

# The Density of States of hole-doped Manganites: A Scanning Tunneling Microscopy/Spectroscopy study

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Variable temperature scanning tunneling microscopy/spectroscopy studies on single crystals and epitaxial thin films of hole-doped manganites, which show colossal magnetoresistance, have been done. We have investigated the variation of the density of states, at and near the Fermi energy ( $E_f$ ), as a function of temperature. Simple calculations have been carried out, to find out the effect of temperature on the tunneling spectra and extract the variation of density of states with temperature, from the observed data. We also report here, atomic resolution images, on the single crystals and larger range images showing the growth patterns on thin films. Our investigation shows unambiguously that there is a rapid variation in density of states for temperatures near the Curie temperature ( $T_c$ ). While for temperatures below  $T_c$ , a finite DOS is observed at  $E_f$ , for temperatures near  $T_c$  a hard gap opens up in the density of states near  $E_f$ . For temperatures much higher than  $T_c$ , this gap most likely gives way to a soft gap. The observed hard gap for temperatures near  $T_c$ , is somewhat higher than the transport gap for all the materials. For different materials, we find that the magnitude of the hard gap decreases as the  $T_c$  of the material increases and eventually, for materials with a  $T_c$  close to 400 K, the value of the gap approaches zero.

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## I. INTRODUCTION

The phenomenon of Colossal Magnetoresistance (CMR) in hole-doped rare-earth manganites has, in recent times, been the subject of intense research efforts [1–4]. These oxides belong to the  $ABO_3$  class of perovskite oxides and contain a mixed valency of Mn, which occupies the B site. The A site is occupied by rare-earth ions like Nd, La etc. or by divalent ions like Pb, Ca etc. These oxides, therefore, have the general formula  $Re_{1-x}Ae_xMnO_3$ , where Re is La, Nd etc. and Ae is Ca, Pb etc. There are a number of basic issues which need to be resolved to understand the unusual transport properties of these materials. One of the interesting properties is the sharp peak in resistivity ( $\rho$ ) close to its ferromagnetic transition temperature ( $T_c$ ). The peak in  $\rho$  is generally believed to arise from an insulator-metal like transition on cooling below  $T_c$ . Since the system shows a transition from an insulator like state above  $T_c$  to a metallic state below  $T_c$ , it is likely that there is a change in the density of states (DOS) at the Fermi level ( $E_f$ ), near  $T_c$ . The change in the DOS at  $E_f$  ( $n(E_f)$ ) is thus ushered in by changing the temperature. This issue is of fundamental importance as  $n(E_f)$  will decide the nature of charge transport in the material. Questions like the existence of a gap in the DOS at  $E_f$ , localization of states near  $E_f$  etc. are still unresolved. We formulate the following definite questions which we would like to seek answers to: (1) Is there a finite DOS at  $E_f$  below  $T_c$  i.e. in the metallic state, and if so, whether it has a temperature dependence? (2) Does a gap open up in the DOS near  $E_f$  above  $T_c$ , i.e. in the paramagnetic insulating state and if so whether it is temperature dependent?

In this paper we report our extensive investigations

of the DOS of these materials as a function of temperature, using variable temperature scanning tunneling spectroscopy. We have carried out our studies on epitaxial thin films and single crystals of various compositions. Mainly we have studied two systems, namely,  $La_{0.8}Ca_{0.2}MnO_3$  epitaxial thin films and single crystals of the system  $La_{1-x}Pb_xMnO_3$ .

## II. EXPERIMENTAL DETAILS

Single crystals of  $La_{1-x}Pb_xMnO_3$  were grown by the flux method using PbO and  $PbF_2$  as solvents [5]. The flux ratio has been optimized to lower the growth temperature, to combat the high volatility of the flux. In addition, the heating, soaking and cooling temperatures have been optimized. The precursors, homogenized in a ball mill, are transferred to a Platinum-Iridium crucible and closed tightly with a Platinum lid. The growth process is carried out in a cylindrical resistive furnace, controlled by a programmable temperature controller. The charge is soaked at 1050°C for 24 hours and slow-cooled in steps of several ramp rates ranging from 0.2 to 1.5°C/hour to 850°C, and thereafter furnace-cooled to room temperature. Crystals of typical dimensions  $1.5 \times 1.5 \times 1.5 \text{ mm}^3$  are obtained by this method. The composition of the as-grown crystals are found by EDX analysis. The lead content is varied by changing the charge-to-flux ratio. Single crystals of the compound  $(La_{1-y}Nd_y)_{1-x}Pb_xMnO_3$  are grown by a similar method (this compound will be, hereinafter, referred to as  $(NdLa)_{1-x}Pb_xMnO_3$ , which signifies that the Nd and La concentrations are  $\sim (1-x)/2$ , for the particular compound studied here).  $La_2O_3$ ,  $Nd_2O_3$  and  $MnCO_3$  are dissolved in the ratio 1:1:4 in the flux

mixture of PbO-PbF<sub>2</sub> and crystal growth initiated as in the case of La<sub>1-x</sub>Pb<sub>x</sub>MnO<sub>3</sub>. Here, crystals of typical dimension,  $2.5 \times 2.5 \times 1.5$  mm<sup>3</sup> were obtained.

