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Magnetic relaxation behavior in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$

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We have carried out a systematic magnetic relaxation study, measured after applying and switching off a 5 T magnetic field to polycrystalline samples of La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. The long time logarithmic relaxation rate (LTLRR), decreased from 10 to 150 K and increased from 150 to 195 K in La$_{0.5}$Ca$_{0.5}$MnO$_3$. This change in behavior was found to be related to the complete suppression of the antiferromagnetic phase above 150 K and in the presence of a 5 T magnetic field. At 195 K, the magnetization first decreased, and after a few minutes increased slowly as a function of time. Moreover, between 200 and 245 K, the magnetization increased throughout the measured time span. The change in the slope of the curves, from negative to positive at about 200 K was found to be related to the suppression of antiferromagnetic fluctuations in small magnetic fields. A similar temperature dependence of the LTLRR was found for the Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ sample. However, the temperature where the LTLRR reached the minimum in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ was lower than that of La$_{0.5}$Ca$_{0.5}$MnO$_3$. This result agrees with the stronger ferromagnetic interactions that exist in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ in comparison to La$_{0.5}$Ca$_{0.5}$MnO$_3$. The above measurements suggested that the general temperature dependence of the LTLRR and the underlying physics were mainly independent of the particular charge ordering system considered. All relaxation curves could be fitted using a logarithmic law at long times. This slow relaxation was attributed to the coexistence of ferromagnetic and antiferromagnetic interactions between Mn ions, which produced a distribution of energy barriers.

I. INTRODUCTION

In addition to the known magnetoresistance effect in manganese perovskites,[1] compounds such as La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ present a real-space ordering of Mn^{3+} and Mn^{4+} ions, called charge ordering (CO). These materials show, close to the charge ordering temperature (T_{CO}), various anomalies in resistivity, magnetization and lattice parameters as a function of temperature, magnetic field and isotope mass.[2–5] Microscopically, CO compounds are particularly interesting due to the coexistence of ferromagnetic and antiferromagnetic phases at low temperatures.[6] However, a relatively small external magnetic field destroys the CO phase and enforces a ferromagnetic orientation of the spins.[4] Moreover, electron microscope analysis has revealed convincing evidence that the CO is accompanied by the orientational ordering of the 3d^3 orbitals on the Mn^{3+} ions,[7] called orbital ordering (OO). Recently, x-ray resonant scattering experiments[8] suggested that CO (a long-range interaction) drove the OO (a short range interaction) near T_{CO}.

Neutron powder diffraction and magnetization studies in La$_{1-x}$Ca$_x$MnO$_3$ samples, with $x = 0.47$, 0.50, and 0.53, have shown that the Curie temperature (T_C) was approximately 265 K in all cases.[9] Huang *et al.*[9] also reported the formation of a second crystallographic phase (A-II) at 230 K. Moreover, they found that the A-II phase had the same space-group symmetry (*Pnma*) and lattice parameters as the original F-I phase, but it differed in the weak Jahn-Teller distortions of the MnO$_6$ octahedrons. Furthermore, the A-II phase ordered antiferromagnetically with a CE-type magnetic structure below 160 K. In addition, both Huang *et al.*[9] and Radaelli *et al.*[2] observed a rapid change of the lattice parameters between 130 and 225 K in La$_{0.5}$Ca$_{0.5}$MnO$_3$. This was associated with the development of a Jahn-Teller distortion of the Mn-O octahedra, as well as partial orbital ordering.

The physical properties in CO manganese perovskites arise from the strong competition among a ferromagnetic double exchange interaction, an antiferromagnetic superexchange interaction, and the spin-phonon coupling. These interactions are determined by intrinsic parameters such as doping level, average cationic size, cationic disorder, and oxygen stoichiometry. Magnetic relaxation studies are a useful tool to study the dynamics of these competing interactions.

Fisher *et al.*[14] studied the time relaxation of resistivity and magnetization in colossal magnetoresistance compounds such as La$_{1-x}$A$_x$MnO$_3$ (with $A = $ Sr, Ca and $x = 0.3$, 0.35).

They found that the relaxation rate was temperature dependent and slowed down when the temperature was far from T_C. The spin-spin relaxation time (τ_{ss}) as a function of temperature in $La_{0.5}Ca_{0.5}MnO_3$ was measured by Dho *et al.*[10] using ^{55}Mn and ^{139}La nuclear magnetic resonance. They found a general decrease in τ_{ss} with increasing temperatures. However, τ_{ss} showed hysteretic behavior in zero field cooling and field cooling measurements, approximately in the same temperature interval where the change in lattice parameters was most pronounced.

The relaxation of electrical resistivity in $Pr_{0.67}Ca_{0.33}MnO_3$, after a large change in applied magnetic field, which induces a transition from a ferromagnetic metallic state to a charge ordered insulator phase or conversely, was studied by Anane *et al.*[11] They found an abrupt change in the resistivity, which indicated a metal to insulator transition. Smolyaninova *et al.*[12] reported the time dependence of the resistivity and magnetization in a $La_{0.5}Ca_{0.5}MnO_3$ sample at low temperatures. They fitted all the curves to a stretched exponential time dependence and explained their results using a hierarchical distribution of relaxation times.

However, to our knowledge, studies of magnetic relaxation curves $[M(t)]$ in charge ordered compounds are not reported for a wide temperature interval. Here, we present a general magnetic characterization of two polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$. In addition, in both cases M(t) curves were systematically measured for several temperatures. We found an unusual temperature dependence of the relaxation curves in the region approximately between the Néel (T_N) and Curie temperatures. These results could be interpreted as a consequence of the strong competition between ferromagnetic and antiferromagnetic interactions. A short version of these results were reported elsewhere[13] by some of us.

II. EXPERIMENTAL PROCEDURES

Polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ were prepared from stoichiometric amounts of La_2O_3, $CaCo_3$, and Mn_3O_4 by standard solid-state reaction method. Purity of these starting materials was more than 99.99%. As most of the rare earth oxides absorb moisture from the air, La_2O_3 has been preheated at $1000\,^{\circ}C$ for 12 h. All the powders were mixed and grinded for a long time in order to produce a homogeneous mixture. First, the mixture was heated at $1100\,^{\circ}C$ for 12 h and after that it was grinded and heated several times at 1100, 1200, and $1300\,^{\circ}C$. After the single-phase material was reached, as checked by x-ray scattering, a pellet was pressed and sintered at $1400\,^{\circ}C$ for 24 h.

