Temperature Dependent Tunneling study of La$_{0.625}$Ca$_{0.375}$MnO$_3$ Thin Films

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Abstract. The tunneling measurements on La$_{0.625}$Ca$_{0.375}$MnO$_3$ strain free epitaxial thin films with an insulator-metal transition temperature ($T_{IM}$) of 250 K were performed using variable temperature scanning tunneling microscopy and spectroscopy (STM/S). We find a depression in the DOS with a finite zero bias conductance (ZBC) signifying the presence of a pseudogap (PG) at all temperatures. With cooling, the ZBC is found to increase together with an increase in the PG energy of about 0.2 eV near the transition. The PG is a signature of the polarons while the increasing ZBC, in agreement with the bulk insulator-metal transition indicates the presence of free carriers at the Fermi energy.

1. Introduction

The colossal magnetoresistance (CMR) behavior in manganites [1] near their ferromagnetic metallic (FM) to the paramagnetic insulating (PI) state transition at $T_{IM}$ is of significant scientific and technological interest. The Zener double exchange[2] mechanism that explains the CMR behavior was found to be insufficient in understanding the detailed physics of manganites. The Jahn-Teller interaction [3] is rather strong in manganites and it can give rise to electron trapping in the local lattice deformations [4]. This lattice deformation together with the trapped electron is termed as polaron. The polarons can move depending on their detailed nature either by thermally assisted hopping or by a coherent transport. In the former case it has to overcome an energy barrier as it moves from a lattice site with lattice deformation to an undeformed site. In the latter case the polaronic wave function spans more than one lattice site either because of its intrinsic large polaron (LP) nature or because of a large scale coherence at low temperatures. The role of polarons in PI state is well accepted and the recent experiments, such as neutron scattering [5], optical conductivity [7], Angle Resolved Photoemission Spectroscopy (ARPES) [13], and tunneling [8, 9], also indicate the presence of polarons in the FM state. ARPES [10, 11] and point contact spectroscopy [12] show a depression in the DOS at $E_F$ signifying a pseudogap (PG) in the FMM state. This gap has been interpreted as the polaron binding energy which is needed to create a free electron. The tunneling measurements so far have shown a hard gap in the FM state [9, 16, 8] which is not consistent with bulk and transport measurements. The presence of the energy gap is an unusual phenomenon in the metallic state. The electronic inhomogeneities on manganites’ surface were also investigated by STM experiments [15] which strongly support the phenomenon of phase separation in manganites. Therefore, in order to probe the intrinsic inhomogeneities and the PG observed in the manganites, we performed the
2. Experimental setup

La$_{0.625}$Ca$_{0.375}$MnO$_3$ (LCMO) films of thickness 200 nm were grown on (110) plane of NdGaO$_3$ (NGO) substrates using pulsed laser deposition under very slow growth mode. The films were mounted on STM holder with a conducting silver epoxy and transferred into STM chamber in a very short time (< 30 min) to minimize the time of exposure to air. The STM cryostat was evacuated to high vacuum (~10$^{-4}$ mbar). Incidently, these measurements were repeated a number of times over three months and in between the sample was stored in a vacuum (~10$^{-2}$ mbar) desiccator. The nature of spectra was found same in each times of measurements.

The STM cryostat was dipped in liquid nitrogen and the temperature was varied using a heater wound around a copper enclosure surrounding the STM. Tunneling spectra were acquired using modulation method using ~50mV ac-modulation. More details on this STM/S measurements have been reported earlier [16]. We kept the junction resistance values same for all the local spectra taken at different locations and different temperatures to ensure the same 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 [17] by plotting the normalized conductance (dI/dV)/(I/V), i.e. dlnI/dlnV. However, at V=0, dlnI/dlnV=1 by definition, so for comparison of the DOS at E$_F$, we directly look at dI/dV value or I-V spectrum slope at V=0.

3. Results and Discussion

The T$_{IM}$ of LCMO films has been observed to be 250 K by four probe resistivity measurement as shown in Fig.1a. The absolute resistivity is in mΩ-cm range and the ratio of the resistivity at transition to that at low temperatures $\rho(T_{MI})/\rho(100K)$ is ~30. This ratio is not so high as compared to some of the narrow bandwidth manganites where the ratio is in 10$^3$ range. Thus we would expect less change in DOS near E$_F$ across T$_{IM}$ as compared to the narrow bandwidth manganites.

