Electroresistance of Perovskite Manganites

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A comprehensive delineation of current-voltage-temperature space is given for $La_{0.66}Sr_{0.33}MnO_3$ and $La_{0.8}Li_{0.2}MnO_3$. The first shows little electroresistance; the second exhibits marked electroresistance over a wide temperature range.

1. Introduction

Electronic oxide materials have grown in prominence recently, as exemplified by a renewal of interest in the semiconductor ZnO [1], the development of high-temperature superconductor technologies based on oxides [2], and extensive studies of perovskites of general form ABX_3, where X is oxygen [3]. Specifically, the perovskite manganites have drawn attention because of the metal-insulator transition (MIT) that occurs in these and the related phenomenon of "colossal magnetoresistance" (CMR) [4]. More recently, the "electroresistance" of the manganites, or the change in electrical resistance with current (in other words, a non-linear current-voltage (I-V) characteristic) has been the subject of concentrated study [5,6]. Non-linear electrical characteristics have been observed in single crystal [7,8], polycrystalline [7], and thin film [5,9] samples of lanthanum manganites. Grain boundary junctions [10] and *p-n* structures involving lanthanum manganites [6,11] also exhibit non-linear I-V characteristics.

The compound $Pr_{0.63}Ca_{0.37}MnO_3$ has been examined in detail by Guha *et al*. [8]. It exhibits a charge-ordered insulating (COI) state below the charge-ordering temperature T_{CO} of about 240 K. The COI state is easily destabilised by magnetic field or optical radiation. The I-V characteristic is linear at temperatures above T_{CO}, but becomes non-linear at temperatures just below T_{CO}. At still lower temperatures, the I-V curves indicate negative differential resistance (NDR) for currents of the order of 1 mA and greater. Simultaneously observing an increase in the magnetisation of the sample using a SQUID, the authors conclude filaments of ferromagnetic metallic (FMM) phase are induced in the sample by the current and are the origin of the NDR. Biskup *et al*. [7] report a detailed study on $R_{1-x}Ca_xMnO_3$, with R = Pr, Nd, Ho and Er, and $x = 0.3$–0.5. At high enough voltages, all specimens exhibit NDR. They conclude that Joule heating is an important factor, even at low current densities, but that heating itself is a result of non-linearities produced by the double-exchange mechanism [7].

"Giant electroresistance" – the dramatic reduction in electrical resistance with increasing current – has been reported in epitaxially-grown thin films of $La_{0.67}Ca_{0.33}MnO_3$ by Zhao and co-workers [5]. An extension of this work [9] considers the dependence of the effect on film thickness and attributes the observed effects to the co-existence of a FMM phase with the COI phase. (These two papers do not present I-V curves as such.)

The work reviewed so far involves nominally homogeneous material. Other research has involved studying junctions that, less surprisingly, also give rise to non-linear electrical characteristics. Non-linear I-V characteristics observed in bicrystal grain boundary junctions in thin films of $La_{0.67}Ca_{0.33}MnO_3$ are attributed to magnetically-induced band-bending at the grain boundary [10]. Hole-doped $La_{0.7}Ca_{0.3}MnO_3$/electron-doped $La_{0.7}Ce_{0.3}MnO_3$ [11] and $La_{0.67}Ca_{0.33}MnO_{3-\delta}$/Nb-doped $SrTiO_3$ [6] have been used to realise *p-n* junctions, which exhibit characteristic rectifying I-V curves.

While resistivity (ρ)-temperature (T) curves (equivalently, V-T curves at constant I) have been presented in the literature for some time, and I-V curves (at constant T) have been the focus more recent work, a comprehensive delineation of the three-dimensional I-V-T space, such as given in this paper, does not appear to have been presented previously.

2. Experimental details

We have measured I-V characteristics of perovskite manganites over the temperature range 10–300 K. The electrical measurements were made using a conventional four-terminal arrangement. It was found for the higher-resistivity samples that identical results were obtained using a two-terminal method. The sample electrodes were fashioned using silver paint. The current was supplied, and the voltage measured, by a Keithley Model 2400 SourceMeter. The samples were mounted in a Janis Closed-Cycle Refrigerator System (CCS-350R) and the temperature regulated by a CryoCon System 31 controller. The data are displayed as surface plots.

Figure 1 illustrates the method for a very elementary test specimen, an Allen-Bradley resistor. The front-right panel gives the I-V curve at room temperature; it is linear. The I-V curve for the lowest temperature (here, 10 K) is given on the back-left panel. For the resistor used, this is again linear. The back-right panel gives the V-T characteristic at the maximum current employed (here, 1 mA). Since the current is constant on this vertical plane, this curve also gives, within a constant multiplicative factor, the ρ-T curve. From this curve it may be seen that as the temperature is decreased, the resistance increases, characteristic behaviour of an insulator. The next most simple example, a diode (IN914), is shown in Figure 2. The surface plot may be interpreted as before. In this case, the I-V curve is strongly non-linear at all temperatures, as expected, and the resistance increases rapidly at low temperatures, also as expected. (The “drips” at zero current indicate the noise in this condition.) These two test specimens illustrate classic ohmic and diodic/rectifying behaviour, respectively.

