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Metastability in the electroresistance of electronic oxides

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Abstract
Electroresistance (ER) may be defined as the change in electrical resistance with applied current or voltage. We have studied ER and the metal-insulator transition (MIT) over the range 10 to 300 K in the lanthanum/calcium manganites $La_{1-x}Ca_xMnO_3$ for $x = 0 - 0.5$. The MIT varied between 80 K and 245 K, depending on the composition. A correlation between the ER and MIT was observed. In contrast, in $La_{0.8}Li_{0.2}MnO_3$ the maximum ER and the MIT occur at different temperatures. In $La_{2/3}Sr_{1/3}MnO_3$ there is only small ER observed below the Curie temperature. In further examining $La_{0.8}Li_{0.2}MnO_3$ through repeated thermal cycling from 300 K to 10 K to 300 K, a metastability in the resistivity-temperature characteristic became apparent. We describe this phenomenon in detail and discuss its origin and possible utilisation in switching and non-volatile memory applications.

Keywords: Metastability; Electroresistance; Manganites; Perovskites; Metal-Insulator Transition; Thermal Cycling

Introduction
The perovskites, of general chemical formula ABX_3, have many fascinating materials properties. In particular, the manganites, in which B is Mn and X is O, have attracted much interest in recent years. These exhibit phenomena which are both physically significant and technologically important, including colossal magnetoresistance (CMR), the metal-insulator transition (MIT) and electroresistance (ER).

We have recently reported on ER and the MIT in the lanthanum/calcium manganites $La_{1-x}Ca_xMnO_3$ for $x = 0 - 0.5$ (Knott *et al.* 2008). Data was taken at many currents in the range -1 to $+1$ mA and over many temperatures in the range 10 to 300 K, allowing a comprehensive picture of the resistance and ER as a function of current and temperature to be built up. The MIT was found to vary between 80 K and 245 K, depending on the Ca fraction. The ER and MIT were seen to be correlated.

In contrast, in $La_{0.8}Li_{0.2}MnO_3$ ER is decoupled from both the CMR and MIT observed in that compound (Lewis 2008a). The voltage across a bulk, polycrystalline sample was measured for $\sim$2000 applied currents I in the range $\pm$1 mA at $\sim$300 temperatures T in the range 10 to 300 K. At low temperature and low current, the ER is significant. As temperature increases, the ER reaches a maximum well below the temperature of the MIT where CMR is greatest. It is concluded that ER in this material is not accounted for by a phase separation (PS) percolation model. $La_{2/3}Sr_{1/3}MnO_3$ is different again. This material is insulating at room temperature and below. Only a small ER observed below the Curie temperature (Lewis 2008b).

In $La_{1-x}Li_xMnO_3$ trivalent La is replaced with monovalent Li. This greatly increases the proportion of Mn^{4+} relative to Mn^{3+}. CMR is observed over a wide temperature range for a wide range of x values (Wang *et al.* 1998a; Wang *et al.* 1998b; Wang *et al.* 2000; Ye *et al.* 2000). The material has also been investigated in high temperature (Shih and Fung 2005), infrared (Lewis *et al.* 1999) and mm-wave (Lewis *et al.* 2002) studies. In examining this material more extensively, we have found that the resistance (and hence the ER) sometimes exhibits marked "jumps" on thermal cycling. This phenomenon of metastability is the subject of the present paper.

Metastability has been previously observed in various manganite systems. For example, Yuzhelevski *et al.* (2001) report metastable resistive states in $La_{0.82}Ca_{0.18}MnO_3$, which they attribute to a spin-polarized tunnel conduction mechanism. In related work, Dikovsky *et al.* (2002) report conductivity oscillations in the current-induced metastable states in the same material. A further, detailed study has been made by Markovich *et al.* (2004). More recently, Quintero *et al.* (2007) investigated electric-pulse-induced resistance switching in manganite systems. They suggest that the mechanism is the doping control of the electronic state of the interface oxide. To our knowledge, the present paper is the first report of metastability in the system $La_{1-x}Li_xMnO_3$.

