Signature of phase coexistence in electron doped manganite

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Abstract.
We investigate the temperature evolution of the electronic structure of La$_{0.2}$Sr$_{0.8}$MnO$_3$ using Mn K-edge extended x-ray absorption fine structure (EXAFS) and state-of-the-art high resolution photoemission spectroscopy. This compound undergoes a transition from cubic paramagnetic metal to tetragonal C-type antiferromagnetic insulator around 265 K ($T_N$). EXAFS results exhibit a direct link between the temperature induced change in resistivity and the structural parameters of the MnO$_6$ octahedra. The high resolution photoemission spectra reveal a gradual evolution of the spectral function exhibiting a pseudo gap at 300 K to a hard gap around 205 K. The appearance of hard gap much below the transition temperature suggests the coexistence of two phases in the vicinity of the phase transition temperature, which might be important in the understanding of phase separation scenario widely discussed in this class of materials.

The physics of manganites [1] are mainly governed by the interplay between the charge, spin, orbital and lattice degrees of freedom. Such intricate coupling leads to interesting properties like colossal magnetoresistance (CMR), multiferroicity, electronic phase separation, charge, spin and orbital ordering, etc [2]. Nowadays, the phenomenon of electronic phase separation is gaining great attention in the scientific community as it is believed to be a possible origin of CMR effect. La$_{1-x}$Sr$_x$MnO$_3$ is one such compound which shows this effect but for $x<0.5$ compositions. As this property arises due to coexistence of metallic/ferromagnetic and insulating/paramagnetic phases, it is equally important to understand the behavior of the insulating phase which is dominant for $x>0.5$ region of the phase diagram. So the best compound which serves this purpose is La$_{0.2}$Sr$_{0.8}$MnO$_3$ as it is cubic at room temperature. In addition to this, it lies far away from the phase boundary region thereby getting rid of the complications arising due to the coexistence of different $e_g$ electron densities. This compound undergoes various phase transitions from paramagnetic to C-type antiferromagnetic, metal to insulator, cubic to tetragonal at $\sim$ 265 K [3, 4, 5]. Another important aspect of this large band width system is the strong role played by electron phonon coupling on the transport properties. To understand the above behaviors across the region of phase transition both at the electronic and local structural level, we have carried

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out temperature dependent ultraviolet, x-ray photoemission and Mn K-edge x-ray absorption spectroscopic experiments. Our results reveal signature of co-existence of two phases in a wide temperature range and portrays the importance of fluctuations in the Mn 3d orbital occupancies to understand such phase coexistence.

The sample was prepared by standard solid state route and characterized using x-ray diffraction (XRD), scanning electron microscopic, resistivity, specific heat and dc magnetization measurements [3, 4, 6]. The details of the temperature dependent Mn K-edge EXAFS measurements and photoemission spectroscopic techniques are given elsewhere [3, 4]. The band structure calculations were carried out for La$_{0.25}$Sr$_{0.75}$MnO$_3$ in the C-type antiferromagnetic phase by using a linearized muffin-tin orbital method within the atomic sphere approximation (LMTART 6.61).

The resistivity measurements exhibit hysteresis during the warming ($\rho_w$) and cooling ($\rho_c$) cycles [3]. This can be clearly seen in the normalized resistivity, $(\rho_c - \rho_w)/\rho_c$ shown in Fig (1a) that reveals a dip at $\sim 265$ K and a peak at $\sim 225$ K, which signals interesting behaviors occurring around these temperatures. Such hysteresis is indicative of first order phase transition. Since the transport property is mainly governed by the hopping of Mn 3d electrons among various MnO$_6$ octahedra, the local structure associated to MnO$_6$ octahedron plays an important role in deriving the electronic properties in this system.

