Spectral evolution in an insulator exhibiting linear specific heat

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Abstract. In this work, we investigate, using state-of-the-art high-resolution photoemission spectroscopy, the spectral evolution of an antiferromagnetic insulator, La$_{0.2}$Sr$_{0.8}$MnO$_3$, exhibiting linear specific heat. Experimental spectral functions exhibited Fermi liquid-like energy dependence at all the temperatures studied. Room temperature spectra possess finite density of states at the Fermi level that vanishes, generating a soft gap at about 265 K (the magnetic transition temperature). High-resolution spectra reveal a hard gap in the magnetically ordered phase (C-type antiferromagnet). These results indicate the signature of an amorphous phase, presumably magnetic in nature, coexisting with the long-range ordered phase in these materials.

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1. Introduction

The specific heat of an electron gas has a linear dependence on temperature and the specific heat coefficient, $\gamma$, can be expressed as $\gamma = (\pi^2 / 3) k_B^2 n(\epsilon_F)$, where $k_B$ is the Boltzmann constant and $n(\epsilon_F)$ is the density of states (DOS) at the Fermi level, $\epsilon_F$. Here, $\gamma$ is a linear function of $n(\epsilon_F)$. However, various experiments reported a finite value of $\gamma$ in insulating materials such as vitreous silica, germania, selenium, etc [1]. Subsequently, it was proposed in [2, 3] that in insulating materials, the charge carriers can tunnel through the potential barrier among various local minima. The energy difference between the local minima will vary continuously in an amorphous system, which leads to a linear term in specific heat. Interestingly, various studies of manganites reveal large $\gamma$ in insulating crystalline compositions [4, 5]. In order to explain such anomalous observations, it was suggested that the DOS at $\epsilon_F$ is finite but localized, which gives rise to finite $\gamma$ and insulating transport. The other suggestion is the possibility of a spin glass phase [6].

Hole-doped manganites [4], [7]–[11], in general, have attracted a great deal of attention during the last two decades following the discovery of colossal magnetoresistance (CMR), leading to potential technological applications. In addition, a plethora of interesting phases are observed due to the interplay between spin, charge, orbital and lattice degrees of freedom. While the CMR effect observed at low doping levels attracted a great deal of attention, the higher doping regime also displays an interesting and complex phase diagram, as shown in figure 1(a) in the case of La$_{1-x}$Sr$_x$MnO$_3$ [12, 13]. Clearly, the system exhibits a complex evolution to different phases as a function of doping and temperature. The systems lying in the proximity of a phase boundary are susceptible to exhibit phase separation or coexistence of multiple phases. For example, phase coexistence is observed in the composition range $0.5 < x < 0.6$, where the system lies in the proximity of the phase boundary involving ferromagnetic and antiferromagnetic ground states. In such cases, the systems may lead to spin amorphicity that contributes as finite $\gamma$ in the specific heat data.

However, the observation of finite $\gamma$ in the insulating materials far away from compositions having phase co-existence is curious. For example, La$_{0.2}$Sr$_{0.8}$MnO$_3$ undergoes a transition from the paramagnetic metallic phase to the C-type antiferromagnetic insulating phase (moments in the $ab$-plane are antiparallel and inter-plane coupling is ferromagnetic) at about 265 K. Although the low-temperature phase is highly insulating, the value of $\gamma$ in La$_{0.2}$Sr$_{0.8}$MnO$_3$ is found to be $\sim 5.6$ mJ/(mole K)$^{-1}$ [14]. This value is close to those observed in other compositions exhibiting metallic conductivity where the conduction electron density at the Fermi level is finite [4]. The crystal structure of La$_{0.2}$Sr$_{0.8}$MnO$_3$ is perovskite derived with small tetragonal distortion (very close to the cubic structure), as shown in figure 1(b). Detailed structural analyses of a variety of samples (single- and poly-crystalline form) consistently indicate high-quality single phase. Various structural studies based on x-ray scattering and neutron diffraction did not indicate signatures of charge or orbital ordering at this doping concentration [12, 13].