Polycrystalline samples of $Nd_{0.5}Sr_{0.5}MnO_3$ were prepared by the sol-gel method.[15] Stoichiometric parts of Nd_2O_3 and $MnCO_3$ were dissolved in HNO_3 and mixed to an aqueous citric acid solution, to which $SrCO_3$ was added. The mixed metallic citrate solution presented the ratio citric acid/metal of 1/3 (in molar basis). Ethylene glycol was added to this solution, to obtain a citric acid/ethylene glycol ratio 60/40 (mass ratio). The resulting blue solution was neutralized to pH~7 with ethylenediamine. This solution was turned into a gel, and subsequently decomposed to a solid by heating at

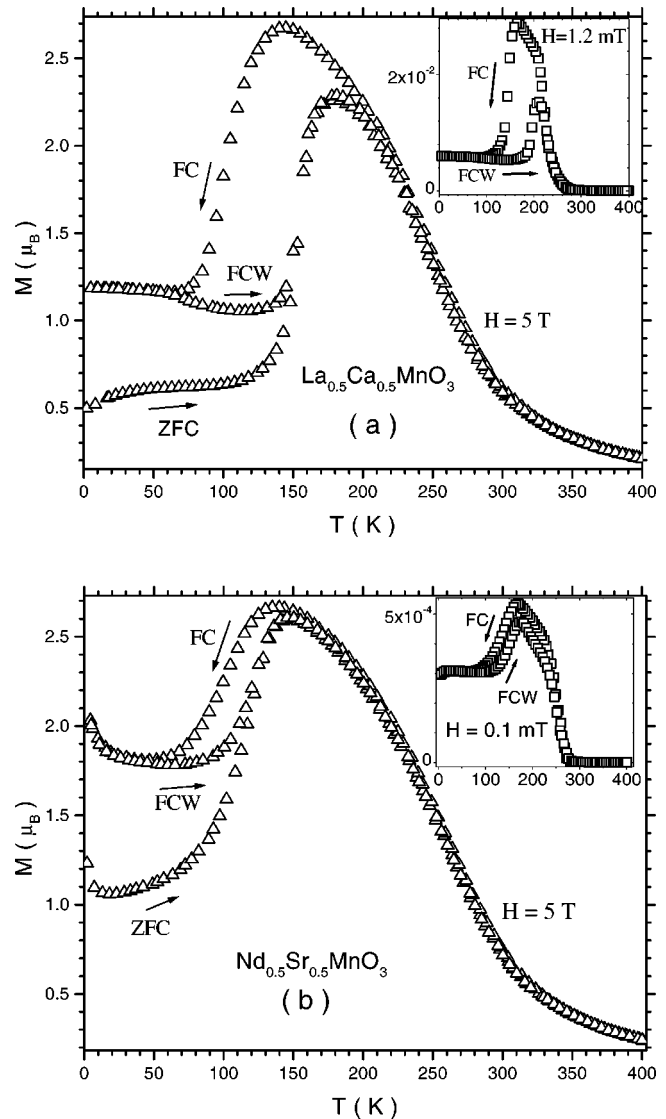FIG. 1. Magnetization vs temperature, measured with an applied magnetic field of 5 T for (a) $La_{0.5}Ca_{0.5}MnO_3$ and (b) $Nd_{0.5}Sr_{0.5}MnO_3$ samples. The insets show the same type of measurements with (a) $H=1.2$ mT and (b) $H=0.1$ mT. Magnetization is given in Bohr magnetons per manganese ion. Arrows show the direction of temperature sweep. The large hysteresis makes these compounds particularly interesting to study their relaxation behavior.

$400\,^{\circ}C$. The resulting powder was heat-treated in vacuum at $900\,^{\circ}C$ for 24 h, with several intermediary grindings, in order to prevent formation of impurity phases. This powder was pressed into pellets and sintered in air at $1050\,^{\circ}C$ for 12 h. X-ray diffraction measurements did not show any peak associated to either impurities or starting materials, indicating the high quality of the samples.

The magnetization measurements reported here were done with a Quantum Design MPMS-5S SQUID magnetometer (UFSCar-São Carlos). Besides, in order to rule out possible machine-dependent effects we repeated part of the relaxation measurements using different techniques and equipments (a Quantum Design PPMS magnetometer operating with the

extraction method and another Quantum Design MPMS SQUID magnetometer) in two other laboratories (ETH-Zurich and Unicamp-Campinas, respectively). The results were consistent and reproducible in all cases.

The relaxation measuring procedure was the following: first, the sample was heated to 400 K in zero magnetic field; second, the remanent magnetic field in the solenoid of the SQUID magnetometer was set to zero; third, the sample was cooled down in zero magnetic field until the stable working temperature was reached; fourth, an applied magnetic field (H) was increased from 0 to 5 T at a rate of 0.83 T/minute and maintained for a waiting time $t_w = 50$ s; fifth, H was decreased to the end field (H_{end}) of zero at the same rate; finally, when H was zero (we defined this time as $t=0$) the $M(t)$ curve was recorded for approximately 3 h. In the future we will call this procedure as ''the standard.'' However, in the case of Fig. 5, measurements were done after step four. We have measured also the profile of the remanent magnetic field trapped in the superconducting solenoid after increasing H to 5 T and its subsequent removal. Within the experimental region the trapped magnetic field was smaller than 1.1 mT.

III. RESULTS AND DISCUSSION

A. Magnetization versus temperature measurements

Figures 1(a) and 1(b) show the temperature dependence of the magnetization measured with $H=5$ T for La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ samples, respectively. The insets show the same type of measurements with (a) $H=1.2$ mT and (b) $H=0.1$ mT. Data in the main frame are shown for zero field cooling (ZFC), field cooling (FC), and field cooling warming (FCW) conditions (see the arrows), while the ones in the insets are shown for FC and FCW conditions. The large hysteresis at a magnetic field as high as 5 T is a clear evidence of the intrinsic frustration in the equilibrium configuration of the spin system, which could

not be only associated to grain boundary defects. This feature makes these compounds particularly interesting to study their relaxation behavior.

We fitted the small field magnetization data for both samples, using temperatures above 300 K, to a Curie-Weiss law $M/H \sim \mu_{eff}^2/(T-T_\Theta)$, where M/H was the dc susceptibility, μ_{eff} was the effective paramagnetic moment and T_Θ was the Curie-Weiss temperature. The μ_{eff} and T_Θ values were $5.5\mu_B$ and $5.7\mu_B$, and 252 and 254 K for La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ samples, respectively. The positive values of the Curie-Weiss temperatures were an indication of the preferential ferromagnetic interaction between spins in this temperature range.