We employed EXAFS to probe the structural change of MnO$_6$ octahedron, which is the ideal tool due to its element specificity. The bond lengths with respect to the Mn ions were obtained by fitting the EXAFS spectra using UWXAS 3.0 software [3]. In Fig (1b), we show the evolution of the Mn-O bondlengths as a function of temperature. We find that all the Mn-O bondlengths in the MnO$_6$ octahedra are not identical. The best fit corresponds to two short ($R_1$) and four long ($R_2$) Mn-O bonds [7]. $R_1$ and $R_2$ exhibit an unusual temperature dependence across the phase transition temperature. On cooling the sample from 300 K, the distortion (difference between $R_1$ and $R_2$) gradually reduces. At about 265 K, all the Mn-O bond lengths become identical. Further lowering of temperature leads the distortion to become prominent again. The difference between $R_1$ and $R_2$ is the largest at around 245 K and reduces further at lower temperatures.

Interestingly, the temperature dependence of $(R_1-R_2)$ follows the trend of the normalized
resistivity data shown in Fig. 1(c). This suggests a direct connection between the local structural parameters and the transport properties.

In order to investigate the microscopic origin of this phenomena, we show the valence band spectra collected at different temperatures and photon energies in Fig. 2. All the spectra exhibit four distinct features marked by A, B, C and D as shown in Fig. 2(a). The relative photo-ionization cross section of Mn 3\textit{d} states compared to O 2\textit{p} states is dominant in Al K\textalpha, which becomes much smaller in He II energies [8]. This helps to identify the character of these features that can be confirmed further by the results from band structure calculations [9]. The calculated density of states (DOS) are shown in Fig 2(b). From the comparison of the spectra at two different energies and the calculated results, it is evident that the peaks A and C correspond to the bonding and anti-bonding states of Mn 3\textit{d} and O 2\textit{p} orbitals having \textit{t}_{2g} symmetry. The feature B can be attributed to the non-bonding O 2\textit{p} states. The peak D corresponds to the \textit{e}_{g} anti-bonding states and mainly contributes to the states at and very close to the Fermi level (\textit{\epsilon}_{F}).

The valence band spectra collected using x-ray source does not show markable temperature dependence except for the peak D. On the other hand, all the features in the He II spectra undergoes significant changes. This suggests that O 2\textit{p} states are very sensitive to temperature and \textit{t}_{2g} bands are not influenced significantly. The increase in intensity of the features at higher binding energy at lower temperatures suggests that the valence electrons are getting more and more local character as the compound...
enters into the C-type antiferromagnetic phase. This is also apparent by the decrease in intensity of the feature D with temperature as shown in Fig. 2(a) and 2(c) at Al Kα, He II and He I energies.

In Fig. (2d), we show the temperature evolution of the spectral DOS (SDOS) at $\epsilon_F$ obtained by dividing the experimental spectra by the Fermi-Dirac distribution function. Here, all the spectra are normalized by the intensity at 1 eV binding energy. At room temperature, the DOS exhibit a pseudogap at $\epsilon_F$. The intensity at $\epsilon_F$ gradually reduces with the decrease in temperature. No hard gap was observed at the phase transition temperature of 265 K although the compound becomes insulating. A hard gap is observed at much lower temperature ($\sim 205$K). Such gradual evolution of the gap with temperature suggests coexistence of low temperature phase above $T_N$ as found in other systems [10] and the high temperature phase below $T_N$; phase coexistence in a wide temperature range [2]. We have verified that this trend of spectral evolution is independent of the background function and normalization procedures. These results evidently indicate a relation to the observation of hysteresis in the transport measurements much below $T_N$.

In summary, we have studied the temperature dependence of the electronic properties and its relation to the local structural parameters of La$_{0.2}$Sr$_{0.8}$MnO$_3$ using Mn K-edge EXAFS and high resolution photoemission spectroscopy. The MnO$_6$ octahedra undergo interesting temperature evolution across the first order phase transition that signals the importance of fluctuations in the Mn 3d orbital occupancy across $T_N$. The high resolution photoemission spectra reveal a pseudogap in the metallic phase, which gradually evolves into a hard gap at about 205 K, much lower than the metal to insulator transition. This suggests signature of phase separation occurring in a wide temperature range in this system.

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