In this paper, we report our results on La$_{0.2}$Sr$_{0.8}$MnO$_3$ obtained by employing high-resolution photoemission spectroscopy. This technique, based on the photoelectric effect, helps us to probe the DOS directly. Thus, the presence of disorder-induced localized states at the Fermi level can be probed directly, which will help to resolve the puzzle mentioned above. We find that the DOS at $\epsilon_F$ is finite at room temperature, suggesting a metallic phase, consistent with the conclusions drawn from the transport measurements. An antiferromagnetic transition
Figure 1. (a) Phase diagram as a function of $x$ in La$_{1-x}$Sr$_x$MnO$_3$. The paramagnetic (PM) metallic phase (A) at high temperatures undergoes a change to ferromagnetic (FM) metallic phase (B) or via short-range (SR) ordered phase (C) to phase-separated (PS) metallic (D) or antiferromagnetic (AFM) metallic (E) phase, or antiferromagnetic insulating phase (F). (b) Crystal structure of La$_{0.2}$Sr$_{0.8}$MnO$_3$. (c) SEM image of the sample studied, exhibiting the large grain size of the single phased material. (d) XRD pattern of the sample, revealing the clean high-quality phase of the sample.

leads to an energy gap at $\epsilon_F$. The spectral function exhibits Fermi liquid-like energy dependence at all the temperatures studied.

2. Experimental details

The samples were prepared by the solid-state reaction route as reported elsewhere [15]. The scanning electron microscopic (SEM) image (see figure 1(c)) reveals the large grain size ($\sim 3 \, \mu$m) that could be achieved by long sintering at the final preparation temperature. The energy dispersive analyses of x-rays on different grains and at different locations on the same grain indicate the absence of impurity phase and the homogeneity of the composition. A room temperature powder x-ray diffraction (XRD) experiment was carried out using a Philips X’Pert
Figure 2. (a) Magnetic susceptibility as a function of temperature, exhibiting an antiferromagnetic transition at 265 K. (b) The O 1s spectrum exhibiting high purity of the sample.

diffractometer with Cu Kα radiation. All the reflections were indexed with a cubic structure (space group Pm̅3m) with a lattice parameter of 3.826 Å (see figure 1(d)). No trace of impurities was found in the XRD pattern, as shown in the figure. The dc magnetization measurement (4–330 K), carried out at a 5 T field in a superconducting quantum interference device (Quantum Design), exhibits a distinct hump at about 265 K (see figure 2(a)), indicating a transition to the antiferromagnetic phase.

Photoemission measurements at different temperatures were carried out using monochromatic Al Kα (hν = 1486.6 eV), He I (hν = 21.2 eV) and He II (hν = 40.8 eV) sources and a Gammadata Scienta analyzer (SES2002). The energy resolutions for x-ray photoemission (XP) and He I and He II measurements were 0.3 eV, 1.4 meV and 4.2 meV, respectively. The base pressure during the measurements was 4 × 10⁻¹¹ Torr. The sample surface was cleaned by scraping in situ with a diamond file. No intensity was observed for the C 1s signal. A typical O 1s spectrum collected at room temperature is shown in figure 2(b); it exhibits a sharp feature A at 529 eV binding energy and a weak feature B at about 531.3 eV binding energy. Feature B can be attributed to the surface oxygens and/or adsorbed impurities. The complete dominance of feature A ensures high purity of the samples.

3. Calculational details

Band structure calculations were carried out by using a linearized muffin-tin orbital method within the atomic sphere approximation (LMTART 6.61) [16]. The muffin-tin radii used are 3.523, 3.523, 2.025 and 1.591 au for La, Sr, Mn and O, respectively. The charge density and effective potential were expanded in spherical harmonics up to l = 6 inside the sphere. The exchange correlation functional of the density functional theory was taken from the paper by Vosko et al [17]. The convergence in the total energy was set as 10⁻⁵ Ryd per cell. (8,8,8) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate DOS. Calculations were performed for La₀.₂₅Sr₀.₇₅MnO₃ in the C-type antiferromagnetic phase.