Epitaxial films of La<sub>0.8</sub>Ca<sub>0.2</sub>MnO<sub>3</sub> (referred as LCMO), were prepared by pulsed laser ablation on LaAlO<sub>3</sub> substrates, using the procedure described in ref. [6].

The resistivity of the samples were measured by four-probe van der Pauw method (for the single crystals) or four probe linear method (for the thin film). The magnetoresistance was measured using a superconducting solenoid.

Scanning Tunneling Microscopy/Spectroscopy (STM/S) was done in a home-made variable temperature STM. The schematic diagram of the STM/S setup is shown in figure 1. The STM was operated from 100 K up to 375 K. During the experiment the STM chamber is kept in a cryopumped environment and all other pumps are disconnected from the system.

Since we have operated our STM from temperatures up to 375 K and down to 100 K, we have chosen samples having a wide range of  $T_c$  to get data for a good range both above and below  $T_c$ . The single crystals' surfaces were scraped mechanically to expose a fresh surface before loading it in the STM. The thin films was cleaned with methanol before loading it in the STM chamber. Mechanically cut Pt-Rh(13%) tips were used for all the tunneling experiments. The samples were baked at about 370 K, in a vacuum of  $5 \times 10^{-6}$  torr, for 24 hours prior to the STM/S measurements. The STM chamber was then cooled to liquid nitrogen temperatures and the chamber was isolated from the external pumps. The samples were further baked, at around 340 K, in a cryopumped environment for 5-6 hours to avoid condensation of residual gases on the sample surface. The samples were then imaged at various magnifications and at different temperatures. The images obtained also served as a test of the cleanliness of the sample surface. The images were taken in the constant current mode, with the tip bias kept at 1.5 V and the tunneling current, during imaging was stabilized at values ranging from 1 to 2 nA (exact values are specified for the particular images). Reproducible images were obtained over long durations indicating that the surfaces were stable and only after obtaining reproducible images, tunneling spectroscopy was carried out. This ensured the cleanliness of the sample surface before the  $I - V$  spectra were recorded. We found that if gases like Nitrogen are made to condense on the surface, most of the features in the  $I - V$  curves are washed out and the surface cannot be imaged. During data acquisition no external pumps were used and only the cryopump placed inside the chamber was used to retain the vacuum.

For recording the  $I - V$  spectra, the tip bias was kept at 1.5 V and the tunneling current ( $I_t$ ) was stabilized at a particular value. The feedback was then put to hold mode and the tip bias was swept between  $\pm 1$  V at a

frequency of 6 Hz and a set of  $I - V$  curves thus obtained, were recorded digitally using a 16 bit AD card. The gain of the current amplifier is  $10^8$  V/A and the least count of the AD card is  $300 \mu\text{V}$ , so the minimum measurable current with this setup is about 3 pA. The data were recorded at a rate of 7.2 KHz. A set of 5  $I - V$  curves were averaged. The  $dI/dV - V$  and  $d \ln I / d \ln V - V$  curves were obtained by numerical differentiation of such average  $I - V$  curves. This procedure was repeated for different values of stabilization currents and at different points on the sample surface, at each temperature.

To determine the exact value of the gaps observed, variable distance tunneling measurements were carried out for one sample ((NdLa)<sub>0.73</sub>Pb<sub>0.27</sub>MnO<sub>3</sub>). This was done only for positive tip bias (filled states of the sample). The procedure followed was the same as above except, the tip bias was swept from 0.01 to 2 V instead of  $\pm 1$  V and the feedback was kept in the sample mode. With an active feedback loop the tip went closer to the sample for lower biases, in order to keep the  $I_t$  constant. This gave us a large dynamic range for the measurement of  $I_t$  and we were able to measure the correct voltage value for which the  $I_t$  goes to zero and hence the correct energy value for the band edges. For details of this method see ref. [7].