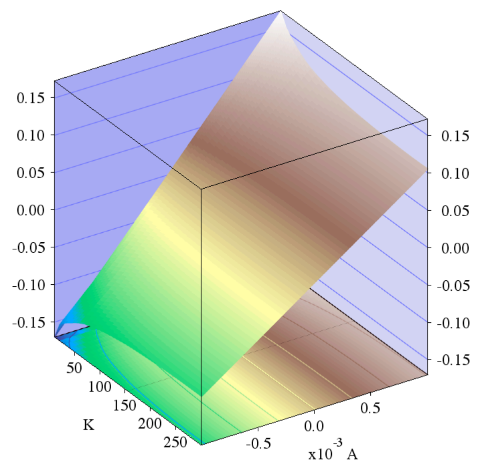

Figure 1: Allen-Bradley resistor. Voltage (vertical axis) as a function of temperature and current.

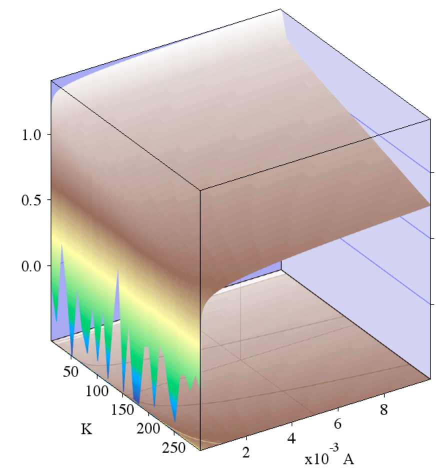

Figure 2: IN914 diode. Voltage (vertical axis) as a function of temperature and current.

3. Results and discussion

We report measurements on two samples based on the perovskite $LaMnO_3$. The La site is then occupied in different ways. (a) In one sample, denoted LSMO, 33% Sr occupies the La site [12]. (b) The other sample, labelled LLMO, has the La site 20% Li [13].

Figure 3 gives the data for LSMO, $La_{0.66}Sr_{0.33}MnO_3$. The I-V characteristic is close to linear at all temperatures. It is seen, at all currents, that $dV/dT > 0$ at all temperatures. Thus this material is metallic at all temperatures, consistent with earlier work showing that the series $La_{1-x}Sr_xMnO_3$ is metallic at room temperature and below for $x > 0.25$ [12].

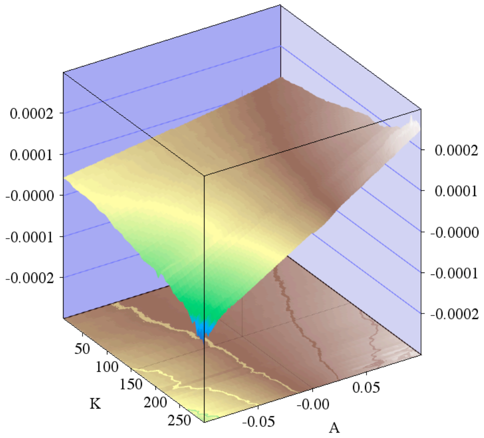

Figure 3: $La_{0.66}Sr_{0.33}MnO_3$ (LSMO). Voltage (vertical axis) as a function of temperature and current.

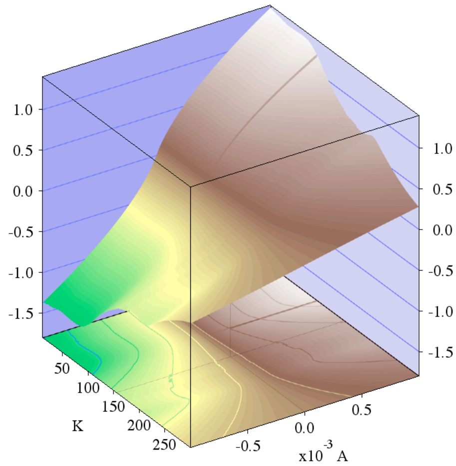

Figure 4: $La_{0.8}Li_{0.2}MnO_3$ (LLMO). Voltage (vertical axis) as a function of temperature and current.

The sample LLMO, Figure 4, generally increases in resistance as the temperature decreases, although there is a broad maximum around 200 K near the magnetic transition [13]. We observe a noteworthy development in this material. The I-V curve changes strikingly with temperature: from ohmic at room temperature, to very non-linear at low temperature. At low temperatures, the resistance decreases with current; in a word, the material exhibits electroresistance. We suggest the explanation for the behaviour observed in Figure 4 is that at low temperature there is a coexistence of metallic and insulating phases. This coexistence is more likely to occur in polycrystalline samples, such as employed here, than in single crystal samples, where the phase transition would be expected to be more abrupt. Any metal-insulator phase boundary would be expected to act as a Schottky barrier, and so diodic behaviour (rapidly increasing V with I) would result. In the "reverse" direction, that particular barrier will be highly resistive, but the current will flow through other, favourably oriented barriers, leading to the symmetric but non-linear I-V.

4. Conclusion

We observe the electrical resistance of two perovskite manganites as a function of temperature and current. The metallic sample, LSMO, exhibits near linear I-V characteristics at all values of I; in other words, little electroresistance. For the sample LLMO below the transition temperature we observe a striking non-linearity in the I-V characteristic; in other words, strong electroresistance.

Acknowledgments

This work is supported by the Australian Research Council. We thank F. Gao and X. L. Wang for provision of samples.

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