Electric field driven destabilization of the insulating state in nominally pure LaMnO$_3$

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Abstract

We report an electric field driven destabilization of the insulating state in nominally pure LaMnO$_3$ single crystal with a moderate field which leads to a resistive state transition below 300 K. The transition is between the insulating state in LaMnO$_3$ and a high resistance bad metallic state that has a temperature independent resistivity. The transition occurs at a threshold field ($E_{th}$) that shows a steep enhancement on cooling. While at lower temperatures the transition is sharp and involves a large change in resistance, it softens on heating and is eventually absent above 280 K. When the Mn$^{4+}$ content is increased by Sr substitution up to $x = 0.1$, the observed transition, although observable in a certain temperature range, softens considerably. This observation has been explained as a bias driven percolation type transition between two co-existing phases, where the majority phase is a charge and orbitally ordered polaronic insulating phase and the minority phase is a bad metallic phase. The mobile fraction $f$ of the bad metallic phase deduced from the experimental data follows an activated kinetics as $f = f_0(E) \exp(-\Delta/k_B T)$ with the activation energy $\Delta \approx 200$ meV, and the pre-factor $f_0(E)$ is a strong function of the field that leads to a rapid enhancement of $f$ on application of field, leading to the resistive state transition. We suggest likely scenarios for such co-existing phases in nominally pure LaMnO$_3$ that can lead to the bias driven percolation type transition.

[Online supplementary data available from stacks.iop.org/JPhysCM/25/155605/mmedia]

(Some figures may appear in colour only in the online journal)

1. Introduction

The localization of electronic states due to strong electron–phonon coupling in strongly co-related oxides like RMnO$_3$ (R = rare-earths like La, Pr, Nd, etc) and the effect of external stimulations on these states have been important research topics over the last two decades [1, 2]. In a material like RMnO$_3$, the strong coupling between the electrons and phonons mediated by the Jahn–Teller (JT) distortion leads to the formation of polarons. Below a certain temperature ($T_{JT}$) cooperative JT distortions set in and one obtains a polaronic insulating state accompanied by an orthorhombic distortion of the lattice. Depending on the R ion the value of $T_{JT}$ can vary between 750 K for R = La and 1150 K for R = Nd. At a much lower temperature the antiferromagnetic (AFM) order sets in at the Néel temperature $T_N \approx 150$ K, leading to an A-type antiferromagnetic insulating (AFI) state. The physical properties, including the crystallographic structure
and its temperature evolution through $T_{JT}$, of R MnO$_3$ systems like LaMnO$_3$ have been studied in detail using various techniques, although many important issues still remain unsolved [3–6]. The orthorhombic polaronic insulating state with cooperative JT distortion can be destabilized by hole doping using divalent substitution at the rare-earth site. This leads to an insulator–metal transition with long range ferromagnetic order, the onset of such phenomena as the colossal magnetoresistance (CMR), charge and orbital ordering (COO) and electronic phase separation, which form the complete gamut of phenomena that comprise the field of manganites. In addition to the hole doping, the polaronic insulating state can be destabilized by external stimuli like pressure [7], very high magnetic field [8] and also a high electric field close to $T_{JT}$ [9].

In this investigation we find that an applied electric field of moderate magnitude can induce instability at room temperature or below in the resistive state of a nominally pure single crystal of LaMnO$_3$. This leads to a reversible destabilization of the highly resistive insulating state to a lower resistance bad metallic state. (Note: the lower resistance state is called a bad metallic state because it has a temperature independent resistivity value that, although lower than the insulating state, is higher than those seen in metallic states of manganites obtained after substantial hole doping.) The observed field induced destabilization can be sharp and at lower temperature it can lead to resistance changes of even a few orders of magnitude occurring sharply over a small field range.

