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Polaronic pseudogap in the metallic phase of $La_{0.625}Ca_{0.375}MnO_3$ thin films

Udai Raj Singh, S Chaudhuri, R C Budhani and Anjan K Gupta

Department of Physics, Indian Institute of Technology Kanpur, Kanpur 208016, India

E-mail: anjankg@iitk.ac.in

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Abstract

The electronic density of states (DOS) of $La_{0.625}Ca_{0.375}MnO_3$ (LCMO) strain-free epitaxial thin films with an insulator–metal transition temperature (T_{IM}) of 250 K was probed using variable-temperature scanning tunneling microscopy and spectroscopy. We find a depression in the DOS with a finite zero bias conductance (ZBC) signifying a pseudogap in the 78–310 K temperature range. With cooling, the ZBC is found to increase, indicating an increased DOS near E_F. We interpret the pseudogap as a signature of Jahn–Teller polarons while the ZBC change, in agreement with the bulk insulator–metal transition, optical Drude peak and photoemission experiments, indicates the presence of free carriers at the Fermi energy in the metallic phase. The free carriers are discussed in terms of correlated polaronic states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The hole-doped colossal magnetoresistive (CMR) manganites [1] have attracted much attention in the past two decades for their intriguing physics and application potential. The Zener double-exchange [2] mechanism that explained the CMR behavior was found to be insufficient [3] and this led to a more elaborate theory by Millis *et al* incorporating Jahn–Teller (JT) interaction [4]. As shown by a number of experiments, like the Hall effect [5], transport [6], x-ray spectroscopy [7], scattering [8] and isotope effect [9], the JT small polarons [10] seem to be responsible for the activated resistivity in the paramagnetic insulating (PI) phase of manganites. Several experiments such as neutron scattering [8], optical conductivity [11], photoemission [12] and tunneling [14, 15] have also shown signatures of polarons in the ferromagnetic metallic (FM) phase, although these signatures are weaker, at least the structural ones [8, 7], than those in the PI phase. Moreover, the optical Drude weight [11] and recent angle-resolved photoemission spectroscopy (ARPES) [13] observation of a quasiparticle peak at E_F indicate the presence of free carriers as well in the FM phase.

Besides the theory of Millis *et al* [4], which finds a transformation of small polarons into delocalized carriers at T_{IM}, a number of other models have also been proposed in the recent past. Emin [16] suggested that these delocalized carriers are large polarons with larger spatial extent of lattice deformation. Alexandrov *et al* [17] advocated the splitting of singlet bipolarons at high temperatures into small polarons below T_{IM}. Both these models propose only polaronic states in the FM phase. Another simple model, put forward by Ramakrishna *et al* [18], accounts for the free carriers by having delocalized band states together with localized polarons. In addition, this model proposes a 'coherent small polarons' state at low temperatures to account for the small magnitude of the resistivity. Therefore, both theory and experiment point towards some kind of polaron softening or delocalization with the onset of the ferromagnetic order. However, the detailed physics of the FM phase seems far from being understood. In particular, the role of charge carriers, i.e. whether they are free or polaronic, in the FM state is not yet clear.

The phase separation scenario [19], with two types (in the sense of small polarons and delocalized) of coexisting carriers, is also consistent with a large number of experiments. Phase separation has been established experimentally in some of the narrow bandwidth manganites [20]. In wide bandwidth manganites some tunneling experiments do indicate electronic inhomogeneities but mostly in granular or inhomogeneous samples [21], whereas the homogeneous samples do not seem to show any phase separation [15, 22].