Materials and Methods
The sample synthesis was by conventional solid-state reaction. The precursors (high-purity La_2O_3, $LiCO_3$ and $MnCO_3$ powders) were weighed, mixed, pelletized and sintered at 1100 °C for 24 hours. Electrical contacts were furnished using Ag conductive paint. A standard four-terminal geometry was employed. A Keithley SourceMeter 2400

operating as a current source and voltmeter was used to make the electrical measurements. The variable-temperature measurements employed a Janis CCS350R closed-cycle cooler.

Results and Discussion

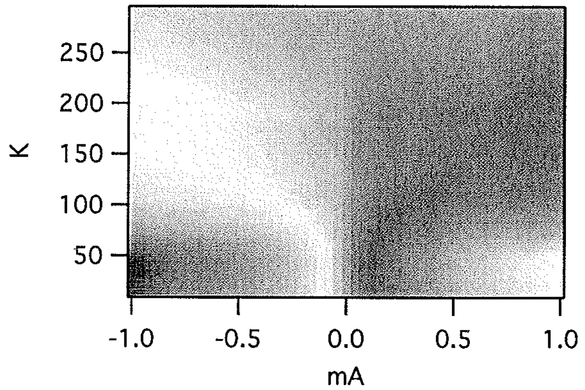

Figure 1: Voltage, V, measured across the sample as a function of current, I, (horizontal axis) and temperature, T (vertical axis).

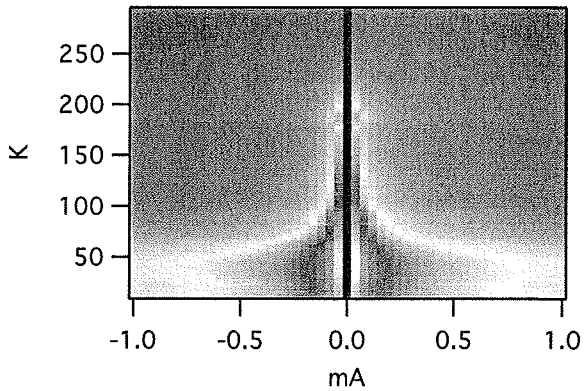

Figure 2: Resistance, R, of the sample as a function of current, I, (horizontal axis) and temperature, T (vertical axis).

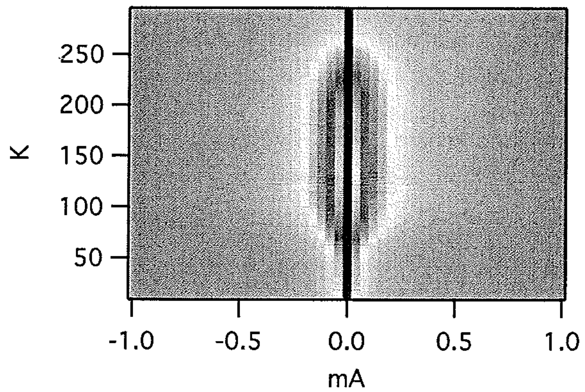

Figure 3: Electroresistance ratio, ER^*, of the sample as a function of current, I, (horizontal axis) and temperature, T (vertical axis).

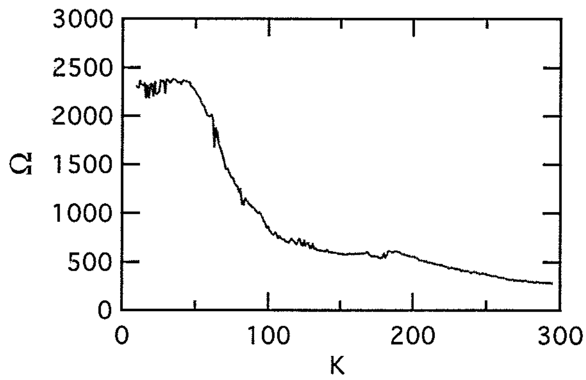

Figure 4: Resistance, R, of the sample as a function of temperature, T, for a current of $+1$ mA.

