# Impedance spectroscopy evidence of the phase separation in $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ manganite

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We have measured electrical resistance $R(T)$, magnetization $M(T)$, and for the first time impedance spectroscopy $Z(T,\omega)$ of polycrystalline samples of $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ compounds. The combined results suggest the coexistence of two metallic ferromagnetic phases below the Curie temperature of the system. The $R(T)$ data exhibit two important features: the occurrence of a metal–insulator (MI) transition at temperatures close to $T_{MI} \approx 170$ K and a large thermal hysteresis below $T_{MI}$. The first feature was found to be associated with the development of ferromagnetism and takes place when the magnetization of the samples becomes about 15% of its saturated value at low temperatures. The second feature suggests two contributions to $R(T)$ below the Curie temperature $T_C$. The $Z(T,\omega)$ data taken from 77 to 300 K and frequency varying from 5 to $10^7$ Hz are much more valuable. These results reveal two well defined bulk contributions to the transport properties of these manganites below ~170 K: one occurring at high frequencies $\sim 4\times 10^6$ Hz and a second one at low frequencies, typically on the order of $1.5\times 10^5$ Hz. An analysis of the $Z(T,\omega)$ data suggests that these contributions are related to the spin lattice relaxation rate of the two distinct phases. Such a result suggests a phase separation below $T_C$ in the compound in complete agreement with recent muon spin relaxation and neutron spin echo measurements performed on manganites.
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The mixed-valent manganites with general formula $Ln_{1-x}T_xMnO_3$ (Ln=rare earth; T=Ca, Sr, or Ba) exhibit rich and interesting physical properties because of the strong interplay between small lattice distortions, transport properties, and magnetic ordering.[1–6] In particular, the magnetic phase diagram of the $La_{1-x}Ca_xMnO_3$ system has been reported recently.[2] In the low Ca doping region, $x<0.2$, the compounds are antiferromagnetic and insulating, due to the superexchange interaction between the $Mn^{+3}$ ions. For $0.2<x<0.5$ the compounds exhibit ferromagnetism and a metallic conductivity owing to the double exchange interaction between $Mn^{+3}$–$Mn^{+4}$ pairs. The $Mn^{+4}$ ions are created by the partial substitution of a divalent alkaline earth for trivalent lanthanum, which corresponds to the creation of holes at the $Mn^{+3}$ sites (hole doping). Furthermore, it has been suggested that the arrangement of these $Mn^{+3}$–$Mn^{+4}$ pairs are confined to small regions of these manganites with dimensions of ~30 Å.[7]

As far as this point is concerned, recent measurements of muon spin relaxation ($\mu$SR) and neutron spin echo in $La_{0.7}Ca_{0.3}MnO_3$ manganite strongly suggested that below $T_C$ two spatially separated phases or regions with very different Mn–ion spin dynamics coexist.[7] One phase was found to display diffusive relaxation near $T_C$ and an increasing volume fraction below $T_C$, suggesting overdamped ferromagnetic spin waves below $T_C$. In the second phase the fluctuation of spins develops over a slower time scale and a decreased volume fraction was found below $T_C$. They also estimated the characteristic length scale of the inhomogeneity of the system to be ~30 Å.[7] These experimental results are in complete agreement with the phase separation predicted theoretically by a number of techniques.[8,9]

In this article, we focus on the transport and magnetic properties of $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ compounds. We have performed temperature dependence of electrical resistance $R(T)$, magnetization $M(T)$, and impedance spectroscopy $Z(T,\omega)$ at temperatures varying from 77 to 300 K. The latter was performed in a large range of frequency ranging from 5 to $10^7$ Hz. These results enabled us to address the issue of phase separation below $T_{MI}$ in these manganites, where MI is metal–insulator.

High quality polycrystalline samples of $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ compounds were prepared with the standard solid state reaction. Details of the sample preparation are described elsewhere.[10] Magnetization $M(T)$ measurements were performed using a commercially available magnetometer from Quantum Design, San Diego, CA. In the zero-field-cooled measurements the samples were cooled