The destabilization of the insulating state that we observe in the case of nominally pure LaMnO$_3$ single crystals is distinct from the field induced resistance state change (both with memory and without memory) that has been seen in manganites with much higher levels of hole doping (typically $x \geq 0.2$) [10–13]. In these manganite systems with higher levels of hole doping (that show ferromagnetic insulating states or charge ordered states) resistive switching has been seen in single crystals [14, 15] and in films [16] and also in nanoscopic regions that can be created by local probes [17, 18]. The creation of ferromagnetic filaments by a high electric field in charge ordered manganites has been reported [13]. Resistive state switching in Schottky junctions involving manganites has also been seen [19]. The above list of observations of resistive state switching is not exhaustive and is indicative. A number of explanations exist for the resistive state transitions in hole-doped manganites. These phenomena range from ionic migration for changes happening near room temperature, particularly in junctions [20], electron heating [21], Joule heating [22, 23] and electric field induced structural changes [24, 18]. However, the observed phenomenon in nominally pure LaMnO$_3$, reported here, is different from those reported in hole-doped systems. In this case, the starting insulating state is a polaronic insulating state with Jahn–Teller distorted MnO$_6$ arranged in a cooperative long range ordered state. The observed characteristics in this case have different field and temperature dependences including a sharp field driven transition. The field driven transition appears to change critically for hole doping around $x \approx 0.1$. In earlier reports involving hole doping with concentration $x \geq 0.15$, the starting insulating state was either a charged ordered state (occurring for hole doping $\geq 0.5$) or a ferromagnetic insulating state (occurring for hole doping $\approx 0.15–0.22$).

2. Experiment

The experiments were carried out on three nominally pure single crystals of LaMnO$_3$ having different dimensions and also on one crystal of Sr substituted La$_{0.9}$Sr$_{0.1}$MnO$_3$ to establish the generality of the phenomenon and the extent of its sample dependence (see the supplementary information available at stacks.iop.org/JPhysCM/25/155605/mmedia). All crystals were grown by the floating zone technique. Sample LaMnO$_3$-1 was grown in Kolkata while samples LaMnO$_3$-2 and LaMnO$_3$-3 were grown in Moscow [25]. The La$_{0.9}$Sr$_{0.1}$MnO$_3$ crystal was grown in Moscow. To establish the quality of the samples, we performed high temperature powder x-ray diffraction to identify the crystallographic features associated with the cooperative Jahn–Teller transition near $\sim 750$ K (data given in the supplementary information available at stacks.iop.org/JPhysCM/25/155605/mmedia). In addition, we performed a series of electron spectroscopies and electron energy loss spectroscopy and energy dispersive analysis of x-ray (EDAX) to qualitatively ascertain the Mn$^{4+}$ content that occurs even in nominally pure LaMnO$_3$. We used vacuum evaporated chrome–gold contact pads and thin Cu wires for the electrical contacts on the crystals in a four probe configuration (see the inset of figure 2). Resistivity measurement for all three LaMnO$_3$ samples and the La$_{0.9}$Sr$_{0.1}$MnO$_3$ sample was performed in the four probe configuration with low current shown in figure 1.

For the measurement of $I$–$V$ characteristics, we used a voltage source and the applied bias ($V_{app}$) was applied

Figure 1. The resistivities ($\rho$) of the LaMnO$_3$ and La$_{0.9}$Sr$_{0.1}$MnO$_3$ single crystals used in the experiment. The resistivities were measured with a very low current in a four probe configuration. Fits of the resistivity data for the LaMnO$_3$ crystals to the adiabatic polaronic model are shown in the inset. The activation energies $E_a$ are noted. For the La$_{0.9}$Sr$_{0.1}$MnO$_3$ crystal the ferromagnetic transition occurs at 145 K.

Figure 2. The $I$–$V$ characteristics for the LaMnO$_3$ single crystal showing abrupt resistive switching with low current. The inset shows the magnetic field configuration with low current shown in figure 1. For the measurement of $I$–$V$ characteristics, we used a voltage source and the applied bias ($V_{app}$) was applied
across the sample in series with a standard resistor $R$, used as a current limiter. The value of the series resistor $R$ was selected to be much less than the sample resistance at low bias to ensure that it did not control the current through the circuit. When the sample goes to the low resistive state after the bias driven transition, the current in the circuit increases and it reaches the compliance limit of our measuring instrument. However, with the presence of the current limiter the total resistance of the circuit remains large enough to avoid the compliance limit. We used a Keithley 2410 source meter to source the voltage and measure the current in the circuit. A separate Keithley 2000 DMM was used for the measurement of the voltage drop $(V)$ between the two voltage probes of the sample. This arrangement allowed us to measure simultaneously the voltage drop across the voltage probes of the sample $(V)$ and the applied bias $(V_{app})$. This arrangement shows the resistive state transition region clearly. (In the region of resistance measurements where there are no compliance issues involved, conventional current sourced measurements were used to confirm that the voltage sourced measurements gave the same data.) In order to avoid Joule heating, we carried out a pulsed mode of measurement with a 50% duty cycle and a 400 ms ON period (see section 3.3). The sample’s surface temperature was maintained within $\pm 1$ K during the entire span of recording the current–voltage characteristics at each temperature.