4. Results and discussions

The calculated DOSs corresponding to the valence band are shown in figure 3. Mn 3d states split into t₂g and e_g bands due to the crystal field of MnO₆ octahedra. The bonding and antibonding
Figure 3. (a) Calculated spin-integrated DOS for the C-type antiferromagnetic phase. The thick line, thin line and dashed line represent the total DOS, Mn 3d PDOS and O 2p PDOS, respectively. Spin-resolved DOS is shown for Mn 3d PDOS with $t_{2g}$ symmetry (b) and $e_g$ symmetry (c) and for O 2p PDOS (d).

t_{2g}$ up-spin bands are centered around $-5 \text{ eV}$ and $-1 \text{ eV}$, respectively; the energy separation is about $4 \text{ eV}$. Almost equal weight of the $t_{2g}$ partial DOS in bonding and antibonding bands indicates its strong mixing with the O 2p electronic states. The down-spin partial DOS appears above the Fermi level as expected for Mn$^{3+}$/Mn$^{4+}$ high-spin state. The bonding $e_g$ bands appear between $-4$ and $-8 \text{ eV}$. The contribution at the Fermi level, $\epsilon_F$, arises primarily due to the up-spin $e_g$ electronic states. O 2p partial DOS has large contributions in the bonding and antibonding energy regions. The non-bonding O 2p contributions appear in the energy range of $-1$ to $-3 \text{ eV}$.

The experimental valence band spectra are shown in figure 4. There are three intense discernible features A, B and C in both XP and He II spectra. First, we discuss the observations in the room temperature spectra. Feature A in the XP spectrum appears at a slightly higher binding energy compared to that in the He II spectrum, whereas features B and C appear to have similar binding energies. The feature C intensity is reduced slightly in the He II spectrum.
when compared to the XP spectrum. The contributions from Mn 3d states are dominant in the XP spectrum and those from O 2p states are dominant in the He II spectrum due to the photoemission cross section. Thus, these observations suggest the strongly mixed character of the features along with a small enhancement in the Mn 3d contribution in feature C. Comparing these results with the calculated DOS, it is evident that feature A represents the photoemission signal from bonding bands (both $t_{2g}$ and $e_{g}$), feature B is the non-bonding O 2p contribution and feature C is the antibonding $t_{2g}$ band. The peaking of feature A at slightly higher binding energy in the XP spectrum is presumably due to the enhanced intensity of the bonding $e_{g}$ band contributions at XP energies. In addition, a weak feature D can also be observed (see the inset) in the vicinity of the Fermi level, which is dominant in the XP spectra and represents the electronic states having $e_{g}$ symmetry, as is evident from figure 3(c). All these spectra exhibit a negligible intensity at the Fermi level, suggesting proximity to an insulating phase. This is consistent with the results of resistivity measurements.

The energy and intensity of the features in the XP spectrum remain almost identical down to 130 K (much below the magnetic transition temperature of 265 K). On the other hand, the He II spectra (normalized by the intensity of non-bonding O 2p signal) exhibit significant spectral weight transfer. Feature A becomes stronger at lower temperatures with subsequent reduction in intensity of feature C. Since the O 2p character is dominant in the He II spectra, this spectral evolution suggests the shift of O 2p eigenenergies towards higher binding energies. The antiferromagnetic coupling among Mn $t_{2g}$ moments in the $ab$-plane is mediated by O 2p electronic states (superexchange interaction). It appears that the onset of antiferromagnetic ordering leads to a higher degree of localization of the O 2p electrons.

The inset of figure 4 reveals significant reduction of intensity of the $e_{g}$ band (feature D) indicating the opening of a hard gap in the antiferromagnetic phase. In order to investigate this
Figure 5. (a) He I spectra at different temperatures. (b) Difference spectra at 260 and 205 K from the room temperature spectrum. (c) The SDOS obtained by dividing the spectra by the Fermi–Dirac function. (d) SDOS plotted as a function of $(\epsilon - \epsilon_F)^2$, revealing Fermi liquid-like energy dependence.

with a better clarity, we probed this energy region with a very high energy resolution of 1.4 meV. The spectra collected at different temperatures are shown in figure 5(a). Evidently, the intensity at $\epsilon_F$ in the room temperature spectrum is weak and a change in intensity is observed near the arrow. To visualize the spectral changes, we have subtracted all the spectra from the room temperature spectrum. The subtracted intensities shown in figure 5(b) exhibit a peak at about 0.3 eV, which increases gradually with an increase in temperature difference. Qualitatively, it is expected that 0.2 electrons in the $e_g$ bands would pin the Fermi level at the lower half of the conduction band, as seen in figure 3(c). Here the experimental results suggest that these electrons have significant local character, which leads to the peak at 0.3 eV and the weak intensity at $\epsilon_F$. Interestingly, the spectral intensity of this local feature shifts towards higher binding energies at lower temperatures, as is also evidenced in the XP spectra shown in the inset of figure 4.