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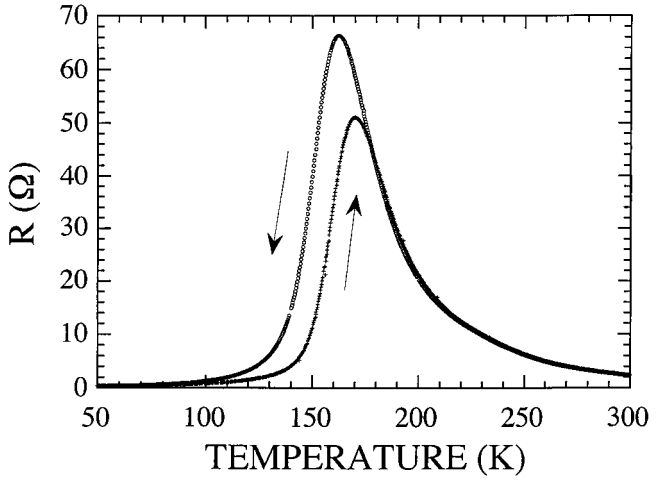


FIG. 1. Temperature dependence of the electrical resistance $R(T)$ of polycrystalline $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ compound. Arrows denote data taken during increasing and decreasing temperature.

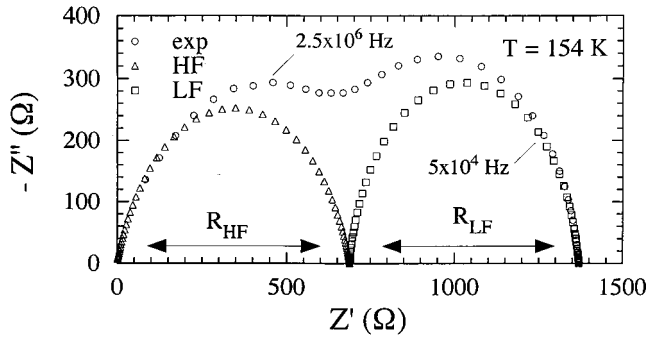


FIG. 2. Impedance spectroscopy $-Z''$ vs $Z'$ diagram for $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$ at $T=154$ K.

down from room temperature to 5 K in zero field before a measured field was applied. In the field-cooled measurements the sample was cooled in an applied magnetic field from room temperature to 5 K. Electrical resistance $R(T)$ measurements were measured with the standard four probe method under two different conditions: increasing and decreasing temperature. Impedance spectroscopy measurements were performed by using the standard two probe method and a HP4192A LF impedance analyzer. The impedance analyzer is connected via HPIB to a model 363 HP controller for collecting, storing, and processing $[-Z''(T,\omega)\times Z'(T,\omega)]$ data in the 5 Hz–13 MHz frequency range. The temperature dependence of the impedance diagram was measured as follows: after collecting the impedance diagram data at room temperature, the sample was cooled down to 77 K. At this temperature, both the $Z''(T,\omega)$ and $Z'(T,\omega)$ data were collected and this step was repeated at several temperatures between 77 and 300 K during the sample warming. All impedance diagrams were corrected for parasite inductances and analyzed using the software for deconvolution of the impedance diagrams that showed more than one semicircle.

It is useful to start the discussion by showing the temperature dependence of the $R(T)$ data which are displayed in Fig. 1. A careful inspection of these results reveals important features of these manganites. First, we have found that the most pronounced feature of both curves is the occurrence of a maximum at a temperature $T_{MI}\approx 160$ and 170 K corresponding to the decreasing and increasing temperature branches, respectively. This maximum is certainly related to the development of the metal–insulator transition in this compound. Second, the $R(T)$ curves taken under different conditions (increasing and decreasing temperature) exhibit a well pronounced thermal hysteresis which was found to exist in a large range of temperature, typically from 60 to 170 K. The observation of such thermal hysteresis is consistent with the coexistence of two different phases with distinct spin-lattice relaxation times.

Some of the observed features in the $R(T)$ data have their counterpart in magnetization data $M(T)$ taken in $H=2.5$ kOe (not shown). First, a saturated moment of the sample at low temperature of ~7.73 emu/mol was observed. Also, it seems that the $R(T)$ transition shown in Fig. 1 occurs at the temperature in which the $(M/H)$ data assume a value close to 15% of 7.73 emu/mol. This indicates that the decrease in the magnitude of $R(T)$ occurs at a given temperature in which the volume fraction of the metallic phase reaches about 15%, which is appropriately close to the three-dimensional percolation threshold. In fact, Kim *et al.*[4] observed a similar behavior in polycrystalline $La_{5/8-x}Pr_xCa_{5/8}MnO_3$ compounds. It was assumed that the volume fraction of the metallic phase is temperature dependent and it increases with decreasing $T$.