\[ \rho = \rho_0 T \exp \left( \frac{E_0}{k_B T} \right) \]  

(1)

Figure 2. Bias voltage $(V_{app})$ versus sample current characteristics for a LaMnO$_3$ single crystal at a few selected temperatures. The inset shows the circuit configuration.

where $\rho_0$ is related to the hopping frequency, length and dimensionality and $E_0$ is the activation energy. The resistivity data given in figure 1 show the difference in the insulating states of the nominally pure LaMnO$_3$ and the lightly doped LaMnO$_{3-x}$, where the presence of a finite amount of Mn$^{4+}$ ($x = 0.1$) changes the nature of the polaronic insulating state. All three samples of the nominally pure LaMnO$_3$ have almost the same activation energy, $E_0 \approx 217-235$ meV (note: the non-linearity in the activation energy around 180 K for LaMnO$_{1.2}$ is due to the magnetic inhomogeneity caused by local ferromagnetic moment/cluster formation), and this matches well with previously reported data [26]. For La$_{0.9}$Sr$_{0.1}$MnO$_3$, $E_0 \approx 145$ meV. With the substitution of a divalent atom like Ca or Sr in the parent LaMnO$_3$, a hole is created in the $e_g$ levels of the 3d-orbital of Mn leading to de-localization of carriers and increase of the conductivity. The introduction of Mn$^{3+}$ dilutes the cooperative JT distortion and enhances the strength of the ferromagnetic double exchange (DE) interaction. For the Sr-doped system, the $x = 0.1$ region is the critical region [27]. In this region of hole concentration, slight variation of Mn$^{3+}$ can change the system from the highly insulating canted antiferromagnetic (CAF) regime to the ferromagnetic insulating (FMI) state at low temperatures. As a result, in La$_{0.9}$Sr$_{0.1}$MnO$_3$, two distinct phases exist, paramagnetic insulating (300–145 K) and ferromagnetic insulating (starting below 120 K), and in between there is a small metallic region (120–145 K) where $\frac{d\rho}{dT}$ is positive. This would also imply the co-existence of complex phases in this region of hole concentration. This complexity makes the $x = 0.1$ region very sensitive to the exact Mn$^{3+}$ concentration. Increase of the Sr concentration to $x > 0.15$ stabilizes the ferromagnetic metallic state [28, 29].

2.2. $I$–$V$ data and bias induced destabilization of the polaronic state in LaMnO$_3$

The $I$–$V$ data were taken as a function of temperature for all three samples and they are qualitatively similar. Here, in figure 2 we show the data for one sample only (LaMnO$_3$-1) and the data for the other two samples are given in the supplementary information (available at stacks.iop.org/JPhysCM/25/155605/mmedia). The data at low $T$ end were limited by the high resistance of the sample which imposes the compliance limit of the voltage source and the current measuring limit of the source meter. It can be seen that after a particular voltage (which we call the threshold voltage) the current through the source meter to source the voltage and measure the current in the circuit.

The four probe low current driven resistivity $(\rho)$ results are shown in figure 1. For all three LaMnO$_3$ samples, the data could be fitted with the adiabatic small polaron hopping model (see the inset of figure 1)

\[ \rho = \rho_0 T \exp \left( \frac{E_0}{k_B T} \right) \]  

(1)
In figure 3(a), we have plotted the sample voltage \( V \) against the applied bias voltage \( V_{\text{appl}} \) at different temperatures. This way of plotting the data \( V \) as a function of \( V_{\text{appl}} \) identifies the sample voltage \( V_{\text{th}} \) at which the transition occurs. When the sample is in the HRS (high resistance insulating state) the voltage drop predominantly occurs across the sample and the sample voltage follows the applied bias. On reaching the threshold voltage \( V_{\text{th}} \), the sample makes a transition to the LRS, leading to a fall in the bias across the sample because the bias now drops predominantly across the limiter \( R \). The inset of figure 3(a) shows an example of the field induced transition and the hysteresis at a representative temperature \( T = 150 \) K, and the threshold voltage \( V_{\text{th}} \) is marked. From this value of \( V_{\text{th}} \), the field \( E_{\text{th}} \) is obtained. In figure 3(b) we show the temperature variation of \( E_{\text{th}} \) for all three samples. All the samples show a steep rise with reduction in \( T \) and have values that are similar (within a factor of 2). \( E_{\text{th}} \) becomes very small \( (<100 \) V cm\(^{-1}\)) for temperatures higher than 290–300 K, beyond which there is no resistive state transition.

