Pseudogap behavior of phase-separated Sm$_{1-x}$Ca$_x$MnO$_3$ : A comparative photoemission study with double exchange

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Using valence band photoemission we have demonstrated the presence of a pseudogap in the near Fermi level electronic spectrum of some of the mixed phase compositions of Sm$_{1-x}$Ca$_x$MnO$_3$ system. The pseudogap was found to grow in size over a large region of the phase diagram of this system, finally leading to a metal-insulator transition. We have made a study comparing the near Fermi level behaviors of this system to those of a canonical double exchange system, namely, La$_{1-x}$Sr$_x$MnO$_3$. This study intends to highlight one of the important differences between the phase separated and double exchange colossal magnetoresistance systems in the nature of their energy gaps across the metal-insulator transitions. These differences could be ascribed to the distortions in the MnO$_6$ octahedra of their structures that regulate the localization of charge carriers. We have discussed our results from the point of view of models based on the idea of phase separation.

I. INTRODUCTION

Although, the double-exchange (DE) mechanism$^{1,2,3}$ could qualitatively explain the phenomenon of colossal magneto-resistance (CMR) in manganites, it was found insufficient to provide a consolidated picture accommodating their intricate transport and magnetic properties. Most of the alternate theories proposed recently$^{4,5}$, are based on lattice polarons of one type or the other highlighting the strong electron-lattice interactions in these systems. These polarons and thereby most of the properties of these Mn$^{3+}$ - Mn$^{4+}$ mixed valent compounds depend on the topology of the MnO$_6$ octahedra in their structure. Among the recently proposed models, the one based on electronic phase separation (PS)$^{6,7}$ has been attracting considerable attention. According the PS model the metal-insulator (MI) transitions in these materials are driven by the percolation of current through ferromagnetic metallic (FMM) domains embedded in an antiferromagnetic insulating (AFMI) matrix. There have been many structural studies showing the co-existence of such metallic and insulating phases$^{8,9,10,11}$ with sizes varying from nanoscopic to microscopic. The cluster-glass (CG) compositions of Sm$_{1-x}$Ca$_x$MnO$_3$ system are some of the materials in which such a phase separation could be unambiguously shown using neutron diffraction, owing to the large sizes of the magnetic domains possible in them$^{8}$. Separation of these magnetic phases in this system has been found to be related to the strong distortions in their GdFeO$_3$-type structure. Also, these distortions control the topology of the MnO$_6$ octahedra of their structure and thereby the one electron band width (W) and the electron localization effects. The near Fermi level ($E_F$) electronic behavior of these phase separated systems could possibly be different from those of the La$_{1-x}$Sr$_x$MnO$_3$ which has long been identified as a canonical DE CMR system$^{12}$ due to its large W. Further, since the term $J_H/W$ ($J_H$ is the Hund’s coupling) which expresses the effective coupling between the $e_g$ and the $t_{2g}$ electrons of the crystal field split MnO$_6$ octahedra in their structure, remains in the weak-coupling regime, the La$_{1-x}$Sr$_x$MnO$_3$ system is regarded as the least affected by the electron-electron and electron-lattice correlation effects among the CMR manganites. On the other hand, the Sm$_{1-x}$Ca$_x$MnO$_3$ with its small W and distorted MnO$_6$ octahedra, is more prone to the electron correlation effects such as the localization of charge carriers.

Recently, there have been many photoemission studies$^{13,14,15}$ highlighting the subtle changes in the near $E_F$ density of states (DOS) associated with the MI transitions in phase separated CMR systems. These shifts in the near $E_F$ spectral weights lead to charge order (CO) gaps and pseudogaps. Such pseudogaps which have been shown to be a generic behavior of CMR systems with mixed phases$^{6,11}$ are closely related to the changes in the W and electron localization. As mentioned before, one expects distinct differences between the mixed phase Sm$_{1-x}$Ca$_x$MnO$_3$ and the DE driven La$_{1-x}$Sr$_x$MnO$_3$ systems in the nature of their energy gaps across the MI transitions. Ultraviolet photoelectron spectroscopy (UPS) is a powerful technique capable of probing the fine changes in the valence band electronic structure. In this paper, we show some of the important differences between the Sm$_{1-x}$Ca$_x$MnO$_3$ and the La$_{1-x}$Sr$_x$MnO$_3$ systems in their near $E_F$ electronic structure using high resolution UPS. The doping dependent pseudogap behavior observed in Sm$_{1-x}$Ca$_x$MnO$_3$ system is discussed here and compared with that of the DE driven La$_{1-x}$Sr$_x$MnO$_3$.
II. EXPERIMENTAL

