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### Electroresistance of La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub>

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The electroresistance of  $La_{0.8}Li_{0.2}MnO_3$  has been measured at many applied currents and temperatures. As the magnitude of the current decreases, the electroresistance becomes more pronounced. Substantial electroresistance is observed over a wide range of temperatures. The greatest effect occurs well below the temperature of the metal-insulator transition. © 2008 American Institute of Physics. [DOI: 10.1063/1.2917443]

 $La_{1-x}Li_xMnO_3$  is of interest as replacing the trivalent La with the monovalent Li increases the number of Mn<sup>4+</sup> ions relative to the number of Mn<sup>3+</sup>, with profound consequences for the magnetic and electrical properties. In pioneering studies of La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub>, Wang *et al.* demonstrated the result is colossal magnetoresistance (CMR) over a wide temperature range.<sup>1–3</sup> Ye *et al.* examined a larger range of *x* values and obtained the same result.<sup>4</sup> Shih and Fung investigated the series to high temperature.<sup>5</sup> Related reports detail infrared optical properties<sup>6</sup> and ferromagnetic resonances in La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub>.<sup>7</sup>

 $La_{1-x}Li_xMnO_3$  is a perovskite of general form ABO<sub>3</sub>. Specifically, it is part of the family of lanthanum manganites (A=La, B=Mn)  $La_{1-x}E_xMnO_3$ , where the *A* sites are partly occupied by another element E. This may be an alkali metal<sup>8</sup> or a monovalent species<sup>9–11</sup> other than Li. Widening the vista, the A site may be occupied by an alkaline earth. The most celebrated example is Ca, in which CMR came to prominence.<sup>12</sup>

Recently, it has been recognized that many materials which exhibit CMR also exhibit colossal electroresistance (CER), that is, the strong dependence of the resistance on the applied current.<sup>13–15</sup> The origin of CER is still controversial. Initial reports correlated CER with CMR,<sup>13,14</sup> supporting a percolative phase separation model of CER. More recent reports show that CER is not always associated with CMR<sup>16,17</sup> and so other explanations of CER may be needed. In the work here, CER is demonstrated in a monovalent *A*-site doped manganite. It is further shown that the CER does not directly correlate with the CMR.

The samples were synthesized by conventional solidstate reaction.<sup>1</sup> High-purity starting materials were weighed, mixed, pelletized, and sintered at 1100 °C for 24 h then ground and repelletized. X-ray diffraction peaks were well indexed by a rhombohedral structure with little evidence of impurity phases. Variable-temperature measurements were made by using a Janis CCS350R closed-cycle cooler. The current was supplied and the voltage measured with a Keithley SourceMeter 2400.

Figure 1 is an ~0.6 megapixel V image against the horizontal I axis and the vertical T axis. [Such extensive data may also be visualized using a surface plot, as exemplified by  $La_{1-x}Ca_xMnO_3$  (Ref. 18) and  $La_{2/3}Sr_{1/3}MnO_3$ .<sup>19</sup>] The image is antisymmetric about a central vertical mirror plane, indicating that the data are symmetric for positive and negative applied currents. Along horizontal slices at the top of the image, the gradient is uniform. This indicates that at high temperatures, the sample is ohmic. Across horizontal slices at the bottom of the image, the steps are unevenly spaced. This indicates that at low temperatures, the sample is electroresistive. Along a vertical slice, the voltage is directly proportional to the resistance (and also directly proportional to the resistivity); it may be seen that as the temperature decreases, the voltage rises and falls more than once.

Figure 2 displays some representative subsets of the data of Fig. 1 as V-I curves. Each curve contains experimental data from -1 mA to -5  $\mu$ A and from +5  $\mu$ A to +1 mA in 1  $\mu$ A steps, 1992 data points altogether. The data at currents near zero were noisy and so the experimental data for I=-4,-3,...,+4  $\mu$ A have been replaced by  $I/(5 \mu$ A)  $\times [V(5 \mu$ A)- $V(-5 \mu$ A)]. The synthetic data are thus 9 points of the 2001 points graphed.

The V-I characteristic was measured from 10 to 300 K in 1 K steps, a total of 291 data sets. Four of these data sets are shown in Fig. 2. The V-I characteristic for T=300 K is linear. The curve for T=200 K is markedly nonlinear. The



FIG. 1. (Color online) Voltage V across  $La_{0.8}Li_{0.2}MnO_3$  sample as function of current I (horizontal axis) in range from -1 mA (left) to +1 mA (right) and of temperature T (vertical axis) in range from 10 (bottom) to 300 K (top); ~0.6 megapixel image.