The change in the resistance at the transition as a function of temperature is shown in figure 4. The size of the hysteresis region, as well as the jump in the resistance at the transition, reduces with increasing temperature and nearly vanishes after 280–290 K. In the HRS the resistivity has a strong temperature dependence (see figure 1). However, the LRS has a resistance that is nearly temperature independent.

The temperature dependences of the HRS and LRS states were investigated by measuring the resistivities at different constant bias voltages going from a very low bias \( (V_{\text{appl}} \approx 1 \) V) to a high bias \( (V_{\text{appl}} \approx 300 \) V) using a four probe method to compare with the resistive state transition as seen in the pulsed I–V data in figure 2. The variation in \( \rho \) with \( T \) measured at different biases is shown in figure 5 for one of the LaMnO\(_3\) samples (sample-2). For lower biases \( (<200 \) V, corresponding to \( E_{\text{th}} < E \)), the sample makes a transition to the HRS on cooling below a certain temperature, and below 100 K we cannot measure the resistivity due to the instrumental measurement limit (marked in figure 5). At higher biases \( (>200 \) V) the resistivity is in the LRS until the lowest temperature, 50 K, due to the steep rise of \( E_{\text{th}} \). These data (along with the data in figure 4) clearly demonstrate the existence of a threshold field for the transition and its steep temperature dependence. At higher temperatures when \( E_{\text{th}} \) is small and applied \( E > E_{\text{th}} \), the sample is in the LRS. On cooling in a fixed \( E \), the \( E_{\text{th}} \) increases sharply, and whenever \( E_{\text{th}} \geq E \), a transition occurs to the HRS. For the sample shown in figure 5, there is a clear resistivity jump in the range of 125–150 K. It can be seen that while the resistivity in the HRS \( (\rho_{\text{ins}}) \) has a strong temperature dependence (the polaronic insulating state), the resistivity of the LRS, which is stable for \( E_{\text{th}} < E \), is nearly temperature independent (marked as \( \rho_{\text{m}} \) in figure 5).

From figure 5, it can be seen that \( \rho_{\text{ins}} \) is equal to or comparable to \( \rho_{\text{m}} \) above 280 K and there is no observable resistivity transition above 280 K. The exact value will depend on the exact crystal used. In the inset of figure 5 we have plotted the percentage of change in resistivity versus
temperature for the three samples. \( \Delta \rho \) is defined as \( \rho_{\text{ins}} - \rho_{\text{m}} \) (we have used \( \rho_{\text{ins}} \) in the denominator and not \( \rho_{\text{m}} \) to avoid unnecessary magnification of the resistance change). It can be seen that the change is nearly 100% below 210 K for all the crystals and it approaches small values for \( T > 280 \) K. While for the other two crystals (LaMnO\(_3\)-2 and LaMnO\(_3\)-3) the data are identical, there are small quantitative differences near the region where \( \Delta \rho \) \( \rightarrow \) 0 for LaMnO\(_3\)-1. This probably reflects the differences in the exact Mn\(^{4+}\) contents of the samples.

2.3. I–V data in the hole-doped system LSMO \((x = 0.1)\) data

To investigate the effect of Mn\(^{4+}\) on the field driven transition, we repeated the measurements in La\(_{0.95}\)Sr\(_{0.05}\)MnO\(_3\) (LSMO \((x = 0.1))\) single crystal where the Mn\(^{4+}\) content is significantly larger than that of nominally pure LaMnO\(_3\). The choice of the doping concentration \( x = 0.1 \) was motivated by the fact that it marks the boundary between the CAF state and the FMI state, as stated before. The \( I–V \) data in LSMO were taken in the same way as for the other crystals (in figure 6(a)). In LSMO the resistive state transition softens compared to that seen in LaMnO\(_3\). The resistive state transition occurs at low temperatures below 50 K, although the \( I–V \) data are strongly non-linear for all \( T \) below 140 K. The minimum field \((\approx 7 \text{ kV cm}^{-1})\) needed to enact the transition is also much larger. In figure 6(b), we plot \( V \) versus \( V_{\text{appl}} \) for 10 and 240 K. The data at lower temperature, \( T \leq 50 \) K, are shown in the inset. For \( T \approx 50 \) K, the sample voltage shows a similar kind of jump to that observed in the three LaMnO\(_3\) samples, showing the existence of an HRS to LRS transition. At higher temperature there is a strong non-linearity leading to a substantial decrease of the sample resistance, showing the precursor of a resistive state transition that may occur at higher bias. Our data are qualitatively similar to those seen by one of us [27] in LSMO single crystal with nominally the same composition. However, there are differences in the detail that will reflect the difference in exact Mn\(^{4+}\) content and also the possibility of co-existence of many phases near the critical concentration \( x = 0.1 \). The data taken by us as well as in [26] show that introduction of Mn\(^{4+}\) gradually changes the nature of the sharp resistive state transition seen in LaMnO\(_3\).