The spectral density of states (SDOS) are extracted by dividing the experimental spectra by the corresponding Fermi–Dirac distribution function. Since the energy resolution is good (resolution broadening is much smaller than the energy range of interest shown here), such an exercise provides a fairly good estimate of the SDOS, as evidenced in other similar systems [18]. The SDOS at room temperature (see figure 5(c)) exhibits a dip at $\epsilon_F$ (pseudogap), which leads to a soft gap at 260 K and a hard gap in the antiferromagnetic phase. It should be noted here that the Neél temperature, $T_N$, marks the onset of the first-order phase transition in this compound, which involves nucleation and the growth process. Hence, the pseudogap can be attributed to the signature of the gapped low-temperature phase nucleated above $T_N$. The band gap below $T_N$ can

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be attributed to the relocation of the Brillouin zone boundary due to global antiferromagnetic ordering in the ab-plane. In addition, the hard gap and vanishing of 0.3 eV features indicate that the \( e_g \) electrons become more localized and shift to higher binding energies in the magnetically ordered phase. A plot of the SDOS as a function of \((\epsilon - \epsilon_F)^2\) exhibits a linear dependence in both paramagnetic and antiferromagnetic phases, indicating Fermi liquid-like behavior of the localized electrons/quasi-particles in such strongly correlated electron systems, as also observed in other similar compounds [19]–[21].

All the above results establish that the low-temperature insulating phase exhibits a finite energy gap at \( \epsilon_F \), although \( \gamma \) is finite and large (similar to that in the metallic phase of these compounds). The electron correlation in the whole series of transition metal oxides in different dimensions is known to be strong [22]–[26]. Thus, it is natural that electron correlation plays a significant role in determining the insulating ground state in these compounds. In such a case, the electrons at the top of the valence band have a sufficiently strong local character due to a large electron–electron Coulomb repulsion strength that leads to the formation of a band gap at \( \epsilon_F \) in the spectral function. In this scenario, the value of \( \gamma \) also vanishes. Thus, one can safely rule out the possibility of the origin of linear specific heat being due to the finite density of itinerant electronic states at the Fermi level.

Since other low-energy excitations involving electron–phonon, electron–magnon, etc do not contribute to the linear term of specific heat, it is clear that some kind of glassy phase/amorphyicity is present in these systems. The issue of phase separation and its implications for the CMR in these systems is widely discussed in [27, 28]. It was also suggested that the magnetic transition is accompanied by the formation of a pseudogap phase [29] similar to that observed in high-temperature superconductors [30]. Thus, it is tempting to correlate the behavior of this compound with those showing precursor effects [29]–[31], phase separations, etc. This is not unrealistic in a correlated system having 20% La concentration at the Sr sites, that is highly susceptible to generating disorder. Moreover, it was found that systems having a well-characterized single phase also exhibit disorder-induced tunneling states [32]. In the present case, the \( e_g \) electrons are found to be localized where the local character increases with a decrease in temperature—this might be a signature of the combined effects due to disorder and electron correlation. These results emphasize the need to consider a phase that has sufficient amorphyicity and/or softness [33], presumably magnetic in nature, co-existing with the antiferromagnetic insulating phase that may be related to the contribution as a linear term of the specific heat.

5. Conclusions

In summary, we have investigated the evolution of the electronic structure of \( \text{La}_{0.2}\text{Sr}_{0.8}\text{MnO}_3 \) with temperature using high-resolution photoemission spectroscopy to probe the origin of the linear term of the specific heat in its insulating phase. We observe interesting changes in the oxygen 2p bands contributing to the valence band spectra. Spectral intensity is finite at the Fermi level in the paramagnetic phase and the electronic states seem to have a dominant local character (the peak in intensity appears around 0.3 eV). The spectral functions close to the Fermi level exhibit the opening of a hard gap in the antiferromagnetic insulating phase via the formation of a soft Coulomb gap at the antiferromagnetic transition temperature. The energy dependence of the spectral function is Fermi liquid-like in all the phases. These results indicate the possibility of an amorphous phase involving localized quasi-particles within the long-range ordered phase.
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