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Conduction mechanisms in pure and doped polycrystalline orthorhombic manganites

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Abstract

In this work we present magnetic and transport measurements as a function of temperature of polycrystalline pure and doped $RMnO_3$ (R=La, Nd and Ho) samples. We have performed AC transport measurement (in the range from DC to 2 MHz) in pellets of $La_{0.7}Ca_{0.3}MnO_3$ annealed at several temperatures, which present different connectivity between grains keeping the same mean grain size (about 1 μm). A large increase of resistance is observed at temperatures below the ferromagnetic order temperature where a metallic regime is expected. The behavior with temperature and frequency of the resistance of low temperature annealed pellets can be explained taking into account that two kinds of conduction paths are present in the sample: low resistive metallic ones, where the carriers percolate through well connected grains and highly resistive channels for high intergrain boundaries that behave as capacitors. In order to obtain the conduction mechanisms for non-doped $RMnO_3$ samples, we have measured the resistance in a large temperature range up to 1400 K. We present a discussion about the deviation of the measured resistance from any kind of polaronic conduction at high and low temperature. The differences in the activation energy with the rare earth ion are also discussed.

Keywords: Magnetically ordered materials; Grain boundaries; Electron–phonon interactions; Exchange and superexchange; Tunneling

1. Introduction

Manganese perovskites $La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba...) have recently attracted much interest because of their potential magnetic applications using their high (up to colossal) magnetoresistance effect [1]. Ca compounds with $0.15<x<0.5$ present an insulator-to-metal transition, at T_{IM}, and para-to-ferromagnetic (FM) ordering, at T_C, both about 265 K for $x=0.33$. The metallic FM state is quite well described by the double-exchange model but polaronic effects due to strong electron–phonon coupling have also to be invoked in the insulator regime where the conduction is achieved by hopping of small polarons. The effect of grain boundaries, grain size, artificially induced boundaries, or films with microcracks [2–4] have been extensively studied since the large values of low temperature low field magnetoresistance is now established to be a spin dependent scattering process at the boundaries [2,5,6].

A comprehension of the detailed mechanisms for the high field magnetoresistance of polycrystalline perovskite oxides is still lacking. Nevertheless, it is now clear that spin polarized scattering at grain boundaries together with the magnetic state of their surface are crucial points in this problem. We have raised the evidence that the connectivity between the grains is of special relevance in the conductivity of the metallic ferromagnetic state of $La_{0.67}Ca_{0.33}MnO_3$ [7] as well as in the low temperature high field magnetoresistance [8]. A poor connectivity can lead to the suppression of the metallic behavior in the ferromagnetic phase. Therefore part of the phenomenology observed in polycrystalline pellets or thin films of mangetoresistive manganites is, in fact, related to extrinsic characteristics as the quality of the surface or the degree of compaction of the grains. Another open question is the conduction mechanism for non-doped manganites.

2. Experimental

Two kind of samples have been studied: 33% Ca doped $LaMnO_3$ and $RMnO_3$ (R=Nd and Ho) powder samples. $La_{0.66}Ca_{0.33}MnO_3$ powders were obtained by standard ceramic process. These pellets were sintered at different temperatures; 200 and 1100°C for 4 h each. The number

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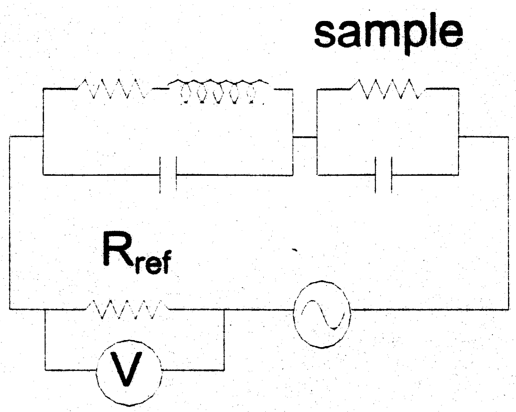

Fig. 1. Equivalent circuit for the experimental set-up in series with the sample, the reference resistance and the voltage supply.

used to label the sample indicates its sintering temperature whose effect is to 'glue' one grain to the other. In that way, connectivity between grains will depend on the sintering temperature [7]. The $x=0.33$ pellets present the same magnetic behavior with T_C at 265 K. Non-doped $RMnO_3$, with R=Y, Er and Ho, crystallizes in an hexagonal structure but can adopt the *Pbnm* one when obtained by citrate techniques involving low temperature treatments [9]. All the studied samples presented the *Pbnm* orthorhombic structure (D_{2h}^{16}, with $Z=4$).