3. Discussion

The discussion section is divided into two parts. In the first part we describe a simple phenomenological model based on a percolation approach to describe the voltage driven resistive state transition. In the second part we explore the likely microscopic scenarios for the phenomenological model.

3.1. A phenomenological model for the transition

The model is based on the basic premises that there is a phase co-existence of two phases in LaMnO\(_3\) below \( T_{\text{JT}} \), one the orthorhombic polaronic insulating phase with resistivity \( \rho_{\text{ins}} \) (the majority phase) and a bad ‘marginally’ metallic resistance phase (the minority phase) which has nearly temperature independent resistivity \( \rho_{\text{m}} \). The rationale for this phase co-existence will be discussed in section 3.2. The volume fraction of the minority phase (or the mobile fraction \( f \) of it that can contribute to conductivity) at room temperature or below is very small in zero applied bias. As a result, the observed \( \rho \) is determined by the \( \rho_{\text{ins}} \). The volume fraction \( f \) can be the total volume fraction of the phase with \( \rho_{\text{m}} \) or, more usefully, it can represent the ‘mobile’ (or de-pinned) fraction of the phase that will contribute to the transport. We make this distinction, because some part of the minority phase can be pinned and will not contribute to the transport. This issue will be elaborated in section 3.2. The conducting volume fraction \( f \) can be enhanced by the applied field \( E \) as well as with increase of the temperature \( T \). The transition to the LRS occurs when \( f \) on application of the field crosses the volume percolation threshold.

The suggested phenomenological model for the resistive state transition is thus a field induced percolation transition between two phases that co-exist below 300 K. In this model the applied field does not create any new minority phase, but enhances its mobile fraction \( f \). \( f \) is also enhanced by the increase of temperature. We evaluated the volume fraction \( f \) from the observed data (\( \rho \) as a function of \( E \)) in the framework of effective medium theory [30],

\[
\rho_{\text{obs}} = \frac{\rho_{\text{ins}} \rho_{\text{m}}}{(1 - f) \rho_{\text{m}} + f \rho_{\text{ins}}} \tag{2}
\]

\[
f = \frac{\rho_{\text{m}} (\rho_{\text{ins}} - \rho_{\text{obs}})}{\rho_{\text{obs}} (\rho_{\text{ins}} - \rho_{\text{m}})} \tag{3}
\]

\( \rho_{\text{obs}} \) and \( f \) are shown in figure 5.

In figure 7(a) we show the data for the volume fraction \( f \) as a function of applied bias (or \( E \)) for different temperatures. For a fixed bias or field, \( f \) is very small at lower temperatures but grows very rapidly as the temperature rises. It can be seen that at \( E = E_{\text{th}} \), \( f \) crosses \( f_c \approx 0.25 \), which is close to
the critical value for volume percolation in 3D, leading to the resistive state transition. From figure 7(a) we find that the growth of the volume fraction $f$ is strongly enhanced by an applied field. At lower temperature, as $f$ is very small compared to the insulating fraction, the effect of the applied bias is stronger, leading to a sharp transition. As the temperature approaches 280–290 K, the decreasing difference between $\rho_{\text{ins}}$ and $\rho_{\text{m}}$ (see figure 5) softens the transition considerably.

The transition at a given temperature $T$, in an applied field $E$, occurs when the fraction $f(E, T) = f_c$. This defines $E_{\text{th}}(T)$ at a given temperature $T$. On application of the field, $f$ grows rapidly. As $f$ increases with the temperature even for a small field, the threshold $f_c$ is reached at a smaller bias at a higher temperature. This ushers in the resistive state transition at a smaller bias at a higher temperature. The steep dependence of $E_{\text{th}}(T)$ on $T$ is thus a reflection of the strong dependence of $f$ on $T$ and $E$, which, as we show below, depend on the thermal activation and field induced de-pinning respectively.