Effective paramagnetic moments could be compared to a simplified theoretical model.[19] Taking the orbital momentum to be quenched in both Mn^{3+} and Mn^{4+}, the theoretical effective paramagnetic moment (μ_{eff}^{th}) in each case reduces to the spin contribution $g\sqrt{S(S+1)}\mu_B$, where S is the spin of the ion (3/2 for Mn^{4+} and 2 for Mn^{3+}) and g is the gyromagnetic factor (approximately 2 in both cases). That gives the theoretical values of $\mu_{eff}^{th}(Mn^{3+})=4.90\mu_B$ and $\mu_{eff}^{th}(Mn^{4+})=3.87\mu_B$. Then, assuming 0.5 Mn^{3+} and 0.5 Mn^{4+} ions per formula unit, it is found

$$\mu_{eff}^{th}(La_{0.5}Ca_{0.5}MnO_3)$$
$$= \sqrt{[0.5[\mu_{eff}^{th}(Mn^{3+})]^2 + 0.5[\mu_{eff}^{th}(Mn^{4+})]^2]}$$
$$= 4.41\mu_B.$$

In the case of the Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ sample the magnetic moment of the Nd^{3+} ions should also be included. The electronic levels of Nd^{3+} ions at high temperatures are well described by $g=8/11$ and the total angular momentum $J=9/2$, which leads to $\mu_{eff}^{th}(Nd^{3+})=g\sqrt{J(J+1)}\mu_B=3.62\mu_B$. Therefore, considering a rigid coupling of the moments of Nd^{3+} ions with the moments of Mn^{3+} and Mn^{4+} ions, we should have

$$\mu_{eff}^{th}(Nd_{0.5}Sr_{0.5}MnO_3) = \sqrt{[0.5[\mu_{eff}^{th}(Mn^{3+})]^2 + 0.5[\mu_{eff}^{th}(Mn^{4+})]^2 + 0.5[\mu_{eff}^{th}(Nd^{3+})]^2]} = 5.10\mu_B.$$

The experimental values of the effective paramagnetic moments are higher than the theoretical ones in both samples. This could be a consequence of cluster formation of Mn^{4+} and Mn^{3+} ions at high temperatures. Similar high values of the paramagnetic effective moments in samples of La$_{1-x}$MnO$_3$ were reported by de Brion et al.[16]

The derivative of the curves in the insets of Fig. 1 showed minima values around 230 and 250 K for La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ samples, respectively. This criterion has been usually employed as a definition of T_C. The maximum magnetization for the FCW curves, using the smaller applied field, was found at 210 K for La$_{0.5}$Ca$_{0.5}$MnO$_3$ and at 176 K for Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. These peaks indicated that antiferromagnetic correlations already existed at these temperatures.

However, the Néel temperature, found from neutron diffraction studies, was $T_N = 160$ K in both cases.[2,9,17,18]

The peak positions in the magnetization curves for both samples are strongly dependent on the cooling conditions and the applied magnetic field. This emphasizes the small energy differences among distinct equilibrium spin configurations. Magnetization maxima occur at lower temperatures in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ than in La$_{0.5}$Ca$_{0.5}$MnO$_3$. Besides, differences between FC and FCW curves, and correspondingly, the hysteresis loop area, are smaller for Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. These results correlate with the stronger ferromagnetic interactions in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, which is evidenced by its higher T_C and a higher value of the magnetization at 2 K.

Ferromagnetic and antiferromagnetic phases coexist at low temperatures for both compounds. The spins at low tem-

peratures align in a CE-antiferromagnetic lattice,[17,18] which is also charge and orbital ordered. As we saw before, in contrast to the La^{3+} ions, the Nd^{3+} ions have an intrinsic total angular momentum ($J=9/2$). Figure 1(b) shows an increase in the magnetization at temperatures approximately below 50 K, indicating a possible short-range magnetic order of the Nd^{3+} ions. A similar increase in the magnetization at low temperatures has been reported for $Nd_{0.5}Ca_{0.5}MnO_3$.[19] Besides, a low temperature specific heat study in $Nd_{0.67}Sr_{0.33}MnO_3$,[20,21] found a Schottky-like peak correlated to the ordering of the Nd^{3+} ions. Our recent specific heat measurements in $Nd_{0.5}Sr_{0.5}MnO_3$ have also confirmed these results.

B. Magnetization versus field measurements

Figure 2 shows representative magnetization versus field curves (M vs H) for the $La_{0.5}Ca_{0.5}MnO_3$ [Figs. 2(a) and 2(b)] and $Nd_{0.5}Sr_{0.5}MnO_3$ [Figs. 2(c) and 2(d)] samples, respectively. The applied magnetic field was cycled in all cases from 0 to 5 T and then back to 0 T again. At 350 K both samples are in the paramagnetic state and the M vs H curves are linear. The first indication of nonlinear behavior is seen at small fields around 270 K. Below 230 K a rapid increase in magnetization at small field values is well defined. This last behavior will be present for all lower temperatures, identifying an easily oriented ferromagnetic component. It is already noted in the curves for 230 K that at small fields the slope has a larger value for the $Nd_{0.5}Sr_{0.5}MnO_3$ sample. This is in agreement with the stronger ferromagnetic interactions in the $Nd_{0.5}Sr_{0.5}MnO_3$ sample.

The start of the hysteretic behavior in the M vs H curves, at about 190 K for $La_{0.5}Ca_{0.5}MnO_3$ and 160 K for $Nd_{0.5}Sr_{0.5}MnO_3$, correlates with the separation of FC and FCW condition curves in Figs. 1(a) and 1(b). The area of the hysteresis loop first increases for lower temperatures and then decreases again. The hysteresis loop area is largest at 160 and 140 K for $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ samples, respectively. Besides, the remanent magnetization, after increasing the applied magnetic field to 5 T and decreasing it again to zero, is maximum at 180 K for $La_{0.5}Ca_{0.5}MnO_3$, corresponding to only 2.7% of the magnetization value at 5 T. However, for the $Nd_{0.5}Sr_{0.5}MnO_3$ case, the remanent magnetization is maximum at 160 K, corresponding to 13% of its value at 5 T.