Polycrystalline samples of $\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ systems were prepared by solid state reactions by mixing $\text{MnO}_2$, $\text{CaO}$ and $\text{Sm}_2\text{O}_3$ or $\text{La}_2\text{O}_3$ in stoichiometric proportions. The powders were first heated at 1000 °C with intermediate grindings and then pressed in the form of pellets. They were then sintered at 1500 °C for 12 h in air with a slow cooling down to 800 °C and finally quenched to room temperature. Details of the sample preparation technique could be found elsewhere. The monophase, homogenous nature of the samples have been checked by x-ray powder and electron diffraction techniques. The cationic compositions, close to their nominal values were confirmed using energy dispersive spectroscopy and iodometric titrations. Magnetic and electrical transport properties of the samples were determined using a magnetometer (equipped with a superconducting quantum interference device) and four probe resistivity measurements. A co-existence of two separate phases of FMM and AFMI domains below 100 K in $x = 0.85$ and 0.9 of the $\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ system were shown earlier using neutron diffraction studies carried out at LLB, Saclay, France on the G41 diffractometer. Consolidated results of these studies is published elsewhere.

Angle integrated ultraviolet photoemission measurements were performed using an Omicron mu-metal ultra high vacuum system equipped with a high intensity vacuum-ultraviolet source (HIS 13) and a hemispherical electron energy analyzer (EA 125 HR). At the He $I$ ($\hbar \nu = 21.2$ eV) line, the photon flux was of the order of $10^{16}$ photons/sec/steradian with a beam spot of 2.5 mm diameter. Fermi energies for all measurements were calibrated using a freshly evaporated Ag film on a sample holder. The total energy resolution, estimated from the width of the Fermi edge, was about 80 meV for He $I$ excitation. All the photoemission measurements were performed inside the analysis chamber under a base vacuum of $\sim 5.0 \times 10^{-11}$ mbar. The polycrystalline samples were repeatedly scraped using a diamond file inside the preparation chamber with a base vacuum of $\sim 5.0 \times 10^{-11}$ mbar and the spectra were taken within 1 hour, so as to avoid any surface degradation. All measurements were repeated many times to ensure the reproducibility of the spectra. For the temperature dependent measurements, the samples were cooled by pumping liquid nitrogen through the sample manipulator fitted with a cryostat. Sample temperatures were measured using a silicon diode sensor touching the bottom of the stainless steel sample plate. The low temperature photoemission measurements at 77 K were performed immediately after the cleaning the sample surfaces followed by the room temperature measurements. In order to make a good comparative study of the two systems ($\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$), we performed all the measurements under exactly same experimental conditions.

III. RESULTS AND DISCUSSION

The phase diagram of the $\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ system published earlier$^{12}$ is shown in Fig. 1 (a). We have chosen five compositions of this system with $x = 0.3$, 0.5, 0.7, 0.85 and 0.9, which are all paramagnetic insulating (PMI) at room temperature. Below 100 K, the $x = 0.3$ sample shows a ferromagnetic insulating (FMI) behavior. A large doping region, $0.40 \leq x \leq 0.7$, shows a CO-AFMI state at low temperatures. The CMR properties of these compositions are strongly dominated by this CO insulating state. The low temperature resistivities (down to 10 K) of these samples were very high ($> 10^4 \Omega$ cm) and are thus insulators. The coexistence of ferromagnetism and metallicity is observed only in the cluster-glass (CG)
region, i.e., \( x \approx 0.9 \), where the resistivity at low temperature (10 K) is \( 10^{-2} \) to \( 10^{-3} \) \( \Omega \) cm, corresponding to that of ‘bad’ metals. The CMR effect is observed in the boundary between CG - state \(( x > 0.85 )\) and CO-AFMI state \(( x < 0.85 )\). Neutron diffraction studies have shown that the last two CG compositions \(( x = 0.85 \) and 0.9\) have coexisting FMM and AFMI phases. Fig. 1(b) shows the phase diagram of the La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\) system, adapted from the work of Chmaissem et al.\(^{18}\).