The temperature dependence of $f$ was found to be an activated process following the relation $f = f_0(E) \exp\left(-\frac{\Delta}{k_B T}\right)$, $\Delta$ being the activation energy. This is shown in figure 7(b) for three representative biases. The thermal activation energy $\Delta$ is found to be in the region of 200–235 meV and largely independent of $E$. The value of $\Delta$ is the same as the activation energy ($E_a$) found in the polaronic state in the three LaMnO$_3$ crystals. Interestingly, The pre-factor $f_0(E)$ increases with $E$. We find that the predominant effect of the electric field $E$ is to change the pre-factor $f_0(E)$. The dependence of $f_0$ on $E$ can be described by $f_0 = C \exp\left(-\frac{E_0}{E}\right)$, where $C$ is a constant and $E_0$ is the scale of the de-pinning field for the pinned minority phase. This is very similar to the relations found in many field driven de-pinning phenomena including charge density wave de-pinning [31, 32]. Thus the joint effect of $E$ and $T$ on the volume fraction $f$ is given as

$$f = C \exp\left(-\frac{E_0}{E}\right) \exp\left(-\frac{\Delta}{k_B T}\right).$$

(4)

To summarize, the observed resistive transition has been described as a bias driven percolation type transition between two states with co-existing phases: the polaronic insulating phase and a lower resistive bad metallic phase. The transition is controlled by two parameters. The first is the mobile fraction $f$ of the more conducting phase that has a steep $E$ and $T$ dependence that is described by equation (2). The second parameter is the relative difference between the two phases $\rho_{\text{ins}}$ and $\rho_{\text{m}}$, as shown in figure 5. This difference determines the magnitude of the resistive jump at the transition. At $T \approx [...$
280–290 K, since \( \rho_{\text{ins}} \rightarrow \rho_{\text{m}} \), the transition is not observable above this temperature.

The creation of Mn\(^{4+} \) by Sr substitution in LaMnO\(_3\) changes the nature of the transition and can gradually suppress it. The data on the single crystal La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\) taken by us along with similar data in [26] show that in most of the temperature range the transport shows strong non-linearity, but \( f \) may not exceed \( f_c \). The strong non-linearity can also be modeled by the phenomenological model described for nominally pure LaMnO\(_3\), where the mobile fraction \( f \) gets enhanced by the applied bias leading to the strong non-linearity. In this case the bias dependence of \( f \) for most of the temperature range is much less steep compared to the nominally pure system.

From the experimental data using a two-phase analysis we find the resistivities of the two phases, \( \rho_{\text{ins}} \) and \( \rho_{\text{m}} \), for La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\). In figure 8 we show the data. The resistivity \( \rho_{\text{ins}} \) in the polaronic insulating state is greatly suppressed by Sr substitution. However, for \( T \geq 150 \) K, the resistivity of the minority phase \( \rho_{\text{m}} \) is identical to the value of \( \rho_{\text{m}} \) that we found for LaMnO\(_3\). This is an important observation that while the creation of Mn\(^{4+} \) suppresses the resistivity of the polaronic insulating state considerably, the resistivity of the minority bad metallic phase is not affected. This suggests that whatever the origin of the bad metallic phase that gives \( \rho_{\text{m}} \) is, it is not created by the deliberate hole doping with Mn\(^{4+} \) that is created by Sr substitution. It can be seen that in the temperature range \( T \geq 150 \) K, as the value of \( \rho_{\text{ins}} \) for the Sr substituted system is lower, it is not very different from the \( \rho_{\text{m}} \). As a result the resistive transition becomes soft and loses the sharpness seen in LaMnO\(_3\). It shows up as a non-linear \( J-V \) curve as \( f \) changes with bias. Below 150 K, when the FM state sets in, there is phase co-existence with a lower resistance ferromagnetic metallic phase. This reduces \( \rho_{\text{m}} \), which, however, recovers below 100 K when the ferromagnetic insulating state sets in. In this region \( \rho_{\text{ins}} \) also rises rapidly on cooling. This leads to a sharp transition at lower temperature. The quantitative details of the transition where one has co-existing phases of different kinds would depend on the exact value of the Mn\(^{4+} \).

3.2. Microscopic scenarios for the phenomenological model

The phenomenological model given above is based on phase co-existence of a relatively low resistance marginally (or bad) metallic phase that has nearly temperature independent resistivity along with the polaronic insulating phase. This was seen to occur in nominally pure LaMnO\(_3\) as well as in La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\). In this section we explore whether there is evidence of such a phase co-existence and a microscopic scenario for such a bad metallic phase.

