Nonlinear conductivity of electronic origin in magnetic oxides: uncommon cases at $E < 1000$ V/cm

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Abstract. We report on electronic transport measurements on polycrystalline, non-metallic samples of doped-LaMnO$_3$, in the ohmic and non-ohmic regimes. The non-ohmic regime has been investigated using d.c. as well as pulsed measurements. Large nonlinear conductivity of electronic origin, was found with pulsed currents in (nominal) La$_{0.8}$Li$_{0.2}$MnO$_3$, LaMnO$_{3+\delta}$ and in La$_{0.8}$Ca$_{0.2}$Mn$_{0.95}$O$_3$ at low temperatures under electric fields $E < 500$ V/cm. Their thermopowers exhibit maxima associated with the onset of (partial) magnetic order. For all samples, including some with perfectly linear pulsed I-V characteristic, the d.c. characteristics show, under similar fields, large nonlinearity and hysteresis, typical of self-heating in samples with activated conductivity.

1. Introduction
Nonlinear conductivity and associated phenomena (hysteresis, noise, switching, breakdown, etc) found in magnetic oxides, in particular in charge ordered (CO) manganites, have attracted considerable attention for more than a decade. Although the thermal theory of non-ohmic conductivity and associated phenomena are known for about a century, many of the recently published I-V characteristics (I-V-C) were obtained using d.c., a.c. or long-duration current pulses (of hundreds of ms or more). Unfortunately, such measurements do not discriminate between nonlinearity of electronic origin and that due to self-heating. We measured the I-V-C of several CO oxides, using both d.c. and short-duration single current pulses$^{1,2}$ and found that in all our samples, for electric fields up to $\sim 1000$ V/cm, the strongly nonlinear d.c. I-V-C mask a perfectly linear or only slightly nonlinear conductivity as obtained with short current pulses. However, using the same technique we did find significant nonlinear conductivity of electronic origin (NCEO) in some non-metallic ferromagnetic oxides, most recently in LaMnO$_{3+\delta}$(LMO$_{3+\delta}$)$^{3}$. By significant we mean that for $E \leq 500$ V/cm the excess current above ohmic ($\Delta J = J - J_0$) is of the order of, or larger than, the ohmic current ($J_0$). Even in such cases self heating takes over the NCEO at unpredictable voltages, when measured using d.c.

The excess oxygen in LMO$_{3+\delta}$ appears as pairs of La-Mn vacancies$^{4}$ that contribute the finite Mn$^{4+}$/Mn$^{3+}$ ratio ($= 2\delta/1-2\delta$) responsible for ferromagnetism. The disorder on the Mn lattice containing Mn vacancies causes non-metallicity. We suggested$^{3}$ that the significant NCEO obtained in this system is due to field enhanced hopping along the Mn chains. In order to learn more about the field and temperature dependence of $\Delta J/J_0$ in insulating FM manganites and their relation to the low-field transport we extended this work to additional polycrystalline doped LaMnO$_3$. 1. Li-doped on the La site (nominal), 2. Li-doped on the Mn site (nominal) and 3. self-doped or Ca-doped with vacancies on the Mn-site. Substitution of trivalent ions (La and Mn) by monovalent ions (Li) or by vacancies is more efficient than by the common divalent ions for increasing the Mn$^{4+}$/Mn$^{3+}$ ratio. The largest NCEO was obtained in La$_{0.8}$Ca$_{0.2}$Mn$_{0.95}$O$_3$(LCMO) and in LMO$_{3+\delta}$; their relatively low resistances allowed us to extend the measurements below liquid nitrogen. It will be shown that the temperature dependence of the thermopower is correlated with the magnitude of the NCEO.