At about 170 K and fields around 1 T, a linear magnetization field dependence with a small slope, characteristic of the gradual destruction of an antiferromagnetic phase, starts to be observed in both samples. This small-slope linear behavior disappears around 3 T, because a ferromagnetic phase is induced by the high magnetic field. The complete suppression of the antiferromagnetic phase is no longer seen in our data below about 150 K, because magnetic fields higher than 5 T would be required. Gang Xiao *et al.*[4] reported M vs H curves for $La_{0.5}Ca_{0.5}MnO_3$ with fields up to 20 T. They found that the field for a complete destruction of the antiferromagnetic phase increased from approximately 3.5 T at 164 K to 11 T at 4.2 K and that the transition was of first order. Similar results have been reported for $Nd_{0.5}Sr_{0.5}MnO_3$.[22]
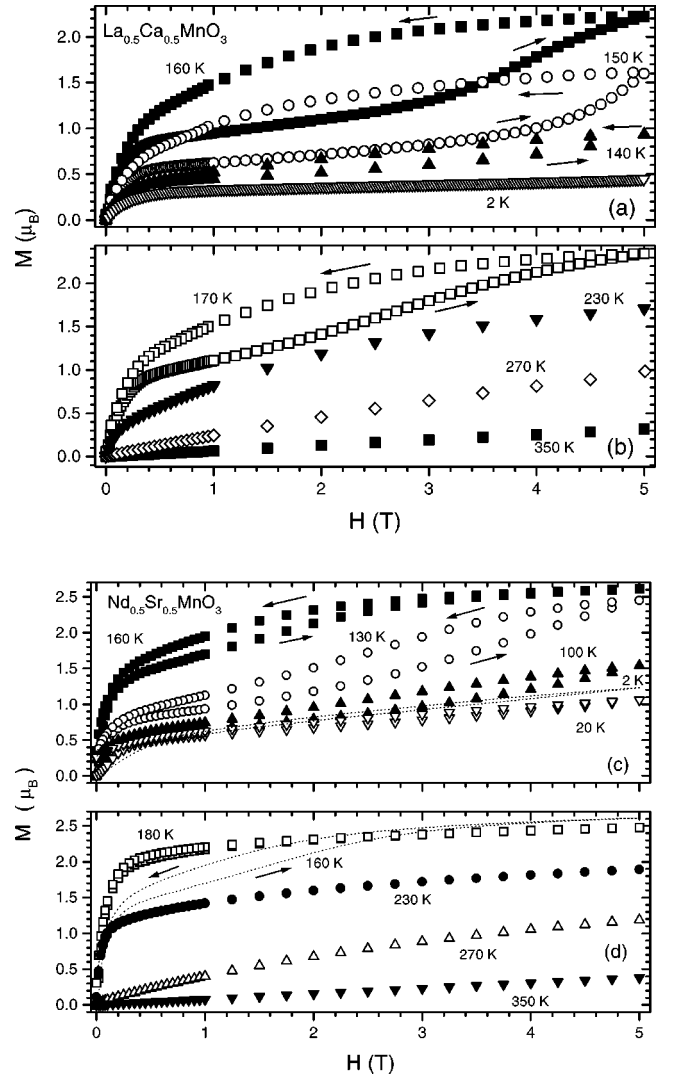

FIG. 2. Magnetization vs applied magnetic field for representative temperatures in $La_{0.5}Ca_{0.5}MnO_3$ (a) and (b) and $Nd_{0.5}Sr_{0.5}MnO_3$ (c) and (d) samples. Magnetization is given in Bohr magnetons per manganese ion. The applied magnetic field was cycled in all cases from 0 to 5 T and then back to 0 T again. Ferromagnetic and antiferromagnetic interactions coexist in both compounds, leading to charge and orbital ordered phases.

In a simplified thermodynamical model, the ferromagnetic (FM) and antiferromagnetic (AFM) charge ordered states correspond to two local minima in the free energy, with large and small magnetization values, respectively. A potential barrier U separates these local minima. An external magnetic field tends to stabilize the FM state due to the gain ($-MH$) in the free energy rather than the AFM charge ordered state ($M \sim 0$). Hence, the potential barrier is expected to vary with the field. The sum of the Zeeman and thermal energies should cover the energy difference between the AFM and FM states in order to favor the AFM-FM transition, explaining the smaller transition magnetic fields for higher temperatures.

Figure 2(c) further shows that for high fields the magnetization at 2 K (dotted lines) is higher than at 20 K (open down triangles). This result correlates with the increase in

magnetization at low temperatures, observed for $Nd_{0.5}Sr_{0.5}MnO_3$ [Fig. 1(b)] but not for $La_{0.5}Ca_{0.5}MnO_3$ [Fig. 1(a)]. As we have mentioned before, Nd^{3+} ions, unlike La^{3+} ions, have an intrinsic magnetic moment. Thus, this increase in magnetization could be related to short-range magnetic ordering of the Nd^{3+} ions at low temperatures.[20] Above 1.5 K no long-range order of Nd^{3+} ions was detected in neutron diffraction studies of $Nd_{0.5}Ca_{0.5}MnO_3$.[19]

C. Relaxation measurements

Figure 3 shows magnetic relaxation measurements, after applying and removing a 5 T magnetic field, from (a) 10 to 150 K, (b) 150 to 195 K, and (c) 195 to 245 K in a $La_{0.5}Ca_{0.5}MnO_3$ sample. To facilitate the comparison between curves at different temperatures, the magnetization in each case was normalized to the corresponding value at $t = 0$, and time was plotted in a logarithmic scale. These curves were denoted as $m(t) = M(t)/M(0)$. The mean slope of each curve at long times, or long time logarithmic relaxation rate (LTLRR), decreases systematically with increasing temperatures from 10 to 150 K. It is important to note that slopes in Figs. 3(a) and 3(b) are negative. The fractional change in magnetization, between the first and the last measurement, increases from 1% at 10 K to about 20% at 150 K. This qualitative behavior has been usually explained considering the increase in the thermal energy, which stimulates the random alignment of the spin and, as a consequence, a decrease in the magnetization.

As can be seen in Fig. 3(b), and contrary to the previous interval, the LTLRR between 150 and 195 K increases with temperature. The fractional change in magnetization goes from 20% at 150 K to 0.9% at 195 K. Note from Fig. 2(a), that above 150 K an applied magnetic field of 5 T completely destroys the antiferromagnetic phase. These results correlate with the change in the temperature dependence of the LTLRR at 150 K. Roughly speaking, between 150 and 195 K the system seems to remember its previous 5 T ferromagnetic orientation. After removing the applied magnetic field, it starts to relax at a slower rate, even in the presence of greater thermal excitations. We will see below that, in this temperature range, the increase in thermal energy is compensated by a rapid increase in the pinning energy of the spin system.