### III. RESULTS

In figure 2 we show the resistivity data of the samples studied. The materials, as expected, show a peak in  $\rho$  at a temperature close to  $T_c$ . We designate this temperature, where the peak in  $\rho$  occurs, as  $T_{IM}$ . The resistivities of the single crystals are much less than that of the thin film. However, due to the small size of the crystals, the absolute values of  $\rho$  have uncertainties. The details of the samples are given in table I. Some of the quantities were not measured due to experimental limitations, but the essential quantities for our subsequent analyses and conclusions have been measured. The resistivities are shown in zero field or in an applied field (3 or 6 Tesla). For the LCMO film the maximum magnetoresistance (MR) is in excess of 80 % for an applied field of 6 T. For (NdLa)<sub>0.73</sub>Pb<sub>0.27</sub>MnO<sub>3</sub> the maximum MR (at 3 T) is nearly 70 %. Here we have defined the MR as  $(\rho(0) - \rho(H))/\rho(0)$ . It can be seen from the data on the (NdLa)<sub>0.73</sub>Pb<sub>0.27</sub>MnO<sub>3</sub> system that the  $T_c$  and  $T_{IM}$  can be varied over a large temperature range by substituting Nd in place of La. This is expected, because the  $T_c$ , in these materials, decreases as the average A-site cation radius ( $\langle r_A \rangle$ ) decreases. Here A-site refers to the A-site of the ABO<sub>3</sub> structure. Substitution of smaller Nd in place of La thus leads to the reduction of  $T_c$  [8,9].

Figure 3 shows an atomic resolution image obtained for the sample La<sub>0.6</sub>Pb<sub>0.4</sub>MnO<sub>3</sub>. The distance between the brighter spots is  $4.02 \pm 0.2 \text{ \AA}$  as derived from our

calibration done on graphite. These materials have a pseudo-cubic structure and the unit cell is nearly cubic or rhombohedral with  $\alpha \approx 60.52^\circ$  (for a perfect cube,  $\alpha = 60^\circ$ ), as obtained from x-ray structure determination. The Mn-O-Mn distance in these materials is around 3.87 Å. The distance observed by us is thus close to this distance and the difference can arise due to the uncertainty in calibration. One may thus argue that the surface exposed has Mn-O-Mn chains. However, we have not been able to ascertain, unambiguously, the chemical identity of the imaged atoms. To determine the chemical identity of the atoms, further studies involving bias dependent imaging of the surface have to be performed. We also observe a distortion from the perfect square array, as can be seen from the  $4.02 \text{ Å} \times 4.02 \text{ Å}$  parallelogram drawn in figure 3.

Figure 4 shows a  $853 \text{ Å} \times 906 \text{ Å}$  image of the LCMO thin film. This image shows atomically smooth terraces, which end in atomic level steps as marked by the arrows. These are typical growth patterns often observed in thin film samples of these oxides [10,16].

Figure 5 shows the  $dI/dV - V$  ( $G - V$ ) curves for two of the samples,  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  single crystal and LCMO thin film. In our subsequent discussions we have referred to these curves. We have shown the data for three distinct regions,  $T < T_c$ ,  $T \approx T_c$  and  $T > T_c$ . To avoid overcrowding of data, we have shown only a cross-section of the data taken.

The  $G - V$  curves, for all the samples, show qualitative variations with temperature, when the temperature is changed across the  $T_c$ . This is obvious directly from the  $G - V$  curves. Before a detailed discussion of the results, we point out some preliminary observations which can be made from the  $G - V$  curves shown above, which are common to all the samples studied. For  $T < T_c$ , the  $G - V$  curves resemble those for a good metal, like platinum. There is a finite value of the zero-bias conductance ( $G_0$ ), and the  $G - V$  curves are parabolic. The parabolic nature of the  $G - V$  curves is essentially a property of the tunneling barrier [15]. This is expected as the metallic state is stabilized below  $T_c$ . For comparison we show, in figure 6, the  $G - V$  curve for a  $500 \text{ Å}$  film of platinum at 307 K. The inset shows the  $G - V$  curve for the same film at 134 K. The calculated curves shown in the figure are discussed later in section IV B. The film was grown on a fire-polished glass surface using electron-beam evaporation, in a base pressure of  $10^{-8}$  torr.

As the temperature is increased to  $T \approx T_c$ ,  $G_0$  goes to zero and a gap like feature opens up near zero bias i.e. the Fermi level. As the temperature is increased further to  $T > T_c$ ,  $G_0$  becomes non-zero again and the gap like feature vanishes. But these  $G - V$  curves are qualitatively different from the metal-like  $G - V$  curves for  $T < T_c$ . We will see below that this particular feature of the tunneling data for  $T > T_c$  implies the existence of a soft gap near  $E_f$ , with additional contributions to  $G_0$

arising due to finite temperature.