Figure 1 gives the raw data obtained in our experiments – the voltage, V, across the sample as a function both of the current, I, shown on the horizontal axis, and the temperature, T, shown on the vertical axis. There are 57 different currents at each of 287 different temperatures, or about 15k pixels altogether in the image. Such large data sets may also be visualised using surface plots, as in Knott *et al.* (2008) and Pond and Lewis (2008). The data in Figure 1 may be compared with that of Figure 1 of Lewis (2008a). The overall appearance is similar, although in detail the two differ. This is likely to be a result of the slightly different sample preparation methods. The sample used in the earlier paper underwent a second stage of grinding, pelletization and heating, involving partial melting. This method of synthesis results in a sample of higher density and larger grain size (Wang *et al.* 2000).

Figure 2 gives the resistance as calculated at every point in Figure 1 according to $R = V/I$ (that is, we plot resistance in the normal sense, not differential resistance, dV/dI). The image again comprises $\sim$15k pixels. In considering horizontal slices through Figure 2, it is clear that the resistance varies with current. Such behaviour has been termed "electroresistance". More formally, we may define the electroresistance ratio ER^* according to $ER^* = [R(I) - R(1\ mA)]/R(1\ mA)$. The electroresistance ratio ER^* is plotted against the current and temperature axes in Figure

3. It may be seen that the electroresistance appears over a wide temperature range and is greatest at low currents.

In considering vertical slices through Figure 2, the resistance-temperature relationship is obtained (at a given current). Figure 4 shows one such slice, corresponding to highest current used, +1 mA. From either Figure 2 or Figure 4 it may be seen that the resistance generally increases as the temperature decreases. There is a small peak at around 200 K. This corresponds to the MIT. A broad, low-temperature peak at around 50 K is thought to be due to grain boundaries in the sample. In this particular data set, taken as the sample was cooled, there is no sign of metastability.

For reasons yet to be fully determined, the same sample under the same experimental conditions sometimes exhibits metastability – the sudden switching of the resistance to a much lower or higher value. An example of this phenomenon is given in Figures 5 to 8.

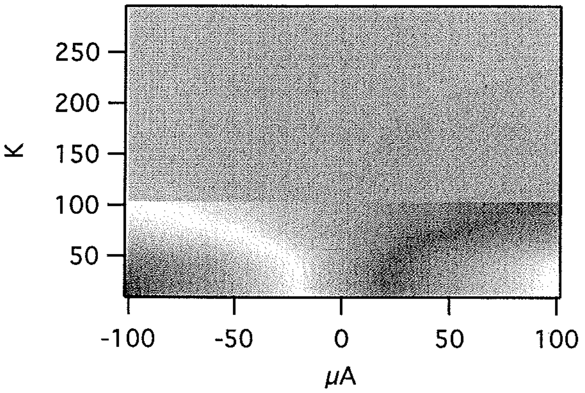

Figure 5: Voltage, V, measured across the sample as a function of current, I, (horizontal axis) and temperature, T (vertical axis), during cooling.

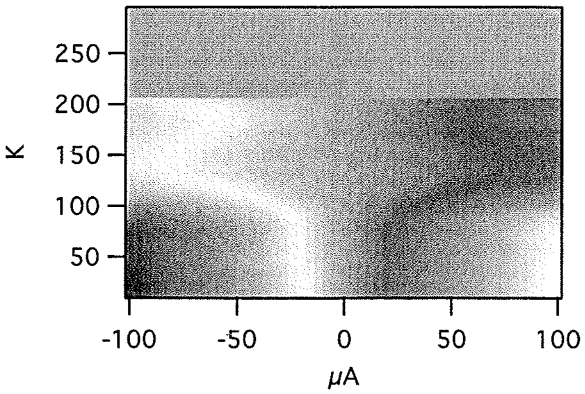

Figure 6: Voltage, V, measured across the sample as a function of current, I, (horizontal axis) and temperature, T (vertical axis), during warming.