The inset in Fig. 3(b) reproduces the relaxation curve before normalization for 195 K and the corresponding error bars. Notice that, in spite of the experimental error, this curve clearly shows that the magnetization first decreases, and after approximately 4 min, increases with time. This behavior is qualitatively different from the curves measured at lower temperatures. We would like to stress here that this unusual increase in the magnetization is stable during a long time interval (about 3 h). The inset in Fig. 3(c) shows the $M(t)$ curve for 200 K, error bars here are about the same size of the symbols. In this case, no decrease in magnetization was measured, but a monotonic increase with time (approximately $62 \times 10^{-5} \mu_B$ per Mn ion in 218 min) was observed. The experiment at 200 K was also repeated with a sample of the same compound having only 9% of the origi-

nal mass. A similar increase of magnetization with time ($88 \times 10^{-5} \mu_B$ per Mn ion in 218 min) was found in this last case.

Figure 3(c) shows $m(t)$ curves, using the standard relaxation procedure, from 195 to 245 K. Notice that in contrast to Fig. 3(b), all curves in Fig. 3(c), except the one at 195 K, show values above 1. In other words, the magnetization increases with time (curves here have positive slopes) above the $M(0)$ value in each case. Furthermore, the fractional change in magnetization is systematically higher with higher temperatures: from 0.9% at 195 K to 80% at 240 K. However, $M(0)$ decreases with higher temperatures, as shown in Fig. 1(a).

We also repeated the standard relaxation procedure at 210 K, but now with an increasing waiting time in each case $t_w = 50$ s, $t_w = 500$ s, and $t_w = 5000$ s. We would like to stress that in the last case t_w was longer than 1 h. The normalized increment in the magnetization was higher the longer the 5 T magnetic field remained applied. Values of $M(0)$ also increased for longer t_w. These measurements confirmed the presence of the unusual relaxation, independently of the value of the waiting time. A plausible explanation could be that the remanent trapped field in the sample after removing the $H = 5$ T, which was higher for longer t_w, was causing a self-alignment of the spins and an increase in magnetization. Therefore, these results could be reflecting intrinsic information about the interactions in the sample.

The curve at 245 K, also shown in Fig. 3(c), presents a smaller fractional change in magnetization with respect to the one at 240 K. This is probably associated with the transition of the system to the paramagnetic phase. Magnetic relaxation measurements were also done between 245 and 350 K. In this temperature interval we did not find a systematic variation of the LTLRR, probably due to the small values of the absolute magnetization. Nonetheless, above 260 K, the $M(t)$ curves always showed the usual decreasing behavior with time.

The change in the temperature dependence of the LTLRR above 195 K could be correlated with the gradual disappearance of the antiferromagnetic fluctuations even at small applied magnetic fields. This is reflected in the gradual suppression of the hysteresis in the M vs H curves [see Fig. 2(b)], and also by the peak in the FCW curve in the inset of Fig. 1(a). However, although antiferromagnetic fluctuations are reduced for higher temperatures, the ferromagnetic interactions also weaken. Therefore, at a given temperature, the competition of these two effects causes the system to return to the usual relaxation behavior.

It is also interesting to note the close overlap between the whole temperature interval where the unusual magnetic relaxation was found (150 to 245 K) and the temperature interval where a rapid change in the lattice parameters (130 to 230 K) were reported.[9,2] This rapid change has been associated to the development of a Jahn-Teller distortion of the Mn-O octahedra, as well as to the partial orbital ordering of Mn ions.[9,2] Therefore, the close overlap between both temperature intervals suggests that the electron-phonon interaction needs to be considered to completely understand this unusual relaxation.
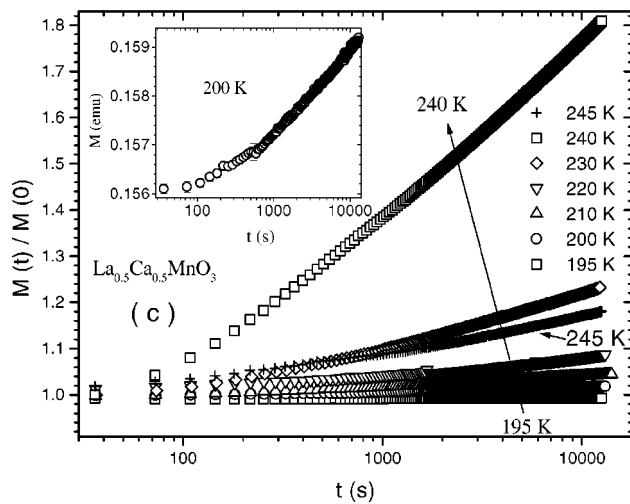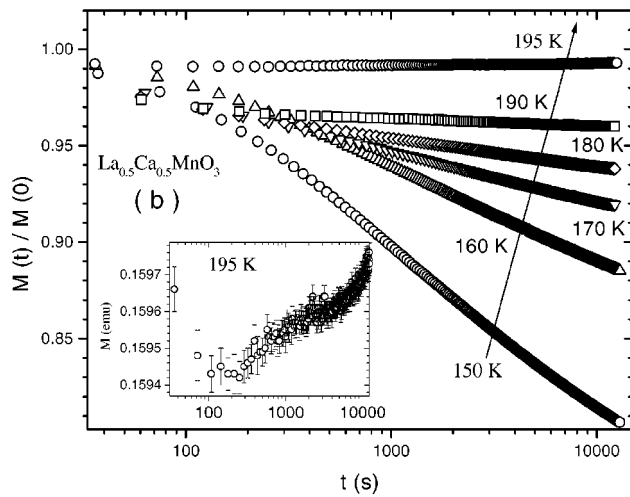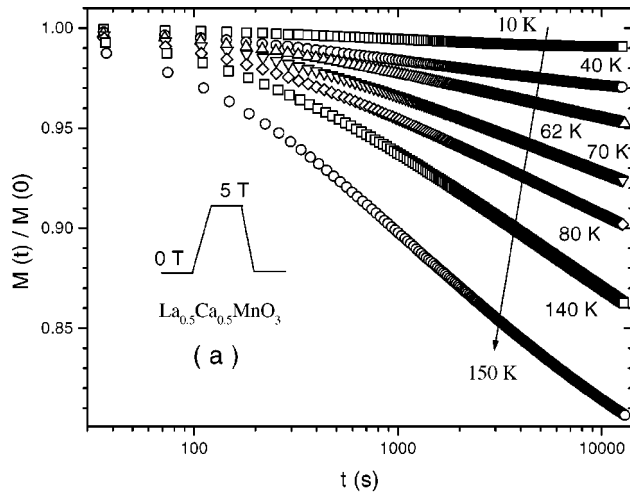
FIG. 3. Normalized magnetic relaxation measurements, after applying and removing a magnetic field of 5 T, in a $La_{0.5}Ca_{0.5}MnO_3$ sample: from (a) 10 to 150 K, (b) 150 to 195 K, and (c) 195 to 245 K. Time is shown in logarithmic scale. The diagram in Fig. 3(a) represents the evolution in time of the applied field. The insets in Figs. 3(b) and 3(c) reproduce details of the curve at 195 and 200 K prior to normalization and with the corresponding error bars. In the last case the error bars have the same dimension of the circles.
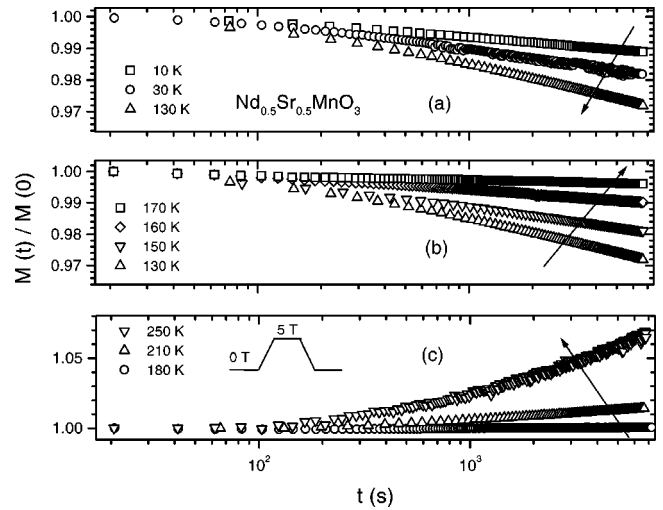