2. Sample preparation and experimental methods
The samples were prepared either by the standard solid state synthesis (SSSS)$^5$ or by wet chemistry$^6$ both followed by sintering. We initially followed the preparation protocols from the literature but...
digressed from these protocols, increasing the number, duration and temperature of heat treatments whenever the resulting samples were not of single phase or disintegrated. The XRD patterns obtained using a Siemens diffractometer showed virtually no traces of impurity phases in the final compounds. The unit cell symmetry and lattice parameters were determined by least-square fitting in the range of $2\theta = 10^\circ - 140^\circ$, collected by step scan of 0.03$^\circ$, 15 secs. step. The (four-probe) d.c. and pulsed I-V-C were measured as described in Ref. 1. and their thermopower (relative to Cu) was measured as in Ref. 2. The preparation method of the investigated samples and their structural properties are summarized in columns 2-4 of Table I and the SEM morphology of six samples is shown in Fig. 1.

**Table 1.** Preparation and structural properties of the investigated samples and the most significant low-field and high-field electronic properties

| Nominal composition       | Preparation       | Crystal system      | Volume/ f.u. ($\text{Å}^3$) | $T(S_{\text{max}})$ (K) | $E_0$ (80 K) V/cm |
|---------------------------|-------------------|---------------------|-----------------------------|------------------------|-------------------|
| $\text{La}_0.8\text{Li}_{0.2}\text{MnO}_3$ | SSSS 1100$^\circ$ C | Orthorhombic (O)   | 58.87                       | -                      | $>$ 1000          |
| $\text{La}_{0.8}\text{Li}_{0.2}\text{MnO}_3$ | SSSS 1450$^\circ$ C + 600$^\circ$ C in $\text{O}_2$ | O close to R | 59.63 | 185 | 140 |
| $\text{La}_{0.8}\text{Li}_{0.2}\text{MnO}_3$ | Wet chemistry + 1200$^\circ$ C | Hexagonal (H) | 58.77 | 180 | 205 |
| $\text{LaMn}_{0.85}\text{Li}_{0.15}\text{O}_3$ | SSSS 1300$^\circ$ C | Rhombohedral (R) | 58.60 | - | - |
| $\text{LaMn}_{0.85}\text{Li}_{0.15}\text{O}_3$ | Wet chemistry + 1200$^\circ$ C | R | 58.60 | 165 | $>$ 1000 |
| $\text{La}_{0.9}\text{Ca}_{0.1}\text{Mn}_{0.95}\text{Li}_{0.05}\text{O}_3$ | Wet chemistry + 1200$^\circ$ C | Monoclinic | 58.87 | 161 | 560 |
| $\text{LaMn}_{0.95}\text{O}_3$ | SSSS 1450$^\circ$ C + 600$^\circ$ C in $\text{O}_2$ | R | 58.62 | - | - |
| $\text{LaMnO}_{3+\delta}$ ($\delta = 0.15$) | SSSS 1450$^\circ$ C + 600$^\circ$ C in $\text{O}_2$ | R | 58.65 | 191 | 85 |
| $\text{La}_{0.8}\text{Ca}_{0.2}\text{Mn}_{0.95}\text{O}_3$ | SSSS 1450$^\circ$ C + 600$^\circ$ C in $\text{O}_2$ | O | 58.95 | 186 | 105 |

**Fig. 1.** SEM images of LLMO(a), LLMO(b) and LLMO(c) (upper row) and of LCMLO, LMO$_{\delta}$, LCMO, (second row). Note the large grains and the melted boundaries of the samples sintered at high temperatures in contrast with those sintered at low temperatures (see Table I).

3. Results and discussion

The resistivity ($\rho$) and the thermopower ($S$) as function of inverse temperature and the pulsed (symbols) and d.c. J-E characteristics of the samples at various temperatures are shown in Figs. 2-4.
Fig. 2. (a) Semilog plot of $\rho$ versus $1/T$ for $\text{La}_{0.8}\text{Li}_{0.2}\text{MnO}_3$ (a,b,c). (b) $S$ versus $1/T$ for the three types of samples. (c) – (e) Log-log plots of $J(E)$ for the three types of samples at various temperatures. Symbols represent pulsed measurements (NCEO) and solid lines- d.c. measurements (self-heating). Significant NCEO is observed at low T for LMO(b) and (c). The insets in (c) and (d) represent $J(E)$ (pulsed and d.c.) on linear scales.