## IV. DISCUSSION

The tunneling spectroscopy data as presented in the previous section need to be analyzed quantitatively before further conclusions can be drawn from them. There are different recipes for obtaining the density of states from tunneling data [11–13]. However, the problem becomes involved if the DOS itself is temperature dependent. This is in addition to the temperature dependence which arises through the Fermi function  $f(E, T)$ . In the following, we have tried to take into account all these effects to derive certain quantitative conclusions about the DOS. We have arranged the following discussion in four subsections, to analyze our data, so that quantitative information about the DOS ( $n(E)$ ) can be obtained to the extent possible. In the first section we analyze the data for energy  $|E - E_f| \geq 0.2 \text{ eV}$  which is the region away from  $E_f$  so that the overall temperature dependence of  $n(E)$  can be obtained. In the second section we analyze the  $n(E)$  near the  $E_f$  for the ferromagnetic region ( $T < T_c$ ). In the third section we analyze the data for temperatures near the transition temperature  $T_c$  ( $T \approx T_c$ ). In the fourth section we have investigated the region close to  $E_f$ , for the paramagnetic regime ( $T > T_c$ ).

### A. DOS for $|E - E_f| \geq 0.2 \text{ eV}$

In this section we discuss the features in the DOS for  $|E - E_f| \geq 0.2 \text{ eV}$ . Figure 7 shows the  $d\ln I/d\ln V - V$  curves for different temperatures, for some of the samples studied.  $d\ln I/d\ln V$  is the normalized conductivity  $(dI/dV)/(I/V)$ . This quantity is generally used as a measure of the DOS, independent of the barrier parameters [12]. The division of the differential conductance ( $dI/dV$ ) by  $I/V$  reduces the effect of the barrier parameters. Within certain limits  $d\ln I/d\ln V$  does give a measure of the DOS [11]. This quantity ( $d\ln I/d\ln V$ ) is not well-defined near zero-bias, when there is a gap like feature in the DOS (low  $G_0$ ) near the Fermi level [14]. Due to this limitation we have calculated  $d\ln I/d\ln V$  outside the region of very low  $G_0$  ( $|V| \geq 0.2 \text{ V}$ ), from the observed data. The tunneling spectra for the low bias region will be discussed in the following sections. From figure 7 we conclude that the DOS for  $|E - E_f| \geq 0.2 \text{ eV}$  changes dramatically with temperature, when the temperature is changed across  $T_c$ . The behavior shown in figure 7(a) is a typical example. For  $T < T_c$ , the DOS has a stronger dependence on energy, on both the filled ( $V < 0$ ) and unfilled ( $V > 0$ ) side than that for  $T > T_c$ . Also the temperature dependence of  $(d\ln I/d\ln V)$  saturates for  $T/T_c < 0.75$ , as shown in the inset of figure 7(b) where we have shown an example for  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ ,

which has a  $T_c > 400$  K (we could not measure  $T_c$  due to experimental limitations, however, the  $T_{IM} = 401$  K).

The temperature variation of  $(d\ln I/d\ln V)$  at a given voltage  $V = 0.9$  volts ( $(d\ln I/d\ln V)_{0.9V}$ ) is shown in figure 8 to find out the extent of variation in  $(d\ln I/d\ln V)$ . We have chosen  $V = 0.9$  volts, as it is away from  $V = 0$  and thus represents states away from  $E_f$ . It can be seen from figure 8 that  $(d\ln I/d\ln V)_{0.9V}$  is higher for  $T < T_c$  than that for  $T > T_c$  (a preliminary observation has been reported in ref. [11] and similar observations have been reported in ref. [16]). This implies that the DOS is higher in value for  $T < T_c$ , in this energy range, and it has a distinct temperature variation as  $T$  changes through  $T_c$ . Eventually, for  $T \ll T_c$ , a temperature independent value is obtained. This was seen before in the inset of figure 7(b). The behavior seen in figure 8 has two noteworthy features. First, there is a distinct peak in  $(d\ln I/d\ln V)_{0.9V}$  at  $T \approx T_c$ . This is

seen in all the samples. Second, the peak is sharper for the single crystal than for the thin film.

For  $T \approx T_c$ , a gap like feature is present in the DOS near  $E_f$  and this results in a very sharp increase in the DOS beyond a particular voltage. This is seen in figure 8 as a rapid increase of  $(d\ln I/d\ln V)_{0.9V}$ , close to  $T_c$ . The increase in DOS at higher energies (away from  $E_f$ ), in the temperature range close to  $T_c$  where there is a gap at  $E_f$ , may imply a transfer of relative spectral weights to higher energies when the gap opens up.