In this paper we report the variable-temperature scanning tunneling microscopy and spectroscopy (STM and STS) studies of strain-free epitaxial $La_{0.625}Ca_{0.375}MnO_3$ (LCMO) thin films with $T_{IM} = 250$ K. The tunneling spectra show a

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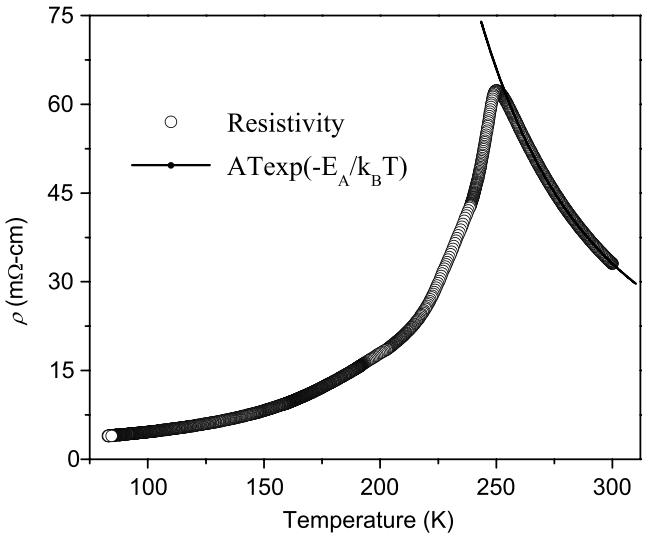

Figure 1. The four-probe resistivity of the LCMO thin film with $T_{IM} = 250$ K. The continuous line is the fitting with polaronic activation behavior with activation energy $E_A = 0.112$ eV.

polaronic pseudogap. The STS images show some electronic inhomogeneities corresponding to small variations in zero bias conductance (ZBC). We also see an increase in the pseudogap energy at T_{IM} with cooling and a rise in the ZBC signifying the build-up of states at the Fermi energy with cooling. This observation, consistent with the bulk resistivity, optical and recent ARPES data, strongly supports a correlated polaron state giving rise to delocalized carriers in the metallic state.

2. Experiment

Epitaxial $La_{0.625}Ca_{0.375}MnO_3$ (LCMO) films of thickness 200 nm were grown on $NdGaO_3$ (NGO) (110) substrates using pulsed laser deposition. The samples, mounted on the STM sample holder with a conducting silver epoxy, were transferred into the STM cryostat in a very short time (<30 min) to minimize the time of exposure to air. The STM cryostat was evacuated to high vacuum ($\sim 10^{-4}$ mbar) before cooling. Tunneling spectra and the STS images were acquired using the ac modulation technique; however, for ZBC comparison direct I–V spectra were used. For the spectra at a fixed point the feedback was switched off while for the STS imaging the feedback was kept on but with a larger time constant so that it does not respond to the ac modulation. In this way one gets a contrast in STS images which actually anticorrelates with the metallicity, i.e. the darker regions have more DOS at E_F while the brighter ones have less DOS at E_F. We kept the junction resistance values the same for all the local spectra taken at different locations and different temperatures to minimize the variation in the tip–sample separation. This is necessary for comparing the absolute values of dI/dV for different spectra at a particular bias voltage. A dI/dV–V spectrum is a convolution of the density of states (DOS) and the energy-dependent matrix element, which can be normalized away [23] by plotting the normalized conductance $(dI/dV)/(I/V)$, i.e. $d\ln I/d\ln V$. However, at $V = 0$, $d\ln I/d\ln V = 1$ by definition, so for studying the variation in DOS at E_F ZBC (dI/dV at $V = 0$) is analyzed.

