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Spectral evolution in an insulator exhibiting linear specific heat

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Abstract. We investigate the spectral evolution of an antiferromagnetic insulator, La$_{0.2}$Sr$_{0.8}$MnO$_3$, exhibiting linear specific heat, using state-of-the-art high resolution photoemission spectroscopy. Experimental spectral functions exhibit Fermi liquid-like energy dependence at all the temperatures studied. Room temperature spectra possess finite density of states at the Fermi level, which vanishes, generating a soft gap, at about 260 K (the magnetic transition temperature). High-resolution spectra reveal a hard gap in the magnetically ordered phase (C-type antiferromagnet). These results indicate an amorphous phase coexisting with the long-range ordered phase in these materials.

The specific heat of an electron gas has a linear dependence with temperature and the specific heat coefficient, $\gamma$, can be expressed as $\gamma = \frac{\pi^2}{3} k_B^2 n(\epsilon_F)$, 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 [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 that leads to a linear term in specific heat. Interestingly, various studies in 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 spin glass phase [6].

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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 goes to ferromagnetic (FM) metallic (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 large grain size of single phased material. (d) XRD pattern of the sample revealing clean high quality phase of the sample.

Hole doped manganites [4], [7]–[11], in general, have attracted a great deal of attention during the last two decades following the discovery that colossal magnetoresistance (CMR) might lead 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 is observed at low doping levels, the higher doping regime also displays interesting and complex phase diagrams, as shown in figure 1(a) in the case of La$_{1-x}$Sr$_x$MnO$_3$ [12, 13]. Clearly, the system lies in the proximity of ferromagnetic and antiferromagnetic ground states; phase coexistence is observed in the composition range ($0.5 < x < 0.6$). Thus, such 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 coexistence is curious. For example, La$_{0.2}$Sr$_{0.8}$MnO$_3$ undergoes a transition from paramagnetic metallic phase to C-type antiferromagnetic insulating phase (moments in $ab$-plane are antiparallel and inter-plane coupling is ferromagnetic). $\gamma$ in La$_{0.2}$Sr$_{0.8}$MnO$_3$ is $\sim$5.6 mJ mole$^{-1}$K$^{-1}$ [14], which is very close to the values observed in metallic compositions [4]. The crystal structure is perovskite derived as shown in figure 1(b). Here, we report our results on La$_{0.2}$Sr$_{0.8}$MnO$_3$ employing high-resolution photoemission spectroscopy. We find that DOS at $\epsilon_F$ is finite at room temperature although the e$_g$ electrons possess strong local character. Antiferromagnetic transition leads to an energy gap at $\epsilon_F$. The spectral function exhibits Fermi liquid-like energy dependence at all the temperatures studied (even in the gapped phase).

The samples were prepared by solid-state reaction route, as reported elsewhere [15]. The scanning electron microscopic (SEM) picture (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 analysis of x-rays on different grains and different location on same grain indicate the absence of the impurity phase and the homogeneity of the composition. The room temperature powder x-ray diffraction (XRD) experiment was carried out using the PHILIPS X’Pert diffractometer with Cu Ka radiation. All the reflections were indexed with cubic structure (space group $Pm\bar{3}m$) with lattice parameter of 3.826 Å, (see figure 1(d)). No trace of impurity is found in the XRD pattern. The dc magnetization measurements (4–330 K), carried out at 5 T field in a superconducting quantum interference device (Quantum Design), exhibits a distinct hump at about 265 K (see figure 2(a)), indicating transition to the antiferromagnetic phase.

The photoemission measurements at different temperatures were carried out using monochromatic Al Ka ($h\nu = 1486.6$ eV), He i ($h\nu = 21.2$ eV) and He ii ($h\nu = 40.8$ eV) sources, and the Gammadata Scienta analyzer SES2002. The energy resolution for x-ray photoemission (XP), He i and He ii measurements are 0.3 eV, 1.4 meV and 4.2 meV, respectively. The base pressure during the measurements was $4 \times 10^{-11}$ Torr. The sample surface was cleaned by scraping in situ with a diamond file. No intensity was observed for C 1s signal. A typical O 1s spectrum collected at room temperature is shown in figure 2(b) exhibiting a sharp feature, A, at 529 eV binding energy and a weak feature, B, at about 531.3 eV binding energy. The feature B can be attributed to the surface oxygens and/or adsorbed impurities. The complete dominance of the feature A ensures high purity for the samples.
Figure 3. (a) Calculated spin integrated DOS for the C-type antiferromagnetic phase. Thick line, thin line and dashed line represent the total DOS, Mn 3d PDOS and O 2p PDOS, respectively. Spin-resolved DOS are shown for Mn 3d PDOS with (b) $t_{2g}$ symmetry and (c) $e_g$ symmetry, and (d) O 2p PDOS.