## B. Tunneling data for $T$ ; $T_c$

For  $T < T_c$ , there is a finite tunneling conductance at zero bias,  $G_0$ . This is expected since, for  $T < T_c$ , the metallic state is stabilized and so we conclude that there is a finite DOS at  $E_f$  ( $n(E_f)$ ). However  $G_0$  also depends on the barrier parameters of the tunnel junction formed between the tip and sample, in addition to  $n(E_f)$  and the temperature. For tunneling spectroscopy done at variable temperature it is difficult to ensure the constancy of these parameters. The usual normalization procedures which remove the effect of the barrier parameters, do not describe the region near zero bias (i.e. near  $E_f$ ) satisfactorily. To remove this dependence on the barrier parameters and also get an estimate of the relative change of  $n(E_f)$  with temperature, we normalize  $G_0$  by the tunneling conductance at 0.9 V ( $G_{0.9}$ ). But  $G_{0.9}$  itself might have a temperature dependence due to the change in DOS with temperature at that energy. We expect that the variation of  $G_0/G_{0.9}$ , due to the variation of  $G_{0.9}$ , can be accounted for if the observed temperature dependence of  $G_{0.9}$  itself, is taken care of by some normalization factor which is independent of the barrier parameters and depends only on the DOS at that energy. Therefore, we plot the quantity:

$$g_{0N}(T) = \frac{G_0(T)}{G_{0.9}(T)} \left( \frac{d\ln I}{d\ln V} \right)_{0.9V,T} \quad (1)$$

where  $(d\ln I/d\ln V)_{0.9V,T}$  is the value of  $d\ln I/d\ln V$  at a sample bias of 0.9 volts and at a temperature  $T$ . This quantity is known experimentally and it is independent of the barrier parameters and depends only on the DOS at that particular energy at a temperature  $T$ . This normalized ratio  $g_{0N}(T)$  in equation 1 is thus expected to mostly reflect the variation arising from the temperature variation of  $n(E_f)$ . The plots of  $g_{0N}$  for three different samples are shown in figure 9. For all the samples  $g_{0N}(T)$  shows a rise below  $T_c$  (or  $T_{IM}$ ) as the material enters the metallic state and it reaches a temperature independent value at lower temperatures. For the epitaxial film the growth of  $g_{0N}$  (and hence of  $n(E_f)$ ) is gradual whereas for the single crystals this rise is rather sharp. *These observations would imply that  $n(E_f)$  grows rapidly below  $T_c$  and reaches a temperature independent value, as in a metal. This is a very important conclusion of our experiment.*

The observed parabolic shape of the  $G - V$  curves and the fact that  $g_{0N}(T)$  has a negligible dependence on temperature below  $T_c$  indicate that the DOS near  $E_f$  is flat in the scale of  $k_B T$  and temperature independent below  $T_c$ , just like a metal. To strengthen this conclusion, quantitatively, we carried out a simple calculation using the expression for tunneling current given below and a constant DOS for both tip and sample. Equation 2 gives the expression for the tunneling current for a trapezoidal barrier [15,11]:

$$I(s, V, W, T) = c \int_{-\infty}^{\infty} N_s \left( E + \frac{eV}{2} \right) N_t \left( E - \frac{eV}{2} \right) \left[ f \left( E - \frac{eV}{2}, T \right) - f \left( E + \frac{eV}{2}, T \right) \right] \tilde{t}(s, E, W) dE \quad (2)$$

where the barrier penetration factor  $\tilde{t}$  is given by

$$\tilde{t}(s, E, W) = \exp \left( -2ks\sqrt{2(W - E)} \right) \quad (3)$$

where  $E$  is the energy of the electron,  $c$  is a constant dependent on the tip-sample effective junction area,  $s$  is the tip-sample distance,  $W$  is the average work function of the tip and sample surface,  $V$  is the bias between tip and sample,  $T$  is the temperature,  $N_t(E)$  and  $N_s(E)$  are the tip and sample DOS respectively,  $k = \sqrt{m}/\hbar$  ( $m$  is the electron mass) and  $f(E, T)$  is the Fermi function at temperature  $T$ . In the above expression all the energies are measured w.r.t.  $E_f$  which is the zero of the energy scale.

Figure 10(a) shows a comparison between an experimental  $G - V$  curve, taken on the LCMO thin film at 160 K ( $T < T_c$ ), and a calculated  $G - V$  curve using constant tip and sample DOS, a tip-sample distance of 6.5 Å and

a work function of 1.2 eV. The good agreement between the observed data and the calculated curves, supports our conclusion that below  $T_c$ , the DOS near and at  $E_f$  is finite and metal-like. For comparison, the experimental and calculated  $G - V$  curves (using again a constant tip and sample DOS and equation 2) for a 500 Å platinum film are shown in figure 6.