In figure 2 we present the angle integrated valence band spectra of the Sm\(_{1-x}\)Ca\(_{x}\)MnO\(_3\) samples taken at 77 K. The main features seen in these spectra are by now well-known and looks similar to those reported earlier on different CMR systems,\(^{19,20,21}\) including the La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\). Features seen in the spectra originate from the bonding and antibonding states of Mn 3d - O 2p hybridization. Detailed discussion on these spectral features could be found elsewhere.\(^{14}\) As in other transition metal oxide compounds, the major contribution to the physical properties of this system comes from the subtle changes in the states near the \( E_F \) (within 2 eV from the \( E_F \)). A high resolution spectra of this region is shown in Fig. 3(a). Intensities of these spectra are normalized at regions above 1.2 eV and below the \( E_F \) and are shifted along the ordinate axis by a constant value for clarity.

Here, we concentrate on the subtle changes in the near \( E_F \) spectral features, marked A and A’ in Fig. 3. Different experiments,\(^{19,20,21}\) and band structure calculations\(^{22,23,24}\) have shown that both these features arise from the Mn \( e_g \) spin-up states of the crystal field split MnO\(_6\) octahedra. The spectra shown, taken at 77 K, demonstrate the finer shifts in the spectral weight from A to A’ as we go across the phase diagram shown in Fig. 1(a). The apparent gaps in the near \( E_F \) DOS resulting from these shifts are usually called ‘pseudogaps’. As mentioned earlier, recent photoemission studies\(^{13,14,15}\) have highlighted the importance of such pseudogaps, particularly for the models based on electronic phase separation.\(^{6,7}\) Fig. 3(a) shows that some finite number of states build up at A’ as we go from FMI \(( x = 0.3 )\) to AFMI \(( x = 0.5 )\) composition. Further increase of \( x \) to 0.7 also results in an increased DOS at A’. Spectra from the \( x = 0.85 \) and 0.9 samples display a distinct feature at A’. In panel (b) we have plotted the spectra corresponding to each composition together with that from the \( x = 0.3 \) for a comparison. It should be noted that, though all the samples with \( x = 0.5, 0.6 \) and 0.7 are AFMI at 77 K the number of states at A’ keep increasing with increase in \( x \) showing that the pseudogap originating from these shifts exist also in the AFMI regime. This building up of DOS at A’ could be associated with the growing FMM domains in the AFMI matrix in the Sm\(_{1-x}\)Ca\(_{x}\)MnO\(_3\) system with progressive Ca doping. The increase in the DOS at A’ should be due to the shift of states from A to A’ following the growth of FMM domains. As we move on to \( x = 0.85 \) and 0.9, the feature at A’ becomes quite prominent. In these compositions, the FMM domains must be large enough leading to the metallic behavior shown by them. This has been confirmed earlier using neutron diffraction studies where we had shown that the Sm\(_{1-x}\)Ca\(_{x}\)MnO\(_3\) system with \( x = 0.85 \) and \( x = 0.9 \) have a unique crystalline structure with FMM clusters embedded in a G-type AFMI background.