Magnetization and DC electric four probes transport measurements in the 350–4 K temperature range were performed in a Squid magnetometer and a multipurpose Quantum Design system, respectively. High temperature resistance measurements, up to 1200 K, were performed in a furnace with platinum electrodes. The AC electric set-up consists in a voltage supply (0–30 MHz) and a 100 MHz digital oscilloscope that measures the voltage drop in a reference resistance connected in series to the sample located inside an Oxford Instruments continuous flow cryostat. The equivalent circuit for the experimental set-up is a LCR circuit in series with the sample, the reference resistance and the voltage supply (Fig. 1).

3. Results and discussion

Fig. 2a shows the DC resistance, normalized to the 300 K value, of $La_{0.66}Ca_{0.33}MnO_3$ pellets sintered at 1100°C (Ca1100) and at 200°C (Ca200). Ca1100 sample shows the usual behavior for this compound. The huge increase in the low temperature resistance of the Ca200 sample is caused by the poor connectivity between grains corresponding to low sintering temperature. Fig. 2b) shows the modulus of the complex impedance $|Z|$, AC measurements, of the 200°C sintered pellet at different frequencies compared to its DC value. The measured resistance decreases as the frequency increases in the low temperature region. The

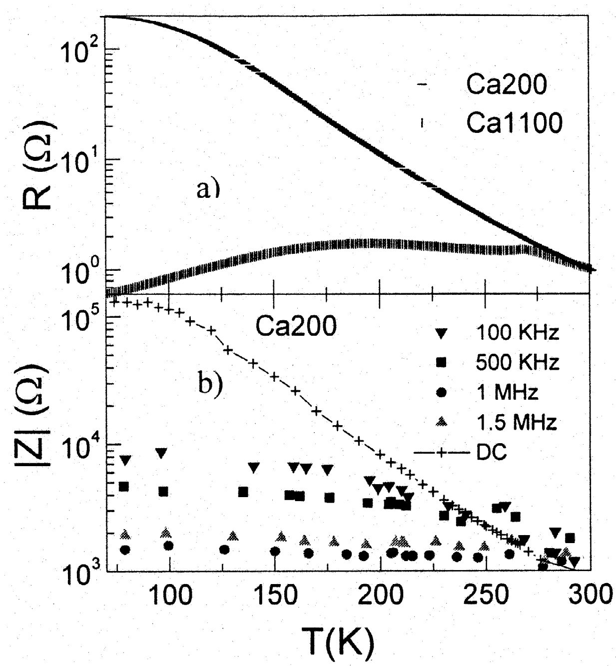

Fig. 2. (a) DC resistance, normalized to the 300 K value, of $La_{0.66}Ca_{0.33}MnO_3$ pellets sintered at 1100°C (Ca1100) and at 200°C (Ca200); (b) AC measurements of the 200°C sintered pellet, at different frequencies, compared to its DC value.

frequency dependence of $|Z|$ at low (77 K) and high (276 K) temperature is shown in Fig. 3.

The observed behavior is perfectly fit using a pure resistance and a capacitor in parallel as the equivalent circuit for the sample. The obtained capacitance value is about 0.6 nF and is almost independent of the temperature. On the other hand, Ca1100 sample shows a resistance independent of the frequency. This behavior can be explained taking into account that, at low temperatures,

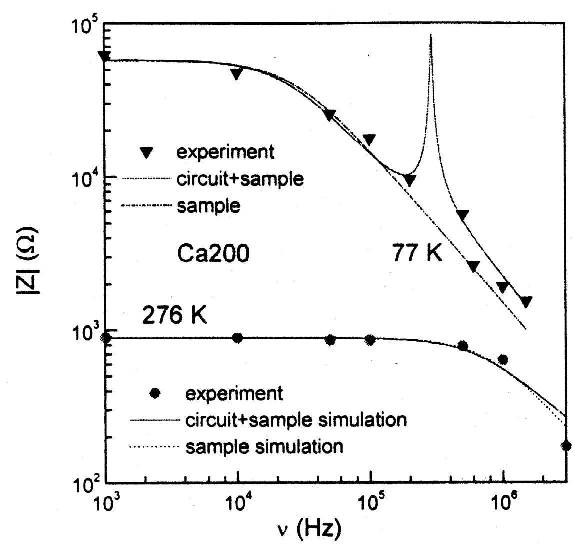

Fig. 3. Frequency dependence of $|Z|$ at low (77 K) and high (276 K) temperature.

carriers are bonded because, to overcome the intergrain boundaries, a thermal energy is necessary but not available. The barriers to intergrain conduction are higher when the contacts between grains are poor. In this way, the measured impedance decreases when the frequency increases since the bonded carriers can follow an AC field: the sample can be described as a pure resistance, corresponding to the paths through the best connected grains, in parallel with a capacitance that represents the intergrain paths with barriers to carrier hopping whose energies are higher than the temperature of the sample. This picture should be valid for all kind of artificial boundaries like grains, scratches, microcracks, etc.