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FIG. 2. (Color online) Voltage V across La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub> sample as function of current I for the temperatures T=10, 100, 200, and 300 K.

curves for T=100 K and T=10 K are also nonlinear but less than for the curve at 200 K. The nonlinearity is expressed below through the calculation of the  $ER^*$ .

The resistance R = V/I is calculated from the data in Fig. 1 at every point to yield the resistance matrix. Figure 3 shows some representative subsets of the data from the resistance matrix as *R*-*T* curves. In Fig. 3, it may be seen that while the magnitude of *R* varies with current (the ER effect), the overall features of the R-T curve are the same at all currents. As T decreases from room temperature, R increases until it peaks at  $T_P \sim 210$  K, then drops before rising again to a second peak at  $T_{P_2} \sim 80$  K, then drops and rises again as T decreases further. Double or triple peaks and a broad, lowtemperature minimum have been previously observed in lanthanum manganites doped with Li (Refs. 1-5) and, more broadly, lanthanum manganites doped with other monovalent on divalent ions on either the A or the B site.<sup>8–11,20,21</sup> Various explanations have been advanced for this rich structure reported in the R-T curves in the lanthanum manganites including grain-size effects,<sup>22</sup> oxidation,<sup>23</sup> percolative phase separation,<sup>24</sup> and phase inhomogeneity.<sup>4</sup> In the present case, it is thought to arise from the grain boundaries in the sample. For the purpose of this paper, the exact origin of the broad, low-temperature peak is unimportant. The main emphasis



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FIG. 4. (Color online) Electroresistance ER\* of La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub> sample as function of current I (horizontal axis) and of temperature T (vertical axis);  $\sim$ 0.6 megapixel image.

here is on the ER, and the main result, as set out below, is that the maximum ER does not coincide with either  $T_P$  or  $T_{P_2}$ .

Figure 4 is an  $\sim 0.6$  megapixel *ER*<sup>\*</sup> image. The data displayed in Fig. 4 are calculated according to  $ER^* = [R(I)]$  $-R(1 \text{ mA})]/R(1 \text{ mA}) \times 100\%$ . The ER is small around three edges of Fig. 4. By definition,  $ER^*$  is zero for the current of 1 mA, the right-hand edge. It was previously noted that the voltage data are symmetric with respect to current. Consequently,  $ER^*$  is close to zero for a current of -1 mA, the left-hand edge. The ER is small at room temperature, the top edge. Moving in from the edges-decreasing temperature or decreasing the magnitude of the current-the ER increases. It is seen that the ER is greatest at the smallest currents employed. Regarding temperature, the ER is greatest at T=170 K. This does not correspond to  $T_P$  or to  $T_{P_2}$ . This is a key result of the paper.

The main results of the paper appear in Fig. 5. Here, ER\*



FIG. 3. (Color online) Resistance R of  $La_{0.8}Li_{0.2}MnO_3$  sample as function of temperature T for the currents I=10, 100, and 1000  $\mu$ A.



FIG. 5. (Color online) Electroesistance ER\* of La<sub>0.8</sub>Li<sub>0.2</sub>MnO<sub>3</sub> sample as function of temperature T for the currents I=10, 100, and 1000  $\mu$ A. The inset shows the magnetoresistance  $MR = [R(B) - R(0 \text{ T})]/R(0 \text{ T}) \times 100\%$ over the same temperature range for the magnetic fields B=4 and 8 T.

is shown as a function of *T*. ER is evident over a very broad temperature range. The inset shows the magnetoresistance at the two magnetic fields B=4 and 8 T, calculated according to  $MR=[R(B)-R(0 \text{ T})]/R(0 \text{ T}) \times 100\%$ . The peak in the ER does not correspond to the peak of the CMR [which has been shown to coincide with the FM transition temperature  $T_C = T_P$  (Ref. 1)]. Thus, ER and CMR are not directly correlated in this system.

It may be seen in Fig. 5 that the ER is greater at smaller currents. As the current goes from 10 to 100  $\mu$ A, the ER decreases but the temperature of the maximum in ER remains fixed at about 170 K. At the largest current shown, 1000  $\mu$ A, *ER*<sup>\*</sup> is zero by definition.

The two main observations reported here for ER in  $La_{0.8}Li_{0.2}MnO_3$  are that it is present over a wide range of temperatures and that the maximum occurs at about 170 K. The first observation may have practical consequences regarding applications. It is of interest as in many other materials, ER is restricted to a narrow band of temperatures. The second observation may spur further investigation of the underlying mechanism. It is of interest as it demonstrates that the maximum in ER does not correspond to the maximum resistance  $T_P$ , nor to the maximum CMR.

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