xMnO_3$ ($T_{mi}=230$ K),[14] followed by a ferromagnetic-paramagnetic transition in the metallic phase at higher temperatures, T_{fp}, has provided another opportunity to study new aspects of these complex transitions. Coupled to the metal-insulator transition is a ferromagnetic-antiferromagnetic transition as well as a sharp change in the lattice parameters.[5,14] As discussed above, the parameters determining the electronic structure of these oxides are more than two orders of magnitude larger than the transition temperature. This indicates that the thermodynamic properties are so finely tuned that they can undergo dramatic changes driven by a low-energy scale like temperature. Novel phenomena such as magnetic-field induced melting of the ordered phase,[12,13] photoinduced insulator-metal transitions,[15] and magnetic-field induced structural transitions[16] confirm that these systems are very close to critical points, and that the systems are truly spin-charge-lattice coupled systems.

In this paper we investigate the electronic structure of $Pr_{0.5}Sr_{0.5}MnO_3$ as a function of temperature using photoemission spectroscopy. The results provide clear spectral changes in the occupied density of states (DOS) across T_{mi}

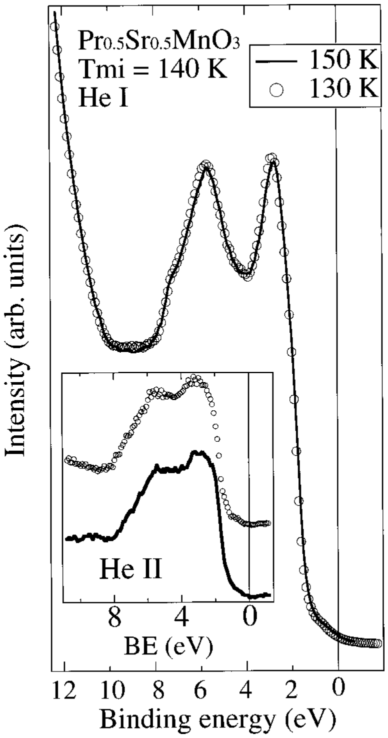

FIG. 1. Valence-band spectra of $Pr_{0.5}Sr_{0.5}MnO_3$ obtained across the m-i/ferro-antiferro transition using He I photons ($h\nu = 21.2$ eV). The spectra at 130 K and 150 K are superimposed to show that negligible changes are obtained over wide energy scales across $T_{mi} = 140$ K. Inset: Valence-band spectra of $Pr_{0.5}Sr_{0.5}MnO_3$ obtained using He II photons ($h\nu = 40.8$ eV).

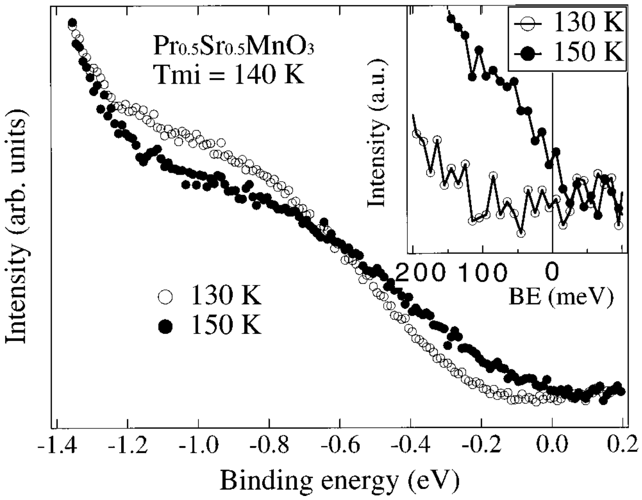

FIG. 2. Spectral changes of $Pr_{0.5}Sr_{0.5}MnO_3$ obtained across the m-i/ferro-antiferro transition showing the gap closure and spectral weight transfer over 1.2 eV from the Fermi level (E_F). Inset: Near E_F region on an expanded scale with better S/N ratio showing a gap of nearly 100 meV below T_{mi} and a finite small DOS at E_F above T_{mi}.

with an abrupt closure of the insulating gap. We discuss the implications of the energy scales and the temperature dependence of the spectral changes in conjunction with transport measurements.

Single-crystal $Pr_{0.5}Sr_{0.5}MnO_3$ was prepared by the traveling solvent floating zone method. The samples were characterized for structure using x-ray diffraction and the electrical and magnetic transitions were confirmed to be as reported earlier.[12] Photoemission spectroscopy was performed using He I and He II photons ($h\nu = 21.2$ and 40.8 eV, respectively) in a homebuilt spectrometer using a 300-mm hemispherical analyzer. Due to low count rates, the energy resolution was set at 70 meV for the near Fermi level spectra. Samples were cleaved *in situ* to obtain clean surfaces and the spectra were reproducible for two samples and on cycling through the charge-ordering transition. The experiments were done on single-crystal surfaces obtained by cleaving, but since the obtained surfaces were not perfectly uniform the spectra had no angular dependence over a variation of the Brillouin zone. The spectra thus correspond to angle-integrated density of states. The spectra were stable up to approximately ten hours after cleaving, beyond which the intensity at E_F decreased gradually and a new feature showed up at about 9.5-eV binding energy due to surface degradation. The samples were mounted on a cold finger of a closed-cycle cryostat and the temperature was measured to an accuracy of +/−2 K using a calibrated Pt resistor.