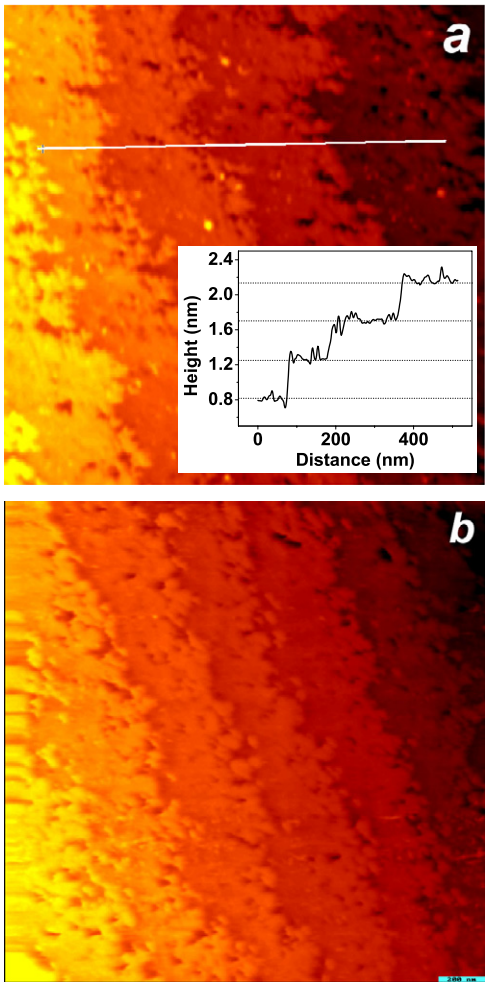

Figure 2. Topographic image of LCMO film at (a) 310 K (area 601 × 601 nm^2, bias = 1.0 V, current = 0.1 nA) and (b) 78 K (748 × 748 nm^2, 1 V/0.1 nA). The inset in (a) shows the line cut with atomic height terraces.

3. Results

Figure 1 shows the four-probe resistivity as a function of temperature for an LCMO thin film with an insulator to metal transition at 250 K. Above 250 K the film shows insulating behavior with a polaron activation gap of $E_A = 0.112$ eV (or 1310 K) as shown by the fitting $\rho = AT\exp(-E_A/k_BT)$ [10] in figure 1. This gap magnitude is in agreement with the earlier work of Jaime *et al* [6]. The absolute resistivity is in the mΩ cm range and the decrease across T_{IM} in resistivity is almost by a factor of two. This change is not so large compared to some of the narrow bandwidth manganites [24]. Thus we would expect a lesser change in DOS near E_F across T_{IM} as compared to the narrow bandwidth manganites.

Figure 2 shows the topographic STM images of this film at 310 and 78 K showing the atomic terraces of 0.4 (±0.05) nm step height and 100–150 nm width. Each terrace has a roughness of about 0.1 nm. The terraces are observed

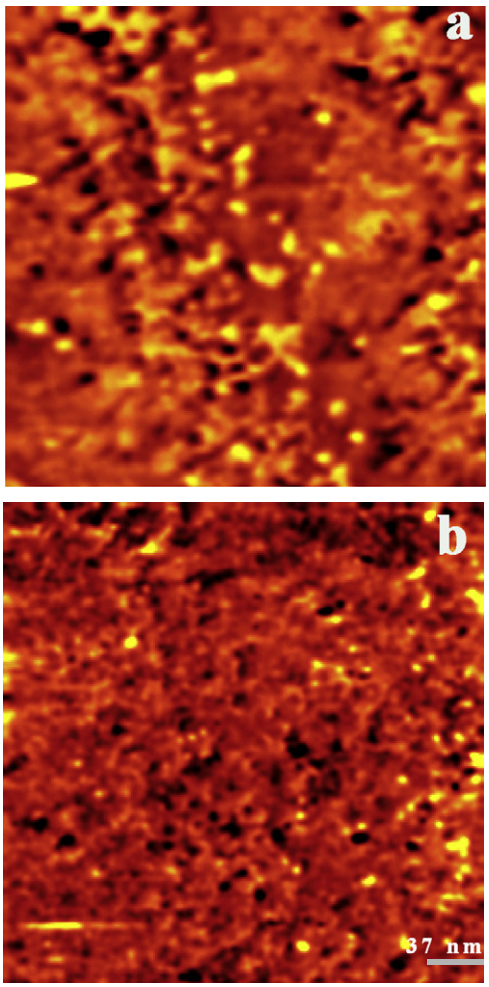

Figure 3. (a) and (b) Show the simultaneous topographic and conductance image (area 304 × 304 nm^2, 1 V/0.1 nA) taken at 78 K. The film surface has been found electronically homogeneous at all temperatures except for some insulating bright regions of 5–10 nm^2 area.

over more than 2 × 2 μm^2 area at all temperatures between 78 and 310 K. The STS images (see figure 3(b)) show little contrast, which consists of some isolated bright spots with a weak contrast in the background. The bright spots show large gap spectra while in other places we see pseudogapped spectra with a small variation in the ZBC that correlates well with the STS image contrast. We believe that these insulating bright spots in STS images correspond to some local chemical defects [24]. We have areas scanned up to 2 × 2 μm^2 with similar conductance inhomogeneities.