The change in conductivity ( $\sigma$ ) below  $T_c$  will arise from a change in the mobility ( $\mu$ ) and/or a change in the carrier concentration ( $N$ ) [ $\sigma = Ne\mu$ ]. The increase in  $\mu$  below  $T_c$  is expected due to the suppression of the spin disorder scattering as the local magnetization builds up. However, if  $n(E_f)$  rises rapidly below  $T_c$ , and builds up from a zero value at  $T_c$ , it is expected that the effective carrier concentration  $N$  also rises as the sample is cooled below  $T_c$ . *The large variation in  $\rho$  near  $T_c$ , may be a consequence largely of a variable  $n(E_f)$ , giving rise to a large variation in  $N$ , with a lesser contribution coming from the temperature dependent mobility  $\mu(T)$ .*

### C. Tunneling data for $T \approx T_c$

For  $T \approx T_c$ , the value of  $G_0$ , goes to zero and a gap opens up in  $n(E)$  near  $E_f$ , as is evident from the  $G - V$  curves shown in figure 5 and the plot of  $g_{0N}$  vs.  $T$  shown in figure 9. The gap ( $2\Delta$ ) is shown for one  $G - V$  curve in figure 5. On heating from below  $T_c$  this gap opens at  $\sim 15$ -20 K below  $T_{IM}$  (or  $T_c$ ) and sharply rises to the maximum value. We denote the temperature where the gap opens as  $T_{gap}$ . It then decreases in magnitude as the temperature is increased further above  $T_c$  and finally disappears as the temperature is increased well beyond  $T_c$  and the observed  $G_0$  becomes non-zero. These observations would indicate that close to  $T_c$  a gap develops in the DOS near  $E_f$ . This gap collapses as the sample is cooled below  $T_c$ . The nature of the DOS near  $E_f$  for  $T \gg T_c$  will be discussed later.

These features are observable both in the epitaxial film and single crystals. However, the transitions are sharper for the single crystals. There is also a very interesting similarity between  $T_{gap}$  and the temperature where the MR of the material shows a peak. It will be interesting to see if such large MR actually arises due to such drastic changes in DOS on the application of a magnetic field, when the sample temperature is near  $T_c$ . In figure 11 the maximum values of the gaps ( $2\Delta_{max}$ ) observed in different materials have been plotted against the  $T_c$  (or  $T_{IM}$ ) of the materials. It is clear that the observed  $2\Delta_{max}$  has a strong correlation with the  $T_c$ . The  $T_c$ 's of these materials are related to the bandwidths. *A material with larger bandwidth has a larger  $T_c$ . The decrease in  $2\Delta_{max}$  as  $T_c$  increases would imply that  $2\Delta_{max}$  decreases as the bandwidth increases. This is an important conclusion.* This also shows that any mechanism that can change the bandwidth, will change the value of  $2\Delta_{max}$

and hence the transport properties close to  $T_c$ . Eventually, for  $T_c \rightarrow 400$  K (as in materials like  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ) the gap is expected to reduce to extremely small values. Interestingly, the largest  $T_c$  observed in these materials is around 400 - 450 K. These values of the gaps, measured by tunneling, are comparable to the transport activation gap in these materials, as estimated from the  $\rho$  vs.  $T$  data, which are  $\sim 0.1$  eV (see Table I).

To verify that the gap is real i.e. the current actually goes to zero within the gap region, we carried out variable separation tunneling spectroscopy, as described in detail in ref. [7]. In this technique, the tip is brought closer to the sample as the bias between the tip and sample and consequently  $I_t$  approaches zero (the particular method used is described in brief in section II). This gives a high dynamic range in the measurement of the tunneling current. This method enables us to effectively measure tunneling currents over a few orders of magnitude, so that we can properly define the band-edges. Although we have not converted the variable distance measurements to constant distance measurements, our purpose, of verifying the band-edges, is still served from just the acquired data. This experiment was done only for positive tip bias i.e. for the filled states of the sample. Therefore we were able to observe the band-edge only for the filled states of the sample. Figure 12 shows the variable distance conductance ( $G_s$ ) data, and it shows the gap feature, denoted by  $\Delta_{var}$ , just like the constant distance tunneling data. The experiment was done at 270 K and the values of  $\Delta_{var}$  and  $\Delta$  (at  $T \approx 270$  K), agree to within 0.01 eV. This combination of the two techniques gives a quantitative foundation to the observed gap.