On the other hand we have explored the conduction mechanisms for nominally pure compounds. Fig. 4 reports the measured resistance, normalized to the 300 K value, of several $RMnO_3$ samples. An intrinsic conduction for these

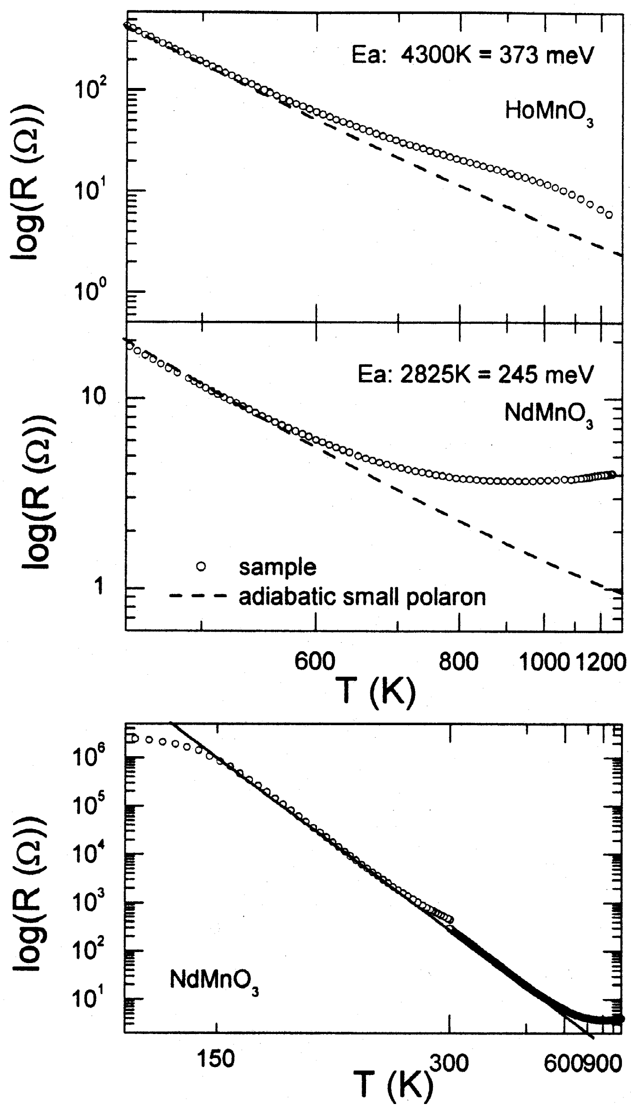

Fig. 4. Measured resistance, normalized to the 300 K value, of several $RMnO_3$ samples and the fitting to adiabatic small polaron behavior.

insulating materials should lead to activation energies of the order of 1 eV, while the obtained values, when fitting to the $R = AT\ \exp\ (E_A/k_BT)$ expression (corresponding to adiabatic small polaron hopping), are in the range from 0.2 to 0.4 eV. Therefore the observed conductivity has to be related to the presence of small amounts of Mn^{4+}. Polaron conduction in pure $LaMnO_3$ has been observed [10]. The value of the reported A constant ($45\times10^{-6}\ \Omega\ \mathrm{cm}\ \mathrm{K}^{-1}$) is comparable with those obtained by us (81×10^{-6} $\Omega\ \mathrm{cm}\ \mathrm{K}^{-1}$ for $HoMnO_3$), which is consistent with a Mn^{4+} content of about 1%. On the other hand, $NdMnO_3$ sample gives a value for the A constant which is 2 times lower, consistent with a lower concentration of Mn^{4+}.