To gain further information regarding the coexistence of phases in $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$, we have performed measurements of the temperature dependence of the impedance spectroscopy from 77 to 300 K. A typical experimental result of $Z(\omega)=Z'(\omega)+iZ''(\omega)$ taken in increasing temperature and at 154 K, which is just below the temperature in which $R(T)$ falls significantly with decreasing temperature, is shown in Fig. 2. The figure displays the $Z'(\omega)$ vs $-Z''(\omega)$ diagram obtained at frequencies varying from 5 to $10^7$ Hz. The frequency $\omega$ decreases with increasing $Z'(\omega)$ values. The experimental curve (open circles) clearly shows two contributions to the $Z(\omega)$ which were obtained by the deconvolution of the data by fitting two semicircles and are also shown in the figure. One of them, at high frequencies and denoted as $R_{HF}$ (open triangles), has a very low electrical resistance. The other one, which is much more resistive, is referred to as $R_{LF}$ and appears at low frequencies (open squares). From an analysis of several $Z(\omega)$ curves taken at different temperatures, we have computed the values of both $R_{LF}$ and $R_{HF}$ which are displayed in Fig. 3. The figure also shows the temperature dependence of the $R_{LF}+R_{HF}$ behavior at the right axis.

The first point to be addressed here concerns the behavior of the total component $R_{LF}+R_{HF}$, which is similar to the $R(T)$ data shown in Fig. 1. This corroborates the assumption that the $R(T)$ curve is comprised of at least two contributions and that the impedance spectroscopy technique is able to separate them. Second, contributions arising from both $R_{LF}$

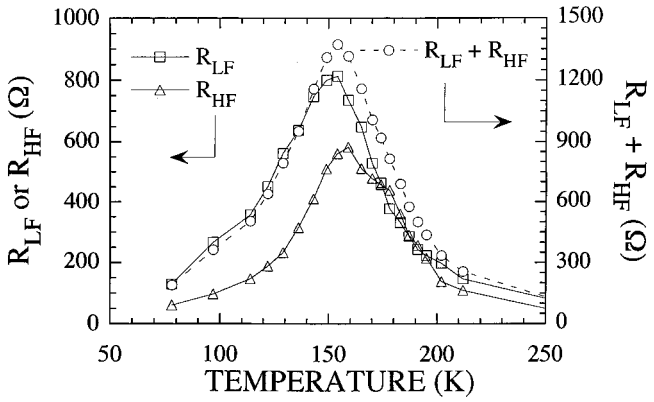


FIG. 3. Temperature dependence of both $R_{LF}$ and $R_{HF}$ components. The figure also shows the temperature dependence of the $R_{LF}+R_{HF}$ at the right axis. The lines are guides to the eye.

and $R_{HF}$ have essentially the same magnitude and temperature dependence down to ≈170 K, the temperature in which ferromagnetism develops and that the $T_{MI}$ occurs in the increasing branch of the $R(T)$ data shown in Fig. 1. Moreover, below 170 K, both curves deviate from each other and increase at a different rate with decreasing temperature down to a maximum value occurring at $T_{max}\approx 155$ and 160 K for $R_{LF}$ and $R_{HF}$, respectively. Below $T_{max}$ both contributions decrease with decreasing $T$ and merge again at ~77 K, in a behavior similar to that observed in the $R(T)$ data. Since both contributions are different below ~170 K, which is the Curie temperature $T_C$ as obtained by the $M(T)$ data, they are related to the development of ferromagnetism in the system. Also, the discussion involving these two components requires consideration of the local Mn–ion spin dynamics of the system. Moreover, it seems that our $R_{LF}$ and $R_{HF}$ data are closely related to the contributions of the spin fluctuation rates to the transport properties of these manganites below $T_C$, as described above.[7]

Our $Z(\omega,T)$ data seem to be in complete agreement with the results discussed in Ref. 7. We have found that the characteristic frequency associated to the $R_{LF}$ component is close to $1.5\times10^5$ Hz, which corresponds to a spin lattice relaxation time of ~6 $\mu$s. This is similar to that found in Ref. 7 of ~2.2 $\mu$s. The same analysis can be made for the $R_{HF}$ component which shows a characteristic frequency of ~4 $\times10^6$ Hz or more appropriately to a spin relaxation time of ~0.2 $\mu$s. Again, our estimate is in complete agreement with the $\mu$SR data of ~0.1 $\mu$s.[7] Thus based on these results, we argued that our $Z(\omega,T)$ data correspond to the contributions to the transport properties of both fast ($R_{HF}$) and slow ($R_{LF}$) Mn–ion fluctuation rates in $La_{0.3}Pr_{0.4}Ca_{0.3}MnO_3$.

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