In nominally pure LaMnO\(_3\) with very small intentional Mn\(^{4+} \), the dominant phase below \( T_{\text{IT}} \) is an orthorhombic polaronic insulating phase which leads to A-type antiferromagnetic ordering below 150 K. However, there is evidence based on neutron scattering studies [33], resonant x-ray scattering [34] and also from optical conductivity experiments [35] that this picture may not be complete, and there is evidence of the presence of a small concentration of a phase that has similarity in structure and electronic properties with the high temperature phase that is found above \( T_{\text{IT}} \). This minority phase can be another orthorhombic/rhombohedral ferromagnetic phase with a considerably smaller unit-cell volume with a ferromagnetic transition temperature near \( T_N \). Based on the above experiments, it has recently been suggested [36] that such a minority phase can be a bad metallic phase. Strong evidence of this comes from pressure induced metallization of LaMnO\(_3\). It has been observed [7] that pressure induced destabilization of the insulating state in LaMnO\(_3\) at 300 K (at pressure \( \geq 32 \) GPa) leads to an orbitally dis-ordered phase that is like a bad metal with temperature independent resistivity. Subsequent x-ray absorption spectroscopy in LaMnO\(_3\) under pressure [37] has shown that although the insulator–metal transition is completed above 32 GPa, there is a co-existing orbitally dis-ordered phase that exists in a wide pressure range above 7 GPa until the transition is complete. Thus, there is evidence that a bad metallic phase with a small volume fraction can co-exist with the insulating phase well below \( T_{\text{IT}} \) in LaMnO\(_3\).

It has been suggested [36] recently that charge transfer (CT) instabilities can lead to dynamic charge disproportionation (Mn\(^{3+} \) + Mn\(^{3+} \) \rightarrow Mn\(^{4+} \) + Mn\(^{2+} \)) in nominally pure LaMnO\(_3\), which can act as an electron–hole (EH) pair. The presence of this instability leads to phase separation between a Jahn–Teller distorted polaronic insulator (the conventional phase) and a phase that behaves as a bad (or marginal) metal comprising EH droplets (Mn\(^{4+} \)–Mn\(^{2+} \) pairs). There is evidence [38, 39] that such a phase is present well below \( T_{\text{IT}} \) and even at 200 K with a finite volume fraction. Increase in temperature leads to an enhanced volume fraction of this phase and the phase transition at \( T_{\text{IT}} \) is envisaged to arise from this phase.

It is suggestive that the bad metallic minority phase, proposed in the phenomenological model above, may be related to this CT instability driven EH droplet phase [36]. The full volume of EH droplets that make the minority phase need not be mobile and can be self-trapped at lattice sites or

Figure 8. Resistivities of LaMnO\(_3\) and LSMO (x = 0.1) in the HRS in comparison to the \( \rho_{\text{m}} \) of the LRS as deduced from the experiment.
may also be trapped by local impurity potentials. The volume fraction ($f$) of the minority metallic phase estimated from the electrical resistance data gives the volume fraction of the mobile phase. The enhancement of $f$ occurs with temperature following an activated process that is very similar to the activation energy seen in transport in the polaronic insulating phase. The electric field applied can lead to de-pinning of the EH droplets from the lattice sites or impurity pinning sites. The nature of the $E$ dependence of $f$ seen by us suggests that this can indeed be the case.

The creation of Mn$^{4+}$ by Sr substitution is likely to be different from the Mn$^{4+}$ in the EH pair. In a very qualitative sense, the Mn$^{4+}$ in the EH pair is like intrinsic doping while that created by substitution is like extrinsic doping. With the creation of more substitutionally doped Mn$^{4+}$, they will dominate over the intrinsic EH pair seen in nominally pure LaMnO$_3$. The inhibition of the resistive state transition in La$_{0.9}$Sr$_{0.1}$MnO$_3$ can be a manifestation of this.

3.3. The issue of Joule heating

Joule heating has been suggested as the sole origin of the resistive state switching observed in manganites [22, 23]. Below we show that this is not the case for the observed switching in the parent manganite samples. To check the contribution of Joule heating in our observed resistive switching, we performed a current level measurement as a function of time for one of the LaMnO$_3$ samples at low temperature with two fixed voltages (in figure 9). We found a nearly constant sample current level with time when a bias of 200 V was stepped to 305 V. These are the voltages just before and after the resistive state switching. If any substantial Joule heating occurred in the sample, the sample resistance and hence the current in the sample would drift with time. We applied 200 V in the sample for nearly 3 min and then suddenly stepped the bias to 305 V, and we observed that the sample current switched to a higher level but stayed constant with the time.