Let us now compare these results from Sm\(_{1-x}\)Ca\(_{x}\)MnO\(_3\) with those from the canonical DE system, La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\). Figure 4 (a) shows the high resolution photoemission spectra of the near \( E_F \) region.
of La$_{1-x}$Sr$_x$MnO$_3$ system taken at 77 K. These spectra are also normalized and displayed in the same way as described earlier. The phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ system (Fig. 1(b)) shows that compositions with $x = 0.2$ to 0.6 are FMM while $x = 0.7$ and 0.8 are AFMI. Correspondingly, our spectra from different metallic compositions also show the presence of a Fermi edge; the hallmark of metallicity. In Fig. 4 (b) we have plotted the spectra from different compositions together with that from the $x = 0.2$ sample. A close observation and comparison of this figure with Fig. 3 (b) will reveal that the spectra from different metallic compositions do not show any distinct feature corresponding to A' as in the case of the Sm$_{1-x}$Ca$_x$MnO$_3$ system. The MI transition in Sm$_{1-x}$Ca$_x$MnO$_3$ (from $x = 0.9$ to $x = 0.3$) was accompanied by the depletion of the feature at A' due to the transfer of some DOS from A' to A; namely the pseudogap. On the other hand, in case of the La$_{1-x}$Sr$_x$MnO$_3$ system we neither find any formation of such a feature at A' nor any shift of DOS. Here, the MI transition is manifested as the opening up of an insulator gap. The plot in Fig. 4 (b), showing the spectra from $x = 0.2$ (metallic) together with that from $x = 0.8$ (insulating) makes this point clear. One can see that the insulator to metal transition here is accompanied by an almost uniform increase in the DOS over the region between 1.2 eV and the E$_F$.

The differences shown by the near E$_F$ spectral changes associated with the doping dependent MI transitions in the Sm$_{1-x}$Ca$_x$MnO$_3$ and the La$_{1-x}$Sr$_x$MnO$_3$ systems could be relevant to the fundamental understanding of the mechanism of CMR. The insulator-metal transition in the La$_{1-x}$Sr$_x$MnO$_3$ system is due to the hopping of the $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$ via the DE and superexchange interactions. These interactions are sensitive to the distortions in the MnO$_6$ octahedra which control the W and the electron correlation effects. With its small W these correlation effects are strong in case of the Sm$_{1-x}$Ca$_x$MnO$_3$. As mentioned before, the mixed phase compositions of this system have FMM domains in a CO-AMFI matrix. With its strongly distorted MnO$_6$ octahedra the C - type AFMI regions could be more prone to the electron localization effects compared to the FMM domains. The charge carriers ($e_g$ electrons) of the AFMI regions should thereby be more localized compared to the $e_g$ electrons in FMM regions. Consequently, this can result in higher binding energies for those $e_g$ electrons in AFMI regions compared to the ones in the FMM domains. As the sizes of these FMM domains increase with Ca doping, the number of itinerant $e_g$ electrons also go up resulting in a shift of spectral weight from A to A'. Conversely, this is the origin of the pseudogap. As Moreo et al. have proposed earlier, this pseudogap could be a generic feature of such phase separated systems. But, the scenario is different in case of the La$_{1-x}$Sr$_x$MnO$_3$ system where such mixed phases do not exist. There the DE and superexchange processes through the undistorted Mn-O-Mn bond lead only to the hoping of $e_g$ electrons with no localization processes or pseudogaps involved.

**IV. CONCLUSION**

In conclusion, we have shown one of the important differences in the near E$_F$ electronic behavior of phase separated and DE systems using high resolution photoemission experiments. Our study of the doping dependent MI transitions in Sm$_{1-x}$Ca$_x$MnO$_3$ compounds shows that the phase separated systems indeed show a pseudogap behavior in their near E$_F$ electronic spectrum over a large region of their phase diagram. A comparison of this system with the canonical DE La$_{1-x}$Sr$_x$MnO$_3$ system reveals the differences in the nature of the gaps associated with the MI transitions between these two systems. These differences could be ascribed to the distortions in the MnO$_6$ octahedra of their crystal structures which regulate the electron - electron and electron - lattice correlation effects determining the localization of charge carriers and thereby the pseudogap behavior.

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