Figure 1 shows the He I ($h\nu = 21.2$ eV) valence-band photoemission spectra of $Pr_{0.5}Sr_{0.5}MnO_3$ obtained at 130 and 150 K, across the metal-insulator transition at $T_{mi} = 140$ K. The spectra are superimposed to show that no temperature-dependent changes occur in the spectral intensity over large energy scales consisting of two prominent features at nearly 6-eV and 3-eV binding energy. A weak intensity feature centered at less than 1-eV binding energy is also observed and is discussed in detail later; the temperature-dependent changes occur only in this feature and have a direct relation with the thermodynamic properties. Comparing with band-structure calculations[6] as well as electron spectroscopy results on the related manganites $La_{1-x}B_xMnO_3$ (B = Ca, Sr, Pb),[8,9] we understand that the 6-eV binding energy feature consists essentially of the O $2p$ derived states while the 3-eV feature has a dominant Mn $3d$ t_{2g} character, with the feature within 1 eV of the Fermi level consisting of Mn e_g derived states. Note that the peak at 3 eV is much more intense compared to the $LaMnO_3$ spectrum,[8] suggesting that the Pr $4f$ occupied states occur at about the same binding energy as the Mn $3d$ t_{2g} derived states. A similar result is known from a resonant photoemission study[17] of $PrNiO_3$ in comparison with $LaNiO_3$, which also crystallize in the perovskite structure, though a resonant photoemission study is awaited for the present system.

In the inset to Fig. 1, we show the valence-band spectra obtained using He II photons ($h\nu = 40.8$ eV) and the spectra are quite similar to the He I spectra discussed earlier. The slight change in relative intensities and broadening of the feature at 3-eV binding energy is consistent with the increase in atomic cross sections due to the Mn $3d$ and Pr $4f$ derived states.[18] It indicates the strong hybridization between the Mn $3d$ and O $2p$ states, pointed out by Pickett and Singh,[6] and also known from earlier electron spectroscopy studies on related manganites.[8,9] In order to investigate the temperature-dependent changes in the e_g derived band we measured the same with better signal-to-noise (S/N) ratio as shown in Fig. 2. The spectra obtained at 130 and 150 K are normalized for total intensity in order to emphasize the changes obtained across the metal-insulator/charge-ordering transition at T_{mi}

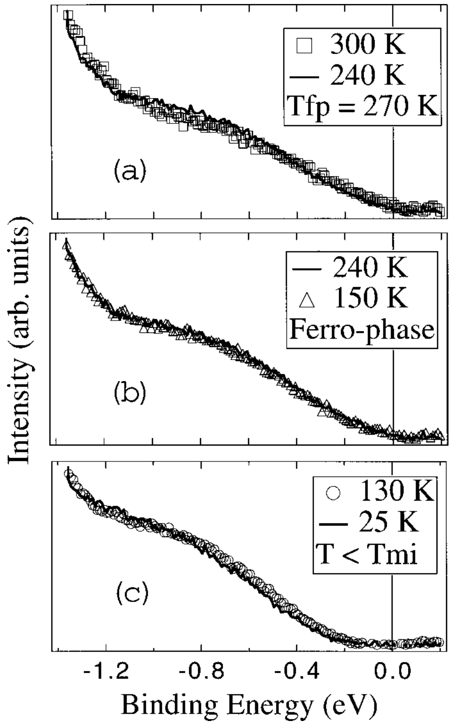

FIG. 3. Temperature-dependent spectra of $Pr_{0.5}Sr_{0.5}MnO_3$ (a) at $T=240$ and 300 K, across the paramagnetic-ferromagnetic transition at $T_{fp}=270$ K showing negligible change at E_F, though small changes are seen further away from E_F, (b) at 150 and 240 K, indicating no changes in the ferrometallic phase as a function of temperature, and (c) at 25 and 130 K, showing negligible change in the insulating phase.

$=140$ K. A clear transfer of spectral weight is observed over an energy scale of about 1.2 eV. In the inset to Fig. 2, we plot the spectra near E_F to get a measure of the gap in the low-temperature insulating phase. The 130-K spectrum shows that $Pr_{0.5}Sr_{0.5}MnO_3$ has a gap of nearly 100 meV in the insulating phase. In contrast, the spectrum at 150 K shows a small but finite DOS at E_F, consistent with its metallic character above T_{mi}. Thus we find the surprising result that the metal insulator transition is accompanied by a spectral weight transfer over an energy scale (~1.2 eV) much larger than the transition temperature ($T_{mi}=12$ meV) as well as the gap in the occupied density of states (nearly 100 meV).