Figure 4 shows the normalized spectra at 246 and 78 K taken at different locations in a particular area together with their average. These spectra are neither metal-like nor pure gap-like and they feature a pseudogap-like depression near zero bias with a finite ZBC. Although the spectra at these two temperatures look qualitatively similar there is a difference in the energy scale of the pseudogap which is quite clear despite the spatial variations in the spectra. To eliminate such variations we have taken an average of several tens of spectra at different places to study the evolution of the DOS with temperature. The corresponding d ln I/d ln V spectra are shown in figure 5. We see that the spectra at all temperatures are quite asymmetric. Such asymmetry is quite common in most transition metal oxides including cuprates [25] and its origin is not quite clear. It could also arise from the effects related to the tunneling matrix element as argued by Ukraintsev [26], particularly for large bias range, which is the case here. We see that for negative bias the kink due to the gap-like feature in the normalized conductance is still visible but much weaker because of a rising background.

The temperature evolution of the normalized spectra across T_{IM} can be described by two features. The first one is the energy scale over which the depression in DOS (representing the pseudogap) occurs, which can be qualitatively deduced from the spectra as the voltage at which there is a change in slope. This can be seen better with the guiding lines corresponding to the low bias and high bias part of the spectra as shown in figure 5. Thus the pseudogap's energy scale increases with cooling by about 0.2 V as can be seen by comparing the spectra above and below 246 K. We have estimated the magnitude (Δ) of the pseudogap at various temperatures as shown in figure 5[1]. The variation of this gap parameter is shown in the inset of figure 5. The magnitude (Δ) of the pseudogap, varying from 0.25 to 0.36 eV, is in agreement with the polaronic energies estimated by Millis [30]. The second feature is the decrease in the slope of the pseudogap edge across T_{IM} with cooling. This can be seen from the guidelines of the low bias region in the same figure. Thus with cooling the gap edge does not really move out to increase the pseudogap but it becomes wider.

The other major result of our measurements is a non-zero DOS at E_F, i.e. the ZBC value is finite at all temperatures and it increases with cooling. We see a clear variation in the ZBC with temperature as seen in figure 6; the zoomed-in plot of the average I–V spectra is also shown in the inset of figure 6. All the I–V spectra used in this plot have been taken with the same junction resistance (1 V/0.3 nA) and each spectrum is an average of several tens of spectra taken at different locations but avoiding the insulating spots. We clearly see that the slope of the I–V spectra near zero bias increases with cooling and, in particular, it has a jump near T_{IM}. This increase in ZBC with cooling is more in line with the bulk transport measurements, low temperature optical Drude weight [11] and the recent ARPES results [13].

The above two results, i.e. increase in ZBC and pseudogap energy scale with cooling, are indicative of some spectral weight transfer from high energy (roughly from 0.35 to 0.50 eV) to lower energies. The pseudogap does not disappear in the FM state of manganite which is unusual for the metallic phase of manganites. The pseudogap has

[1] We have estimated the gap magnitude in two ways which agree with each other. The first one uses the midpoint of the gap edges in the normalized spectra. The second one is by fitting the normalized conductance spectra for positive bias to a function of the form $\sigma_n = 1+\alpha|V|+\beta[1-\exp(-V^2/\Delta^2)]$. Here α is needed to fit the weak linearly rising background while the β and Δ determine the depth and the width of the pseudogap feature, respectively. Although the pseudogap feature exists for both the biases the spectra have noticeable asymmetry and thus fitting for positive sample bias is better than that for the negative bias.