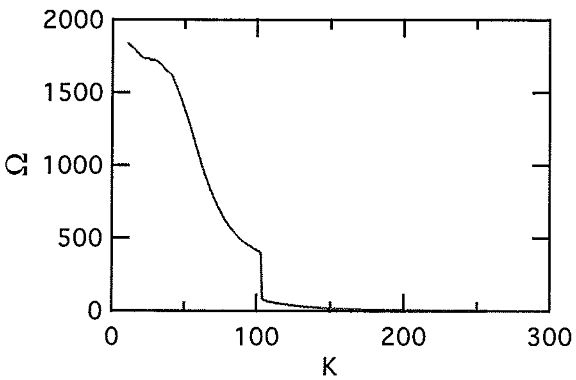

Figure 7: Resistance, R, of the sample as a function of temperature, T, for a current of +100 μA, during cooling.

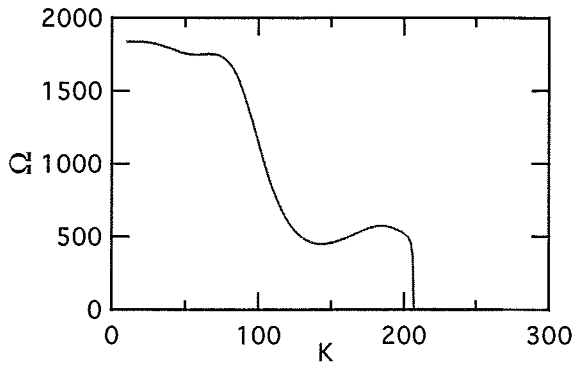

Figure 8: Resistance, R, of the sample as a function of temperature, T, for a current of +100 μA, during warming.

The data displayed in Figures 5 to 8 show data obtained during a single cooling and warming cycle. In cooling, Figures 5 and 7, a sharp rise in resistance occurs at about 100 K. Contrariwise, in warming, Figures 6 and 8, a sharp decrease in resistance is observed at about 210 K.

This type of experiment has been repeated many times with similar, but not identical, results. The general features may be summarized as follows. The temperature at which the jump occurs on cooling varies greatly from run to run: from as high as 260 K to as low as 40 K, and some times not at all (such as in the data shown in Figures 1 to 4). Likewise, the temperature at which the switch occurs on heating varies, from 200 K to 270 K. The usual pattern is a behaviour which may be termed "hysteretic": the resistance switch during cooling occurs at a lower temperature than the temperature of the resistance switch during subsequent warming. In other words, the system tends to stay in either the low-resistance or high-resistance state once it is in that state. It might also be noted that the high-temperature data in Figure 8 does not represent a short circuit, due to a problem with the wiring or contacts, for example. The resistance varies with temperature as shown in Figure 4, but at a much reduced level. Likewise, the high-temperature data in Figure 7 shows a peak at around 200 K (as in Figure 4 and Figure 8), but at a much reduced overall resistance. Thus the phenomenon is intrinsic to the sample and not an experimental artefact. It might also be noted that the maximum current employed in the experiments represented in Figures 5 to 8 is ten times less than that employed in the experiments represented in Figures 1 to 4. So, in contrast to other works on metastability in manganites, the metastability does not appear to be current-induced (Markovich *et al.* 2004) or electric-pulse–induced (Quintero *et al.* 2007), but simply induced by the change in temperature. Another salient fact is that we have never observed metastability in the partially-melted samples (Pond and Lewis 2008; Lewis 2008a).

We do not at present have a full explanation for the metastability observed here. The fact that the resistance is reduced as the temperature increases through the transition temperature would seem to rule out conducting filaments as the origin, as these would be expected to be disrupted as the temperature is increased. Other mechanisms that have been proposed to account for metastability that involve the application of larger electric fields than used here, or magnetic fields, do not seem to be relevant. Given that we have observed the phenomenon in the conventionally prepared samples, but not in the partially-melted ones, it is likely to be related to the greater porosity, lower density, and smaller grain size in the former. While in principle the phenomenon could be exploited in non-volatile memory applications, further work is required to improve the reproducibility of the effect, to which end a fuller fundamental understanding of the mechanism would assist.

Conclusions

We have observed, for the first time to our knowledge, metastability in the resistance state of $La_{0.8}Li_{0.2}MnO_3$. The phenomenon is driven by temperature changes alone and appears to be related to the sample grain structure.

Acknowledgements

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