### D. Tunneling data for $T > T_c$

Above  $T_c$ , the gap near  $E_f$  closes again and  $G_0$  assumes a finite value. This implies, essentially, appearance of finite DOS at  $E_f$ . However the transport in the material is still activated. This is possible only if the new states arising close to  $E_f$  are localized. We have to interpret our tunneling data carefully since, at such high temperatures, the temperature itself plays an important role in determining the shape of the  $G - V$  curves. However, we have carried out numerical calculations again using equation 2, to find out if the observed disappearance of the gap at high temperatures is due to the thermal smearing of the tunneling spectra, and *have found that the disappearance of the gap cannot be explained due to the thermal smearing alone.* In order to explain our tunneling data for  $T > T_c$  we have to make the following proposition. We propose that the gap which developed near  $E_f$  for  $T \approx T_c$ , collapses to a soft, Coulomb gap for  $T > T_c$ . The presence of a soft, Coulomb gap suggests that the states around  $E_f$  are localized. One then has an interplay of Coulomb interaction and disorder. However, further

investigation is required before issues like the existence of a Coulomb gap can be established beyond doubt. At this moment we can only state that using the above model, we can fit our data quantitatively. However, we cannot guarantee that this is the only way to explain the data. In the following, we describe the model calculations which were carried out to determine the nature of the DOS for  $T > T_c$ .

In figure 10(b), we show the comparison of the experimental  $G - V$  curve taken at 328 K (i.e. for  $T \gg T_c$ ) for the LCMO thin film sample, with the calculated  $G - V$  curves (using equation 2) at that temperature. The dotted line shows the calculated curve using a constant DOS for the tip and sample. The tunneling distance and the work function were taken as 2.5 Å and 1.2 eV respectively. This can be taken as the background voltage dependence of  $G$  for the tunnel junction, due to just the barrier parameters,  $s$  and  $W$ . But unlike for  $T < T_c$ , the measured  $G - V$  curve dips below the calculated constant DOS curve for  $|V| < 0.4$  volts, therefore suggesting that there is a dip in the DOS near the Fermi level for  $|E - E_f| < 0.4$  eV. Also, there is a significant asymmetry in the measured  $G - V$  curve. We have calculated the  $G - V$  curve using the model DOS, shown in the inset of figure 10(b), for the sample and a constant DOS for the tip in equation 2 and the same barrier parameters used for the constant DOS calculation, for the bias region  $|V| < 0.4$ . The model DOS is taken as a quadratic function of  $|E - E_f|$ . The value of the model DOS is non-zero at  $E_f$  (which was required for a good match with our experimental data), unlike a Coulomb gap. This could be due to the fact that the DOS, in the presence of a Coulomb gap, has an explicit temperature dependence which results in a change in the width of the Coulomb gap as well as a non-zero value for the DOS at  $E_f$ , at such high temperatures [17]. The calculated  $G - V$  curve using this model DOS is shown as the solid line in figure 10(b). It is interesting to note that the tunneling distance estimated from the  $G - V$  curves for  $T < T_c$  (about 6.5 Å) is much larger than that estimated from the  $G - V$  curves for  $T > T_c$  (about 2.5 Å). This could again be a consequence of the fact that the states near  $E_f$  are localized for  $T > T_c$ . The asymmetry in the experimental  $G - V$  curves for  $T > T_c$ , is reproduced, to a certain extent, by our calculation using the model DOS. Therefore from the analysis given above, we conclude that for  $T > T_c$  a Coulomb (soft) gap is formed at  $E_f$ .

To summarize, our experiment suggests that the hard gap existing close to  $T_c$ , closes at a temperature somewhat higher than  $T_c$  and gives way to a soft gap with localized states near  $E_f$ . This is an important observation. However, more experiments are needed to confirm the above picture.

## V. SUMMARY AND CONCLUSION

From the tunneling studies carried out and the discussion in the above sections, it is clear that the density of states of hole doped manganites show large changes near  $E_f$ , when the temperature is changed across  $T_c$ . This plays an important role in determining the transport properties, like resistance and magnetoresistance, of these materials. When the temperature is changed across  $T_c$ , there is a transfer of spectral weight in the DOS. Below  $T_c$  the metallic state is stabilized and there is a finite DOS near  $E_f$ , which is flat in the scale of  $k_B T$ .

When the temperature is increased from below  $T_c$ , a gap appears in the DOS near  $E_f$ , just below  $T_c$ . The value of this gap is comparable to the transport gap, estimated from the resistivity data above  $T_c$ . The maximum value of this gap is higher for the samples with lower  $T_c$ . It may happen that, if near  $T_c$  the applied magnetic field modifies this feature of the DOS near  $E_f$ , then this will be reflected as a large change in  $\rho$  and can thus be the origin of CMR in these materials. Our experiment suggests that, on heating much above  $T_c$ , the hard gap gives way to a soft gap near  $E_f$ , indicating that the states near  $E_f$  are localized. Opening up of a hard gap can arise from Jahn-Teller effect whereas, a soft gap arises from Coulomb interactions for localized states. Our data suggest that there is a presence of both these factors above  $T_c$ , modifying the nature of DOS.