Fig. 4. (a) Semilog plot of $\rho$ versus $1/T$ for $\text{LaMn}_{0.95}\text{O}_3$, $\text{LaMnO}_{3-\delta}$ and $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_{3-\delta}$. (b) $S$ versus $1/T$ for the three types of samples. (c) Semilog plot of $\rho$ versus $T$. (d) – (f) Log-log plots of $J(E)$ for the three types of samples at various temperatures. Symbols represent pulsed measurements (NCEO) and solid lines- d.c. measurements (self-heating). Large NCEO is observed at low T for LMO,δ and LCMO.

Fig. 3 containing the corresponding data for the three types of samples doped with Li on the Mn sites (see Table I) is added as a supplementary Figure. See also the Supplementary Table IS.

For all samples investigated in this work the resistivity is activated at all temperatures. All ln ($\rho$) vs $T^{-1}$ plots bend from a higher to a lower activation energy at specific temperatures $T_\rho$, associated with the onset of ferromagnetic order. Between RT and $T_\rho$ the resistivity activation energy $\Delta_\rho(T>T_\rho)$
is lowest for LCMLO (110 meV) and highest for LMLO(a) and LCMLO (137 meV). Below $T_p$ the activation energy is constant as in Fig. 2 (a) or decreases with decreasing temperature as in Figs. 3 (a) and 4 (a). Close to RT, the activation energies of the thermopower ($\Delta_\rho$) are much lower (range between ~22 meV for LMO$_{\delta}$ and ~35 meV for LLMO(b)). $\Delta_\rho >> \Delta_4$ is expected for polaron hopping. For all samples, $\Delta_\rho$ decreases with decreasing temperature and for six samples $S(T)$ passes through a maximum ($T(S_{\text{max}})$) at temperatures close to $T_p$. The values of $T(S_{\text{max}})$ are shown in row 5 of Table I.

The pulse J-E characteristics for LLMO (b) and (c), (Fig. 2) for LMO$_{\delta}$, and for LCMO (Fig. 4) exhibit strong nonlinearity at low temperatures, visible even on the log-log scale. Note that although the morphology of LLMO (b) and LMO (c) are very different they exhibit comparable NCEO. The weak nonlinearity of J(E) for LLMO(a) (Fig. 2), LMLO(b) and LCMO (Fig. 3) is barely visible on this scale. The nonlinearity decreases with increasing temperatures and is not detectible above ~ 150 K. For LMLO(a) (Fig. 3) and LMO(a) (Fig. 4) the pulsed J(E) plots are perfectly linear at all temperatures of the measurements. For all samples, with and without NCEO, the d.c. characteristics are nonlinear and exhibit hysteresis, the typical behavior for self-heating.

Analysis of the J(E) plots shows that the dependence of the excess current density $\Delta J$ on the electric field $E$ can be expressed as: $\Delta J/J_0 = (E/E_o)^\alpha$ where $E_o$ and $\alpha$ are fitting parameters. For LMO$_{\delta}$ and LCMO for which J-E measurements could be extended below liquid nitrogen temperature $\alpha>1$ at low temperatures (see Fig. 5(a)), where $\ln p/p_o \propto -T$ (see Fig. 3(c)). Fig. 5(b) shows the semilog plot of $E_o(T)$. $E_o$(80 K) is shown in the last column of Table I.

The most significant observation of this work is revealed by the correlation between the last two columns in Table I: It is seen that measurable NCEO at fields below 500 V/cm appears in samples where $S$ has a maximum. Moreover, the higher $T(S_{\text{max}})$ the larger the NCEO (the lower $E_o$).