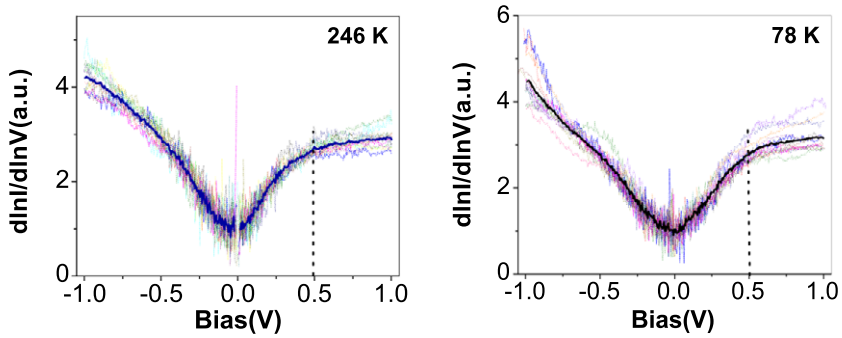

Figure 4. The dotted curves show those spectra that were taken at different places. The solid line curves for 246 K and 78 K show average spectra.

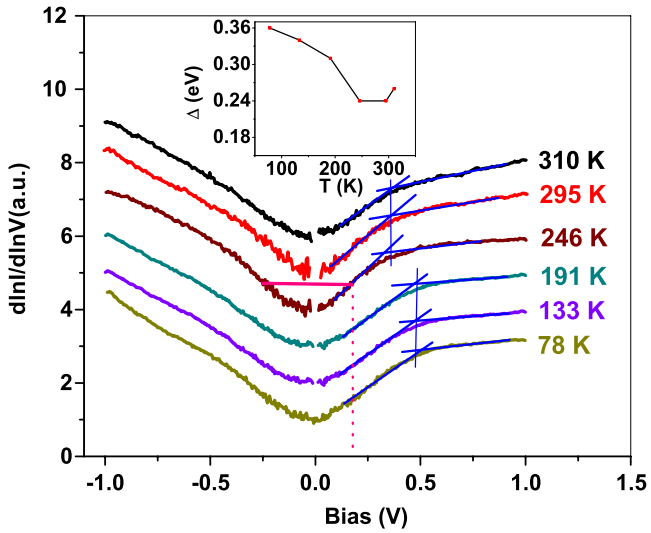

Figure 5. The temperature-dependent spectra taken at 10 GΩ (1 V/0.1 nA) junction resistance. d ln I/d ln V spectra have been offset uniformly for clarity. The inset shows the variation in the pseudogap energy parameter (Δ) with temperature.

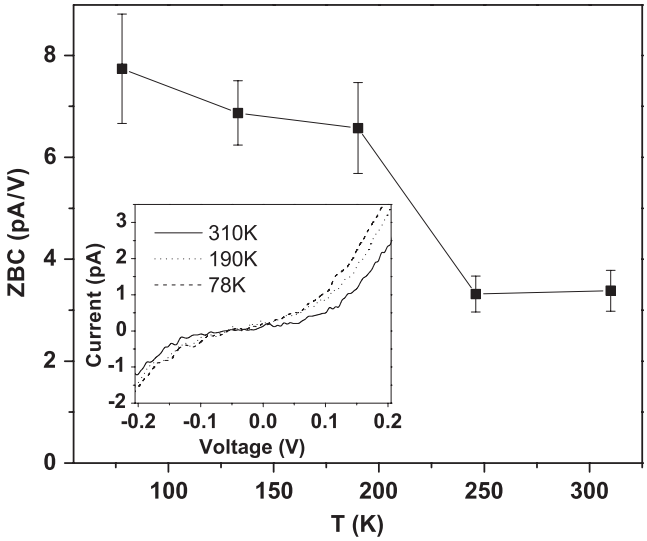

Figure 6. The variation in ZBC with temperature with the error bars showing the rms spread in ZBC. The inset shows representative low bias region of the I–V spectra at three different temperatures taken at the same junction resistances (1 V/0.3 nA).

also been observed by optical, ARPES and recent tunneling measurements [11, 28, 27, 14, 15] and is an indication of JT polarons.