The value of the A parameter should be similar for the $RMnO_3$ series since it is proportional to the Mn^{4+} concentration and to the Mn–Mn spacing within the framework of polaron conductivity. The variation of the activation energies for the conductivity with the rare earth needs special mention. Variation of this activation energy has been reported [10] through the series $La_{1-x}Ca_xMnO_3$, a linear relationship between the Mn^{3+} content and the activation energy was observed, this variation was attributed to the Jahn–Teller distortion, proportional to the Mn^{3+} content. Taking into account that the Jahn–Teller distortion increases monotonically through the series La–Nd–Ho (a measure of this distortion is the relative difference of a and b parameters; c is the long axis), the activation energies obtained by us, 0.245 eV for $NdMnO_3$, 0.373 eV for $HoMnO_3$ and 0.215 for $LaMnO_3$ [11] are in accordance with a monotonous dependence of the activation energy (and hence the polaron binding energy) with the Jahn–Teller distortion.

Fig. 4 shows the behavior of the sample resistance in the high temperature range for $NdMnO_3$ and $HoMnO_3$, at low temperatures the previously mentioned activation energies are obtained. At temperatures close to 700 K a reduction of the activation energies is observed in both samples, this can be tentatively attributed to the presence of a structural phase transition in this temperature range. Finally, the resistance of the $HoMnO_3$ sample shows a fast decrease at temperatures higher than 1000 K perhaps due to intrinsic conduction at high temperatures, this behavior is not observed in the $NdMnO_3$ due to the lower resistivity of this sample. Intrinsic conduction should become apparent at higher temperatures.

Fig. 5 shows the low temperature behavior of the resistivity for the $NdMnO_3$ sample, the high temperature behavior matches the results shown in Fig. 4, whereas at temperatures below $\approx$150 K the resistivity departs from the thermally activated behavior, as is expected from the polaron picture [12]. The activated behavior, present at high temperature, is related to polaron hopping; at temperatures around $\Theta_D/2$ phonon assisted tunneling begins to dominate the polaron motion giving rise to a conductivity dependence $\sigma\propto\exp(-T^{-1/4})$; at lower temperatures a power law for the polaron mobility is expected.

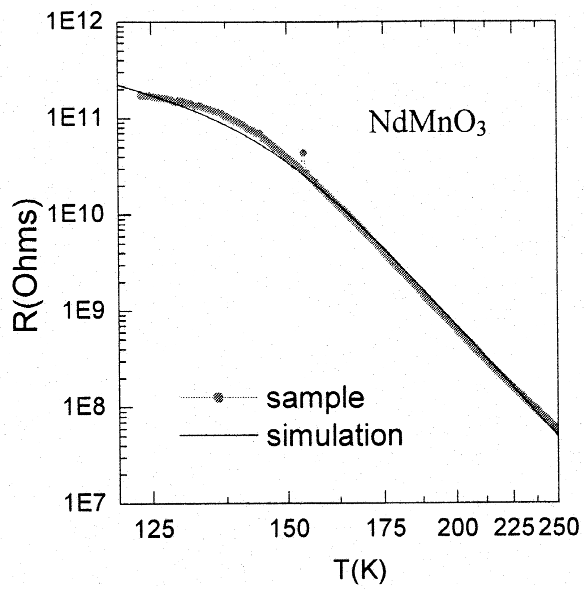

Fig. 5. Low temperature behavior of the resistivity for the $NdMnO_3$.

The resistance has been fitted considering that both mechanisms are happening: polaronic hopping and tunneling. This second mechanism beginning to be dominant at low temperature when polaronic hopping is very much reduced.

4. Conclusions

In summary, we have seen for the doped samples, sintered at two different temperatures and, hence, showing different connectivity between grains, that show different dependence of the resistance with temperature. For samples with poor grain connectivity, at low temperatures, the carriers are bonded inside the grains because they have no thermal energy to overcome the intergrain boundaries. The sample can be described as a pure resistance, corresponding to the paths through the best connected grains, in parallel with a capacitance that represents the intergrain paths with barriers to carrier hopping whose energies are higher than the temperature of the sample.

We explored the conduction mechanisms for the undoped $RMnO_3$ samples and related the smaller value of the activation energy, than that expected, to a presence of small amounts of Mn^{4+}. The activation energies obtained were in accordance with a monotonous dependence of the polaron binding energy with the Jahn–Teller distortion. The reduction in the activation energy value for the Ho an Nd samples, at temperatures close to 700 K, was attributed to the presence of a structural phase transition in this temperature range.

Finally, the resistance for $NdMnO_3$, at low temperatures (below $\Theta_D/2$),was fitted considering that polaronic hopping and tunneling mechanisms were taking place at the same time, being the second process dominant at low temperatures when polaronic hopping is much reduced.

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