In order to investigate changes in the different phases, we have checked for temperature dependence of the valence band from 25 to 300 K. In Fig. 3(a) we plot the valence-band spectra across the ferromagnetic-paramagnetic transition at $T_{fp}=270$ K, which shows very small spectral weight transfer in the Mn e_g derived band from near E_F to about 0.5–1.0 eV below E_F. This suggests that the change in the temperature dependence of the transport properties at the ferro-para transition has a very small contribution from a change in the DOS, particularly at E_F. This is consistent with recent Hall coefficient measurements, which show that carrier density does not depend on temperature or magnetic field above T_{mi}.[19] In Fig. 3(b), we compare the spectra obtained at 150 K and 240 K in the ferromagnetic-metallic phase and find no change in the spectra. A similar behavior is seen in the low-temperature insulating phase below 140 K, with the spectra obtained at 25 K and 130 K showing negligible change [Fig. 3(c)]. These observations are quite consistent with recent studies, which show that while the lattice parameters show a sharp change at T_{mi}, they show negligible changes for $T<T_{mi}$ or for $T>T_{mi}$.[13,20]

Our photoemission spectroscopy results show that the spectral weight transfer at T_{mi} is abrupt and occurs over a very large energy scale (~1.2 eV from E_F), which is an order of magnitude larger than the gap in the occupied DOS, about 100 meV (if we assume the chemical potential to be at the center of the gap, the total gap is estimated to be 200 meV), and which is itself another order of magnitude larger than the transition temperature $T_{mi}=140$ K$=12$ meV. A recent tunneling spectroscopy study[21] of the charge-ordering transition in $Nd_{0.5}Sr_{0.5}MnO_3$ ($T_{mi}=158$ K) reports a value of ~250 meV for the total gap, and thus matches well with the gap measured by us. A difference in magnitudes of energy scales of the transition temperature, the gap, and the spectral weight transfer has also been observed in two other systems: (i) quasi-one-dimensional conductors Dicyanoquinone-diimine (DCNQI)-Cu,[22] which exhibits a charge-density wave transition, and (ii) for the Verwey transition in Fe_3O_4.[23] Recent photoemission and optical spectroscopy results on the Mott-Hubbard system $Ca_xSr_{1-x}VO_3$ have shown that spectral weight transfer over large energy scales determined by on-site U are well explained by changing U/W (where W is the bandwidth) in the dynamical mean-field theory.[24] However, in the present case, a similar situation does not apply because U/W does not change as a function of temperature. Also, while spectral weight transfer over large energy scales (~2 eV) determined by the Hund coupling energy has been observed in the CMR manganites,[5] the charge-ordering transition does not occur in all manganese perovskites, but only close to, or at, a Mn^{3+}:Mn^{4+} ratio of 1:1. In contrast, CMR is observed in all manganese perovskites in the ferromagnetic metallic phase with evidence for polaronic transport.[4,5] Based on these facts, Lee and Min[25] model the charge-ordering manganites as a system in which a competition between nearest-neighbor repulsion and double-exchange results in the first-order ferromagnetic metal-antiferromagnetic insulator transition at T_{mi}. This is analogous to the charge ordering known in Fe_3O_4 (Ref. 26) and $La_{2-x}Sr_xNiO_4$ ($x=\frac{1}{3},\frac{1}{2}$),[27] which share many aspects of an order-disorder transition with charge-ordering manganites. In a very recent study, Mizokawa and Fujimori[28] show from an unrestricted Hartree-Fock calculation that the A-type antiferromagnetic order observed only in the insulating phase of $Pr_{0.5}Sr_{0.5}MnO_3$ (Ref. 20) is due to a breathing-type lattice distortion. Alternatively, the usually observed ''ce'' type order could be favored depending on a specific orbital ordering in the perovskites.[28,29] While the gap obtained in these theoretical studies is of the order of the observed gap, the origin of the energy scale of the spectral weight transfer is not yet understood in the charge-ordering systems. From our studies, it is clear that the spectral weight transfer over large energy scales is a generic feature of the charge-ordering systems. Further theoretical and experimental studies are necessary to clarify the origin of the spectral weight transfer in the charge-ordering manganites. In particular, the answer to the question of whether the transition is driven by nearest-neighbor[25] or superexchange interaction,[28] coupled to a lattice distortion, would also need to explain the simultaneous spectral weight transfer.

In conclusion, the spectral changes in the occupied DOS of $Pr_{0.5}Sr_{0.5}MnO_3$ across the metal-insulator/charge-ordering/ferromagnetic-antiferromagnetic transition are abrupt and over very large energy scales (up to 1.2 eV from Fermi level E_F) compared to the transition temperature $T_{mi} = 140$ K ($\sim$12 meV) and the gap value in the insulating phase ($\sim$100 meV). While no significant changes in DOS are observed in the ferrometallic phase, a weak spectral weight transfer across the ferromagnetic-paramagnetic transition at $T_{fp} = 270$ K is consistent with negligible change in carrier density above T_{mi}.

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