FIG. 4. Normalized magnetic relaxation measurements, after applying and removing a magnetic field of 5 T, for a $Nd_{0.5}Sr_{0.5}MnO_3$ sample. The diagram represents the evolution in time of the applied magnetic field. The curves show the same qualitative behavior found in the $La_{0.5}Ca_{0.5}MnO_3$ compound.

Recently, similarly unusual magnetic relaxation measurements were done by Sirena *et al.*[23] They studied the relaxation of the magnetization in thin films of $La_{0.6}Sr_{0.4}MnO_3$, after applying a 1 T magnetic field during 5 min and then removing it. Their measurements were done during a time window of 8 h. This procedure was repeated for temperatures between 4 and 200 K. They found that, above a temperature labeled as T_{rev}, the magnetization increased with time and T_{rev} decreased with increasing film thickness. However, no clear interpretation was reported for all the results.

Figure 4 shows magnetic relaxation measurements using the standard procedure in the $Nd_{0.5}Sr_{0.5}MnO_3$ sample. The LTLRR was negative at low temperatures and decreased from 10 to 130 K [Fig. 4(a)]. From 130 to 170 K [Fig. 4(b)] the LTLRR was still negative but increased as a function of temperature. The LTLRR became positive, increasing even more, from 180 to 250 K [Fig. 4(c)]. The absolute variation in magnetization, between the first and the last measurement, was 1% at 10 K, 3% at 130 K, and 5% at 250 K. We also performed magnetic relaxation measurements above 250 K, but we did not find a systematic variation of the LTLRR, maybe due to the small values of the absolute magnetization in this temperature range. The temperature where the LTLRR reached the minimum in $Nd_{0.5}Sr_{0.5}MnO_3$ was lower than in $La_{0.5}Ca_{0.5}MnO_3$. This is in agreement with the lower temperature of the maximum FC magnetization for $Nd_{0.5}Sr_{0.5}MnO_3$ (see Fig. 1).

The relaxation curves measured for $Nd_{0.5}Sr_{0.5}MnO_3$ followed the qualitative behavior found for $La_{0.5}Ca_{0.5}MnO_3$. Note also in Fig. 2(c) that, above 130 K and closely related to the change in behavior of the LTLRR, a 5 T applied magnetic field completely destroys the antiferromagnetic phase. In addition, as in the $La_{0.5}Ca_{0.5}MnO_3$ case, there is a rapid change in the lattice parameters for $Nd_{0.5}Sr_{0.5}MnO_3$ between approximately 110 and 250 K. Once more, both temperature intervals (rapid change of lattice parameters and unusual
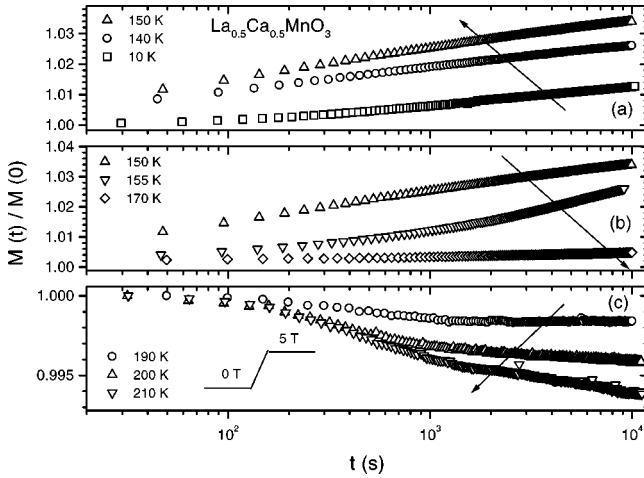
FIG. 5. Normalized magnetic relaxation measurements in the presence of 5 T magnetic field for a $La_{0.5}Ca_{0.5}MnO_3$ sample. The diagram represents the evolution in time of the applied field. The temperature dependence of the relaxation rate values with H_{end} $=5$ T are similar (but with inverted signs) to the ones with H_{end} $=0$.

magnetic relaxation behavior) almost completely overlap. All of these suggest that the temperature dependence of the LTLRR, and the underlying physics, are mainly independent of the particular charge-ordering material.