The topography images of this films at 310 and 78 K temperatures are shown in Fig.1b. The line cut in the image at 310 K (see the inset in Fig.1b) shows atomic terraces of 100-150 nm width separated by 0.4(±0.05) nm height steps. The surface roughness on a particular terrace is found to be less than 0.1 nm. These terraces have been seen at all temperatures between 78 and
Figure 2. a. The spectra in the plot have been offset uniformly for clarity. The continuous lines in a show the best fits to a pseudogapped DOS as described in the text. b. 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 same junction resistances (1 V / 0.3 nA).

310 K and it assures a clean, smooth and defect free surface for STM/STS. The conductance spectra (dI/dV-V) were taken at the same junction resistance of 10 GΩ (bias voltage 1.0 V and tunnel current 0.1 nA) at various temperatures. The average of about hundred spectra at different places was taken to study the evolution of the DOS with temperature.

We present here the temperature dependent dlnI/dlnV spectra in Fig.2a which are neither metal-like nor pure gap-like. We see a depression near zero bias in dlnI/dlnV-V plot with a finite zero bias conductance (ZBC) which also has some temperature evolution as discussed later. Thus this depression in DOS represents a PG, which has also been observed in earlier experiments [10, 11, 13, 12] manganites. To analyze the PG energy scale variation with temperature we have fitted a function of the form $\sigma_n = 1 + \alpha |V| + \beta [1 - \exp(-V^2/\Delta^2)]$ to the normalized conductance for the positive sample bias (i.e. $E < E_F$). Here $\alpha$ is needed to fit the weakly linearly rising background while the $\beta$ and $\Delta$ determine the depth and the width of the PG feature, respectively. The spectra are quite asymmetric and the fitting for positive bias is much better than that for negative bias as shown in Fig.2a. Ukraintsev [18] argued that this asymmetry could be related to the positive bias dependence of tunneling matrix elements but we cannot rule out an intrinsic asymmetry in the DOS here. An asymmetry in tunneling spectra has also been observed in cuprates [20] and it could be an intrinsic nature of such oxides. We see that for negative bias the kink due to gap-like feature in the normalized conductance is still visible but much weaker because of a rising background. The calculated values of $\Delta$ from the fitting curves show that there is an increase in PG energy ($\Delta$) with cooling which is in contradiction with the resistivity data as the sample is more conducting at low temperatures. The $\Delta$ has a value of 0.35 eV for spectra below 200 K while above 240 K $\Delta$ value is 0.24 eV. So there is an increase in the 2$\Delta$ value of $\sim$0.2 eV across $T_{IM}$ with cooling. The value of $\alpha$ is found to increase mildly with increasing temperature and there is a small decrease in the $\beta$ value. This behavior is similar to our recent La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ (LPCMO) tunneling data [16] except for the fact that the gap here is not fully open.

The other major result of these measurements is a non-zero DOS at $E_F$ i.e., the value of dI/dV is finite at zero bias at all temperatures and it increases with cooling. We never see a fully open hard gap at any place and at any temperature. We see a clear variation in the ZBC with temperature as seen on zooming into the average I-V spectra as shown in Fig.2b. All the spectra shown in this plot have been taken with the same junction resistance (1 V/0.3 nA) and each spectra is an average of about hundred spectra taken at different locations. We clearly see that the slope of the I-V spectra near zero bias increases with cooling. This increase cannot
possibly be due to the thermal smearing of the higher energy states as the PG’s energy scale is rising with cooling while the thermal smearing reduces with cooling. This increase in ZBC with cooling is more in-line with the bulk transport measurements and also with the low temperature Drude weight [7, 6] and the recent ARPES results [14].

This temperature variation of ZBC in LCMO is in contrast with our recent LPCMO experiments [16] where the ZBC was found to decrease with cooling. In that work the tunneling data were anticorrelated with the bulk transport but they correlated well with the known CO phase below 210 K. In the present data, the PG has slightly larger magnitude than the resistivity activation gap in PI phase and it further increases in FM phase. This could be attributed to a poorly conducting surface. In most manganites, the surface has been found to be less conducting with weaker ferromagnetic order [19]. However, the fact that the jump in PG occurs at T_{IM} and the temperature variation of ZBC values are in qualitative agreement 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 additional barrier (other than the vacuum barrier) for tunneling into the bulk. Finally we believe from the observation of PG with none-zero DOS at E_F that FM of manganites is polaronic conductor with more delocalized carriers in the metallic phase. It is not clear if the delocalized carriers are also polaronic in nature.

4. Conclusions
Our tunneling experiments find a pseudogap at all temperatures (78-310K) in the strain free epitaxial La_{0.625}Ca_{0.375}MnO_3 thin films. The pseudogap is larger in the FM phase but the the DOS at E_F is larger in the FM state as compared to PI state. The latter result is in agreement with the bulk transport, optical conductivity, and recent ARPES results.

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