References
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**Supplementary data**

**Table IS:** Additional structural and electronic transport properties of the investigated samples

| Nominal composition | Cell constants (Å) | $T_\rho$(K) | $\Delta_\rho$(T$\geq T_\rho$) meV | $\Delta_\rho$(T$\leq T_\rho$) meV | $T(S_{max})$ (K) | $\Delta_s$(RT) meV |
|---------------------|-------------------|------------|-------------------------------|-------------------------------|-----------------|-----------------|
| La$_{0.8}$Li$_{0.2}$MnO$_3$ LLMO(a) | 5.487(2) 5.521(2) 7.774(2) | 121 | 129 | 113 | - | 28 |
| La$_{0.8}$Li$_{0.2}$MnO$_3$ LLMO(b) | 5.520(1) 5.525(1) 7.822(1) | 165 | 125 | 94 | 185 | 35 |
| La$_{0.8}$Li$_{0.2}$MnO$_3$ LLMO(c) | 5.526(1) 13.334(3) | 186 | 130 | 108 | 180 | 30 |
| LaMn$_{0.9}$Li$_{0.1}$O$_3$ LMO(a) | 5.524(1) 13.305(2) | 149 | 137 | 119 | - | 27 |
| LaMn$_{0.9}$Li$_{0.1}$O$_3$ LMO(b) | 5.524(1) 13.306(2) | ~130 | 127 | 12 $T^{1/2}$ | 165 | 20 |
| La$_{0.9}$Ca$_{0.1}$Mn$_{0.9}$Li$_{0.1}$O$_3$ LCMLO | 5.489(1) 5.497(1) 7.804(2) $\beta=90.43^\circ$ | ~220 | 137 | 11 $T^{1/2}$ | 161 | 24 |
| LaMn$_{0.9}$O$_3$ LMO(a) | 5.524(1) 13.310(2) | ~125 | 136 | 11 $T^{1/2}$ | - | 26 |
| LaMnO$_3$+$\delta$ ($\delta=0.15$) LMO$_\delta$ | 5.521(1) 13.329(2) | 179 | 112 | 66$^{**}$ | 191 | 22 |
| La$_{0.8}$Ca$_{0.2}$Mn$_{0.9}$O$_3$ LCMO | 5.513(1) 5.500(1) 7.777(1) | ~240 | 110 | 97$^{**}$ | 186 | 24 |

* The XRD spectrum of this compound contained minute unidentified peaks.
** Below 80 K for LMO$_\delta$ and 90 K for LCMO $\ln(\rho/\rho_o)$.

**Remarks to Table IS**
- Doping on the Mn site is difficult and the blue section of Table IS represents the few successful cases, i.e. single phase and non-brittle.
- $T_\rho$ is the temperature of the bend in the plot of $\ln(\rho)$ vs. $1/T$.
- Above $T_\rho$, the activation energy $\Delta_\rho(T> T_\rho)$ is constant for all samples
- $\Delta_\rho(T<T_\rho)<\Delta_\rho(T> T_\rho)$ for all samples and for some of them is temperature dependent (see column 5 in the Table above).
- $T(S_{max})$ which appears in Table I was included here to show that in most cases it is close to $T_\rho$.
- $\Delta_s = \frac{dS}{d(T^{-1})}$ decreases with increasing temperature (see Figs. 2 (b), 3(b) and 4 (b)). Column 6 of this Table shows its value at room temperature (RT).
Fig. 3. (a) Semilog plot of $\rho$ versus $1/T$ for LLMO (a,b) and LCMLO (see Table I). The inset shows the semilog plot of $\rho$ versus $T^{3/2}$ (b) $S$ versus $1/T$ for the three types of samples. (c) – (e) Log-log plots of $J(E)$ for the three types of samples at various temperatures. Symbols represent pulsed measurements (NCEO) and solid lines- d.c. measurements (self-heating). Very weak NCEO is observed for LMLO(b) and LCMLO.