The 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, 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 after Vosko et al [17]. The convergence in the total energy was set to $10^{-5}$ Ryd cell$^{-1}$. (8,8,8) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate DOS. The calculations were performed for La$_{0.25}$Sr$_{0.75}$MnO$_3$ in the C-type antiferromagnetic phase.

The calculated DOS corresponding to the valence band are shown in figure 3. Mn 3d states split into $t_{2g}$ and $e_g$ bands due to the crystal field of MnO$_6$ octahedra. The bonding and antibonding $t_{2g}$ up spin bands are centered around $-5$ eV and $-1$ eV, respectively; the energy separation is about 4 eV. The 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 appear above the Fermi level as expected for the Mn$^{3+}$/Mn$^{4+}$ high spin state.
The bonding $e_g$ bands appear between $-4$ and $-8$ 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 $-1$ to $-3$ 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. The feature A in the XP spectrum appears at slightly higher binding energy compared to that in the He II spectrum, while the features B and C appear to have similar binding energies. The feature C intensity is reduced slightly in the He II spectrum compared to that in 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 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 the non-bonding O 2p contributions and feature C the antibonding $t_{2g}$ bands. The peaking of feature A at slightly higher binding energy in the XP spectrum is presumably due to the enhanced intensity of the bonding $e_g$ bands contributions at XP energies. In addition, a weak feature D can also be observed (see 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 evident in figure 3(c). All these spectra exhibit negligible intensity at the Fermi level, suggesting proximity to an insulating phase. This is consistent with the results from 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,
Figure 5. (a) He I spectra at different temperatures. (b) Difference spectra at 260 and 205 K from the room temperature spectrum. (c) 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.

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 a subsequent reduction in intensity of feature C. Since the O 2p character is dominant in the He II spectra, these spectral evolutions suggests the shift of O 2p eigen energies 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 with 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 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 enhances gradually with the 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). However, the experimental results suggest that these electrons have significant local character that leads to the peak at 0.3 eV and weak intensity at $\epsilon_F$. Interestingly, the spectral intensity of this local feature shifts towards higher binding energies at lower temperatures, as 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. 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. We note 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 be attributed to the relocation of the Brillouin zone boundary due to 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.

All the above results establish that the low temperature phase is insulating due to the finite energy gap at $\epsilon_F$, although $\gamma$ is finite and large (similar to that in the metallic phase of these compounds). Since other low energy excitations involving electron–phonon, electron–magnon etc do not contribute in the linear term of specific heat, it is clear that some kind of glassy phase/amorphicity is present in this systems. The issue of phase separation and its implications for the CMR in these systems is widely discussed [18, 19]. It was also suggested that the magnetic transition is accompanied by the formation of a pseudogap phase [20] similar to that observed in high temperature superconductors [21]. Thus, it is tempting to correlate the behavior of this compound with those showing precursor effects, phase separations etc. These results emphasize the need to consider a phase that has sufficient amorphicity and/or softness [22] coexisting with antiferromagnetic insulating phase that may contribute as a linear term in the specific heat. This is not unrealistic as $e_g$ electrons are localized and hence, 20% La concentration at the Sr sites in LaSrMnO$_3$ will naturally induce disorder.

In summary, we have investigated the evolution of the electronic structure of La$_{0.2}$Sr$_{0.8}$MnO$_3$ with temperatures using high resolution photoemission spectroscopy to probe the origin of linear term in the specific heat in its insulating phase. We observe interesting change in the oxygen 2p bands contributing in the valence band spectra. Spectral intensity is finite at the Fermi level in the paramagnetic phase and the electronic states seem to have dominant local character (peak of intensity appears around 0.3 eV). The spectral functions close to the Fermi level exhibit 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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