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Sample	Type	$T_c$ (K)	$T_{IM}$ (K)	$E_a$ (eV)	$2\Delta_{max}$ (eV)	$T_{gap}$ (K)
$\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$	Epitaxial thin film	-	196	0.121	0.215	178
$(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$	Single crystal	290	275	0.052	0.156	254
$\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$	Single crystal	338	-	-	0.059	325
$\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$	Single crystal	-	401	0.041	-	-

Table I. The details of the samples studied. The Curie temperature ( $T_c$ ), the temperature where the peak in  $\rho$  occurs ( $T_{IM}$ ), the transport activation gap ( $E_a$ ), the maximum value of the gap in the DOS near  $E_f$  for  $T \approx T_c$ , measured by tunneling spectroscopy ( $2\Delta_{max}$ ) and the temperature where the gap in the DOS opens while heating the sample from much below  $T_c$  ( $T_{gap}$ ) are shown, for the different samples. Some of the values could not be measured due to experimental limitations.



## FIGURE CAPTIONS

Figure 1. A schematic representation of the STM/S setup. The dotted box indicates the STM head, which is kept in a cryopumped environment.

Figure 2. (a) The resistivity and magnetoresistance of the LCMO epitaxial thin film. (b) The resistivity and magnetoresistance of the  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$  single crystal. The inset shows the scaled resistivities of three of the samples studied, (A) LCMO thin film, (B)  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$  single crystal, (C)  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ , showing the variation in  $T_{IM}$ .

Figure 3. Atomic resolution image of  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$  single crystal. The image was taken in the constant current mode, with a tip bias of +1.5 V and a tunneling current of 1.2 nA. The temperature of the sample was 320 K. The parallelogram indicates a cell of size  $4.02 \times 4.02 \text{ \AA}$ .

Figure 4. An  $853 \text{ \AA} \times 906 \text{ \AA}$  image of the LCMO thin film. The image was taken in the constant current mode, with a tip bias of +1.5 V and a tunneling current of 2 nA. The temperature of the sample was 298 K. The atomically smooth terraces are terminated by atomic steps, some of which are marked by the arrows.

Figure 5.  $G - V$  curves at different temperatures for: (a), (b) and (c)  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  single crystal and (d), (e) and (f) LCMO thin film. The gap observed for  $T \approx T_c$  i.e.  $2\Delta$ , is shown for the LCMO sample.

Figure 6.  $G - V$  curve for  $500 \text{ \AA}$  Platinum film, at 307 K. The solid line is the calculated  $G - V$  curve (described in text). The inset shows the  $G - V$  curve for the same film at 134 K. The solid line is the calculated  $G - V$  curve.

Figure 7.  $d\ln I/d\ln V - V$  curves for  $|V| \geq 0.2$  volts at different temperatures for (a)  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  ( $T_c = 338 \text{ K}$ )

(b)  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$  ( $T_{IM} = 275 \text{ K}$ ). The inset in (b) shows the  $d\ln I/d\ln V - V$  curves at two temperatures for  $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$  ( $T_{IM} = 401 \text{ K}$ ), which illustrates that for temperatures well below  $T_{IM}$ , there is no appreciable change in the DOS with temperature.

Figure 8. A plot of the quantity  $(d\ln I/d\ln V)_{0.9V}$  vs.  $T$  for two samples, showing the redistribution of spectral weight with temperature. The solid lines are guides to the eye and typical error bars are shown.

Figure 9. The  $g_{0N}$  vs.  $T/T_c$  plot for  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ , showing that  $n(E_f)$  drops to zero just below  $T_c$ , when the temperature is increased from below  $T_c$ . A typical error bar is shown. The inset shows the  $g_{0N}$  vs.  $T/T_{IM}$  plots for the samples (a) LCMO thin film and (b)  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$  single crystal. The solid lines are guides to the eye.

Figure 10. A comparison of the experimental and calculated  $G - V$  curves for the LCMO thin film. (a) The sample temperature is 160 K. (b) The sample temperature is 328 K, the dashed line showing the constant DOS calculation and the thick solid line showing the model DOS calculation. The inset in (b) shows the model DOS used to calculate the  $G - V$  curve for the bias range  $|V| < 0.4 \text{ V}$ , for  $T = 328 \text{ K}$ .

Figure 11. A plot of the maximum value of the tunneling gap ( $2\Delta_{max}$ ) vs.  $T_{trans}$ , where  $T_{trans}$  is either  $T_c$  or  $T_{IM}$ , as specified in the figure. The dotted line is a guide to the eye.

Figure 12. Variable distance  $G_s - V$  curves for the sample  $(\text{NdLa})_{0.73}\text{Pb}_{0.27}\text{MnO}_3$ , at a temperature 270 K. The gap  $\Delta_{var}$  is indicated by the arrows. The  $G_s$  scale is logarithmic. The inset shows the same curve with a linear  $G_s$  scale and the gap  $\Delta_{var}$  is marked by the arrow.

