4. Discussions

Tunneling measures the DOS, which, in comparison to ARPES, represents the spectral function integrated over all **k** vectors. The recent ARPES experiments [13] find pockets of quasiparticles in a very narrow region of the 2D Fermi surface of a layered manganite. Thus the change in the total DOS at E_F due to this quasiparticle peak would be rather small. The earlier ARPES on bilayer manganites did not observe this peak [29] due to an insufficient **k** resolution. We believe that these quasiparticles at E_F exist in the metallic phase of other manganites as well but require much better **k** resolution to be experimentally detected. The 2D bilayer manganites offer an ideal system for ARPES as they provide excellent **k** resolution. The c-axis tunneling may not be able to probe the in-plane quasiparticles for 2D manganites [14] as the in-plane **k**-states contribute negligibly in c-axis tunneling. In 3D manganites the same **k** resolution is difficult with ARPES since well-oriented surfaces, like 2D cleavable manganites, are not possible to prepare.

The theory of Millis *et al* [4], for a range of JT coupling, finds delocalized states in the FM phase giving a non-zero spectral weight or DOS at E_F. The measured Drude weight [11] is two orders of magnitude smaller than in a typical metal, although it does indicate the presence of metal-like free carriers in the FM phase. However, the exact nature of the mobile charge carriers in the FM state is far from clear. In particular, it is still debatable whether manganites are bad metals because they are homogeneous systems with all (polaronic) carriers having poor mobility or they are a mixture of free carriers and localized polarons.

It seems from various experimental results, including the present one, that we can neither rule out free carriers nor polarons in the FM phase. Thus the coexistence of two types of carriers is a likely scenario. The delocalized carriers in the FM phase could arise in a number of ways, such as large

polarons, band electrons or coherent small polarons. Although our tunneling data cannot differentiate between these scenarios we believe that the small polarons' coherence [12, 18, 31] could be giving rise to the metallic free carriers, particularly in the broad bandwidth manganites.

As compared to our recent STM study on more metallic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films [34] the DOS at E_F is smaller in these LCMO films while it is larger as compared to the less metallic $La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$ films [24]. In fact, for the LSMO films we see a rather broad dip above T_{IM} which evolves into a well-defined pseudogap with a larger ZBC with cooling. This is qualitatively similar to the present LCMO study except for a well-defined pseudogap at all temperatures. Both LSMO and LCMO spectra are also in agreement with the dynamic phase separation [35] scenario, where one can have dynamically coexisting insulating and metallic phases fluctuating over a timescale much shorter than the STM measurement time. The coexisting coherent and localized polarons scenario may be difficult to differentiate from the dynamic phase separation as both involve two types of coexisting entities.

As discussed earlier, the pseudogap increases with cooling, presumably due to larger binding energy of the localized polarons, while we believe that the ZBC increases due to the presence of coherent polarons. In the bilayer manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$, the STM [14] shows an increase in the gap while the ARPES [13] shows a quasiparticle peak at E_F together with a pseudogap that decreases in magnitude in the metallic phase. This qualitative inconsistency also seems to be present in 3D manganites, i.e. with cooling, ARPES on 3D manganites [28] observes a less pronounced pseudogap while with STM we see it more pronounced.

We would like to point out that, in most manganites, the surface has been found to be less conducting with a weaker ferromagnetic order [24, 32]. The breaking of crystal symmetry or oxygen deficiency at the film surface could be affecting the surface's electronic and magnetic properties [33]. We can also not avoid the extreme surface sensitivity of STM/STS (as well as ARPES) measurements, where the surface may act as a barrier in probing the bulk properties of LCMO due to oxygen deficiency or surface contamination. However, the fact that we see a change in pseudogap behavior near T_{IM} and the temperature variation of ZBC qualitatively agrees with the bulk transport makes us believe that the surface here does reflect the bulk, at least qualitatively. It is also possible that the surface provides an additional barrier (other than the vacuum barrier) for tunneling into the bulk.

5. Summary

In summary, our tunneling experiment finds a pseudogap at all temperatures (78–310 K) in the strain-free epitaxial LCMO thin films. The pseudogap energy is larger in the FM phase but the DOS at E_F is also larger in the FM state than in the PI state. The latter result is in agreement with the bulk transport, optical conductivity and recent ARPES results. From this we strongly believe that the IM transition in the broad bandwidth manganites results from a polaronic transition involving the high temperature small polarons giving rise to coherent and delocalized states at E_F.

Acknowledgments

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