Moreover, in order to test the effects of a fixed applied magnetic field on the temperature dependence of the LTLRR, we repeated the standard relaxation procedure in the $La_{0.5}Ca_{0.5}MnO_3$ sample, but in this case we did not remove the 5 T field. Figure 5 shows these relaxation curves and a schematic drawing of the time evolution of the applied magnetic field. As before, the magnetization was normalized and time was shown in logarithmic scale. Here, the LTLRR is positive and increases from 10 to 150 K [Fig. 5(a)] and decreases from 150 to 170 K [Fig. 5(b)]. From 190 to 210 K [Fig. 5(c)] the LTLRR is negative and decreases with increasing temperatures.

The absolute variation in magnetization between the first and the last measurement is 1.2% at 10 K, 3.4% at 150 K, and 0.6% at 210 K. These variations are smaller than in the previous cases, due to the high value of the applied magnetic field. The maximum LTLRR is found here at 150 K, the same temperature where we had found the minimum LTLRR for the case with $H_{end}=0$ T in the same sample. As we have already seen, the antiferromagnetic phase was suppressed completely at 150 K with an applied magnetic field of 5 T.

There is a further change at about 190 K, where the magnetization unusually decreases as a function of time. Again, it is very interesting to note that, the temperature where this change in behavior is found is very close to the one corresponding to the change from negative to positive LTLRR in the relaxation procedure with $H_{end}=0T$. Although the change with temperature of the LTLRR in Fig. 5(c) is very systematic, we must be careful in this case because changes smaller than 1% are difficult to separate from the experimental error [see scale in Fig. 5(c)].

The LTLRR temperature dependence observed in this last experiment with a constant applied field ($H_{end}=5$ T) is very similar (but with inverted signs) to the previous case, when the applied field was removed, leaving only a remanent magnetic field of about 1 mT. In our view, these results eliminate the possibility that the residual field trapped in the superconducting magnet of the SQUID or PPMS magnetometers could be the cause for the observed unusual relaxations.

D. Fitting of relaxation curves

Our relaxation measurements at long time scales follow approximately a logarithmic law $M(t)/M(t_n)=1+S\ln(t/t_n)$. Here, S is called magnetic viscosity, and t_n and $M(t_n)$ are the normalization time and the corresponding magnetization at that moment, respectively.[24,25] This logarithmic relaxation has also been found in spin glass systems,[26] superconductor materials,[27] and mixture of small ferromagnetic particles.[28,29]

The logarithmic relaxation has been attributed to the existence of a distribution of energy barriers separating local minima in the free energy, which correspond to different equilibrium states.[24–29] In our polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ we have a spatially inhomogeneous mixture of ferromagnetic and antiferromagnetic domains, which produce frustration in the interactions among individual spins. This frustration was visualized before in the differences among ZFC, FC, and FCW curves in Fig. 1.

We performed the fitting of all the relaxation curves using the logarithmic law mentioned above, where S was the only free parameter. In order to get information over the whole temperature interval we consider $t_n=1000$ s, removing from the fitting any transient behavior at the beginning of each relaxation measurement. Due to the fact that at long times the relaxation curves are linear in a semilogarithmic plot, S could be considered as a normalized value of the LTLRR.

Figure 6 shows the temperature dependence of S in the cases where the external field is removed ($H_{end}=0$ T) for $La_{0.5}Ca_{0.5}MnO_3$ (close squares) and $Nd_{0.5}Sr_{0.5}MnO_3$ (open circles), and when the external field is kept constant (H_{end} $=5$ T) for $La_{0.5}Ca_{0.5}MnO_3$ (open up triangles). The corresponding error bars associated to the fitting procedure are smaller than the symbols used in all cases and the continuous lines are only guides to the eye. This figure displays the main magnetic relaxation results in a single graph. It is interesting to note the change in the temperature dependence of S between 130 and 150 K. Moreover, S changes sign between 180 and 195 K in all cases.

Note also that to facilitate the comparison among different data sets the curve for $Nd_{0.5}Sr_{0.5}MnO_3$ was multiplied by 5 and the curve for $La_{0.5}Ca_{0.5}MnO_3$ with $H_{end}=5$ T was multiplied by 20. The decrease in the absolute value of S in $Nd_{0.5}Sr_{0.5}MnO_3$ in comparison with $La_{0.5}Ca_{0.5}MnO_3$ (H_{end} $=0$ T) was expected due to the higher internal magnetic field experienced by $Nd_{0.5}Sr_{0.5}MnO_3$. As discussed before, this is associated with the stronger ferromagnetic interactions in $Nd_{0.5}Sr_{0.5}MnO_3$. The same effect, now due to the external magnetic field, was verified in the comparison between the absolute values of S in $La_{0.5}Ca_{0.5}MnO_3$, when the measure-
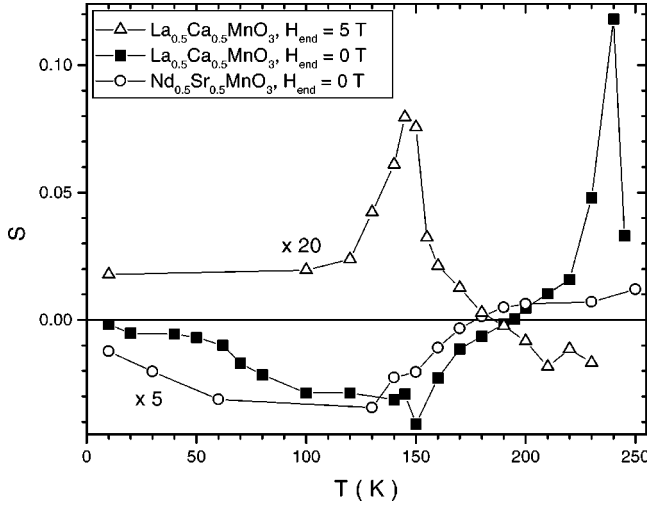
FIG. 6. Results of the fitting of the curves in Figs. 3, 4, and 5 with a logarithmic law at long time scales. S is the magnetic viscosity, which is the only fitting parameter. Measurements were done removing the final external field ($H_{end}=0$ T) for $La_{0.5}Ca_{0.5}MnO_3$ (closed squares) and $Nd_{0.5}Sr_{0.5}MnO_3$ (open circles), and with the final external field constant ($H_{end}=5$ T) for $La_{0.5}Ca_{0.5}MnO_3$ (open up triangles). Lines are only guides to the eye. Note that to facilitate the comparison among different data sets the curve for $Nd_{0.5}Sr_{0.5}MnO_3$ was multiplied by 5 and the curve for $La_{0.5}Ca_{0.5}MnO_3$ with $H_{end}=5$ T was multiplied by 20.

ments were done removing the field ($H_{end}=0$ T) and with the constant field ($H_{end}=5$ T).