We also performed a calculation for the maximum temperature rise in the sample due to the Joule heating considering the heat generated in the sample and dissipated from the sample through the metal base via the GE-varnish and thermal grease.

The heat balance equation in the sample is given as

$$\frac{dT}{dt} = \frac{P}{C_P} - \frac{T}{\tau} + \frac{T_S}{\tau},$$

$$\frac{dT}{dt} + \frac{T}{\tau} - \left(\frac{P}{C_P} + \frac{T_S}{\tau}\right) = 0.$$  

The solution to this equation is given as

$$T(t) = T_S + \frac{P \times \tau}{C_P} \left(1 - \exp\left(-\frac{t}{\tau}\right)\right).$$

Using the measured values of $C_P$ and $R_{Th}$, we evaluated the evolution of $T(t)$ on application of the pulsed power [40, 41]. A typical result for the temperature rise $\Delta T = T(t) - T_S$ as a function of time is shown in figure 10 at $T_S = 150$ K for LaMnO$_3$-1. The highest temperature rise at the maximum power pulse of nearly 300 mW was <3 K (switching pulse in figure 10(b)). In a similar way, calculating the $\Delta T$ for each pulse from 10 to 340 V, we found that the total temperature rise was ~14 K (from figures 10(a) and (b)). This temperature rise (maximum estimated) is not sufficient to generate the kind of resistive transition we observed at 150 K. We found that the temperature rise even at the lowest temperature was ≤4 K with the maximum power applied. This rules out any substantial contribution to the result arising from Joule heating. In general, when the applied voltage across the sample is increased in a step, so that switching in the resistive state occurs, the resistance in response to the step may drift due to Joule heating. We carried out tests and found an absence of such a drift. We have also shown that when data are taken with a constant bias the material makes a sharp transition from a lower resistance state to a higher resistance state at low temperature (in figure 5), which is the opposite of what one would expect if the entire effect were due to Joule heating.

4. Summary

In summary, we observed a sharp transition in the resistive state of nominally pure LaMnO$_3$ at temperatures below 300 K with a moderate applied bias. The field induced resistive state transition seen in this paper is different from those seen in manganites with higher levels of Mn$^{4+}$ content. Thus, the
mechanisms proposed for them are not applicable for the observations made here. In this case the transition occurs between the polaronic insulating state in LaMnO$_3$ and a bad metallic phase that has a temperature independent resistivity. The experiments were carried out on three single crystals. All three crystals, despite differences in their absolute resistivity values, showed qualitatively similar bias induced resistive transitions. At lower temperatures the change at the transition can be as high as four orders of magnitude. The transition becomes softer and is eventually not observed above 280 K. Similar experiments were also carried out on a single crystal of Sr substituted La$_{0.9}$Sr$_{0.1}$MnO$_3$. In this case we found that the increase of Mn$^{3+}$ content on Sr substitution inhibits the resistive state transition.

The observation has been explained as a bias driven percolation type transition between the two co-existing phases mentioned above. The applied bias can change the mobile fraction $f$ of the bad metallic phase, leading to a percolation type transition to the lower resistive state when the fraction $f$ crosses the critical volume fraction for the percolation transition. The mobile fraction $f$ (as estimated from the experimental data) has an activated dependence on temperature with an activation energy of $\approx 200 \text{ meV}$. The fraction $f$ has a dependence on the field of $f = C \exp \left(-\frac{E}{T} \right)$. This leads to rapid enhancement of $f$ on application of field, leading to a sharp transition in the resistive states.

Likely microscopic mechanisms for the co-existing phases have been proposed based on recent suggestions for the appearance and existence such phases. It appears that a bad metallic minority phase can co-exist in nominally pure LaMnO$_3$ due to charge transfer instability driven charge disproportionation [36].

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**Figure 10.** The temperature rise and fall ($\Delta T$) for each ON and OFF pulse (a) from 10 to 190 V and (b) from 200 to 340 V. The total increment in temperature is calculated by adding the $\Delta T$ after each period, i.e. for pulse no 2, 4, 6, ..., 68, indicated in the figure at each pulse position.
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