Some reports[24,25] have claimed that as a first approximation S could be considered proportional to $(k_B T)/U$. In other words, the magnetic viscosity is expected to have two competing factors: the thermal energy, which favors a faster relaxation, and an effective pinning energy of the spin system, which opposes to it. This could be viewed as an effective potential well where the depth corresponds to U and the excitation energy to $k_B T$. However, it is important to stress here that this simple model cannot explain the observed changes of sign in S.

If we consider the absolute value of S as the physically relevant parameter, ignoring the changes in sign, we then find that below 150 K in $La_{0.5}Ca_{0.5}MnO_3$ (130 K in $Nd_{0.5}Sr_{0.5}MnO_3$) the thermal energy increases at a higher rate than U for increasing temperatures. This is due to the increase in the absolute value of S with temperature. On the other hand, between 150 and 195 K in $La_{0.5}Ca_{0.5}MnO_3$ (130 and 180 K in $Nd_{0.5}Sr_{0.5}MnO_3$) the absolute value of S decreases with rising temperatures. This result suggests that the effective pinning energy grows in this interval at a faster rate in comparison with the thermal energy. Above 195 K in $La_{0.5}Ca_{0.5}MnO_3$ (180 K in $Nd_{0.5}Sr_{0.5}MnO_3$) the absolute value of S increases again with temperature, and the predominant role of the thermal energy is recovered.

We also tried to fit the relaxation curves to a stretched exponential dependence $M(t)=M(\infty)-[M(0)-M(\infty)]\exp[-(t/\tau)^n]$, where $M(0)$ and $M(\infty)$ are the magnetizations at times $t=0$ and $t=\infty$, τ is a characteristic relaxation time and n is a parameter that could change between

0 and 1. The value of $n=1$ corresponds to a single exponential dependence, characteristic of only one energy barrier in the free energy. However, if $0<n<1$, that would mean that a distribution of energy barriers and relaxation times are present in the system. This expression has been used before for spin glass systems[26] and also for $La_{0.5}Ca_{0.5}MnO_3$.[12]

The main problem with this kind of fitting is that manganese perovskite samples have a characteristic relaxation time much bigger than that of the usually available total measuring time. This makes the estimation of $M(\infty)$ very difficult. For example, Smolyaninova *et al.*,[12] after 24 h measuring the magnetic relaxation in a similar sample of $La_{0.5}Ca_{0.5}MnO_3$ at 12 K, did not find saturation in the magnetization. Trying to solve this problem we approximated $[M(t)-M(\infty)]/[M(0)-M(\infty)]$ by $M(t)/M(0)$. Even though the fittings are not very good for all temperatures, we found as an order of magnitude for $La_{0.5}Ca_{0.5}MnO_3$ at 150 K and $H_{end}=0$ T, values of $\tau=10^7$ s (approximately 100 days) and $n=0.3$. Repeating the same procedure at 130 K for $Nd_{0.5}Sr_{0.5}MnO_3$ we obtained values of $\tau=10^8$ s (about 3 yr) and $n=0.3$. These results reinforce the idea of the long relaxation times and the wide distribution of energy barriers involved in these samples.

IV. CONCLUSIONS

We performed a systematic study of magnetic relaxation curves after applying and removing a 5 T magnetic field, in polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$. The LTLRR in $La_{0.5}Ca_{0.5}MnO_3$ ($H_{end}=0$ T) decreased from 10 to 150 K and increased from 150 to 195 K. This change in behavior was found to be correlated with the complete destruction of the antiferromagnetic phase in the presence of a 5 T magnetic field above 150 K. At 195 K, the magnetization decreased initially in a very short time interval and after that it increased slowly as a function of time. Moreover, between 200 and 245 K, an increase of magnetization above $M(0)$, was observed. The change from a negative slope to a positive one at about 200 K was found to be related to the suppression of antiferromagnetic fluctuations with small magnetic fields.

A similar temperature dependence of the LTLRR was found for the $Nd_{0.5}Sr_{0.5}MnO_3$ sample. However, the temperature where the LTLRR reached the minimum in $Nd_{0.5}Sr_{0.5}MnO_3$ was lower than in $La_{0.5}Ca_{0.5}MnO_3$, in agreement with the stronger ferromagnetic interactions in $Nd_{0.5}Sr_{0.5}MnO_3$. This suggested that the general temperature dependence of the LTLRR, and the corresponding physics, were mainly independent of the particular charge-ordering sample considered.

We have also measured the relaxation curves in the $La_{0.5}Ca_{0.5}MnO_3$ sample with a constant magnetic field of 5 T. The LTLRR values in this case showed a temperature dependence similar to the previous ones, but with inverted signs. They increased from 10 to 150 K and decreased from 150 to 210 K. The peak in the temperature dependence of the LTLRR was again around 150 K. These measurements also eliminated doubts about a possible influence of the small magnetic field trapped in the superconductor solenoid of the

SQUID magnetometer after removing the field in the standard procedure.

We successfully performed the fitting of all the relaxation curves using a logarithmic law. The slow relaxation was attributed to the coexistence of ferromagnetic and antiferromagnetic interactions, which produced a distribution of energy barriers. The decrease of the absolute value of S with rising temperatures between 150 and 195 K in $La_{0.5}Ca_{0.5}MnO_3$ (130 and 180 K in $Nd_{0.5}Sr_{0.5}MnO_3$) suggested that, contrary to the other intervals, here the effective pinning energy grew at a faster rate than the thermal energy. In addition, a stretched exponential dependence of the relaxation curves at 150 K for $La_{0.5}Ca_{0.5}MnO_3$, and at 130 K for $Nd_{0.5}Sr_{0.5}MnO_3$, showed the existence of very long relaxation times and a wide distribution of pinning energies.

Although further studies would be required to fully understand the temperature dependence of the relaxation in charge ordering compounds, our preliminary findings indicate a correlation between the instability of two competing magnetic phases and the unusual magnetic relaxation. These intriguing results in the relaxation measurements could be a consequence of the competition between ferromagnetic double exchange and antiferromagnetic superexchange interactions.

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