

Magnetic relaxation in bulk and film manganite compounds

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We have investigated the time dependence of the magnetic and transport properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ films and bulk samples. A significant magnetic aftereffect has been observed in all the samples through magnetization and resistivity measurements. The relaxation effects can be described by the addition of a logarithmic to an exponential contribution. The weight of each contribution is strongly temperature dependent, with a relaxation that is predominantly logarithmic at low temperatures ($T < 30$ K) and exponential at high temperatures ($T > 100$ K). As the film thickness is decreased the magnetic relaxation becomes more important and the magnetic viscosity of the system increases. These results point out the important role of structural defects in the magnetic relaxation of the samples.

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I. INTRODUCTION

Manganese oxides of the form $A_{1-x}B_x\text{MnO}_3$ (A : La, B: Sr, Ba, Ca) have a very rich and complex phase diagram due to the competence between antiferromagnetic and ferromagnetic (FM) interactions.¹ Superexchange interaction between Mn^{3+} makes LaMnO_3 antiferromagnetic. An increase of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ concentration by doping the parent compound with divalent cations B induces ferromagnetism and a metal-insulator transition in the $0.2 < x < 0.5$ range, due to Zenner's double-exchange² coupling between Mn^{3+} and Mn^{4+} ions. A "colossal magnetoresistance" effect is observed close to the Curie point.

Even in the ferromagnetic phase manganite compounds present particular characteristics. Ibarra and Teresa³ show by neutron-diffraction experiments that bulk compounds have rather large short-range ferromagnetic ordered regions at temperatures well above the Curie point (T_C). In thin films, the lattice mismatch between the substrate and the manganite reduces ferromagnetic interaction by modifying the angle and distance in the Mn—O—Mn bonds.⁴ The Curie temperature of the films is strongly depressed in relation to that of the bulk compounds but mesoscopic ferromagnetic regions have been observed at $T_C^{film} < T < T_C^{bulk}$ by magnetic-force microscopy.⁵ A high magnetic polarizability and small hysteresis has also been measured in magnetization loops above T_C^{film} .⁶

Several works discuss the existence of a clustered system in similar compounds.⁷⁻⁹ As spin glasses, clustered and ferromagnetic systems present characteristic magnetic relaxation effects their study may provide insights into the magnetic structure of ferromagnetic manganites. A detailed study of the behavior of the magnetic aftereffect could provide evidence to distinguish between a clustered and a ferromagnetic system. Moreover, relaxation measurements may give information about the main mechanism of magnetization change in these samples. Magnetization changes in a ferromagnetic compound,¹⁰ may occur by domain-wall movement, magnetic moment rotation, or nucleation of reverse magnetization within large-volume elements. When a mag-

netic field applied is changed, magnetic materials which exhibit hysteresis present a characteristic time dependence of the magnetization, due to the multiplicity of available metastable states. At constant external field, internal random thermal perturbations may cause an hysteretic system to explore different metastable states.¹¹ Magnetic relaxation is a rather complex phenomenon and many models based both on phenomenological studies and first principles have been proposed to explain it. In strongly interacting materials a slow magnetic relaxation of the form:¹²

$$M(t) = M_0 e^{-(t/\tau)^\beta}, \quad 0 < \beta < 1 \quad (1)$$

called stretched exponential function is usually found, instead of the conventional Debye exponential function ($\beta = 1$).¹² The Debye function is only found in very simple systems where the main relaxation mechanism can be ascribed to the existence of a single-energy barrier opposed to domain-wall movement and magnetic rotation. In many materials relaxation times are distributed in finite ranges, following particular distribution functions $g(\tau)$.¹³ The time change of the magnetization can be described by

$$M(t) = M_0 \left(1 - \int_0^\infty \frac{g(\tau)}{\tau} e^{-t/\tau} d\tau \right). \quad (2)$$

In the simplest case, a constant distribution function over a time interval $[\tau_1, \tau_2]$, and zero outside this range is assumed. This type of magnetic aftereffect is referred to as Richter type. The integral expression can be calculated for different limits. For $t \ll \tau_1$, the magnetization decreases linearly with time t . For $\tau_1 < t < \tau_2$, the magnetization is described by

$$M(t) \cong M_0 + S \ln(t), \quad (3)$$

where S is the magnetic viscosity of the system, function of τ_1 and τ_2 . Finally, the magnetization change tends to zero for $t \gg \tau_2$ in the form

$$M(t) \cong M_0 - A \frac{1}{t} e^{-t/\tau_2}, \quad (4)$$

where A is a constant that depends on τ_1 and τ_2 .

A more complicated behavior has been found in particular spin glasses, where the magnetic relaxation follows a power-law decay for short times and a logarithmic decay¹⁴ or stretched exponential decay¹⁵ at long times.

Due to the close relation between the magnetic and transport properties of these systems, magnetic relaxation should also be measurable in magnetoresistivity measurements. In fact, Helmolt *et al.*¹⁶ reported a logarithmic relaxation of the resistivity in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films for different magnetohistory conditions and related it to the spin structure of the samples.

In this work a study of the magnetic aftereffect in manganese bulk and thin-film samples is presented and discussed in terms of a simple phenomenological model. The temperature and field dependence of the magnetic relaxation has been investigated through magnetization and resistivity measurements. Finally, the influence of the sample size in relaxation mechanisms is discussed.

II. EXPERIMENTAL SETUP AND SAMPLES

We have measured the magnetic aftereffect in bulk samples and sputtered films of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO). Films of different thicknesses t_h varying from 10 nm to 500 nm were grown on (100) MgO and (100) SrTiO₃ substrates, as described elsewhere.¹⁷ The bulk samples were prepared by nitrate liquid-mix reaction.

Magnetic measurements were carried out in a commercial superconducting quantum interference device (SQUID) magnetometer. Magnetization-vs-time curves were measured at several temperatures ($4.2 \text{ K} < T < 300 \text{ K}$) and magnetic fields up to 5 T. Measurements of dc resistivity were made using a standard four-probe technique under magnetic fields up to 9 T in the same temperature range.

The time-dependence data were always acquired after performing a common sequence: the magnetization of the sample was first saturated with a 1 T field, applied parallel to the sample surface. After waiting for 5 min the field was decreased to the desired value ($t=0$). The superconductor magnets used in both magnetic and transport experiments take around 1 min to lower the field from 1 T to zero.

III. RESULTS AND DISCUSSION

The samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ used in this study are ferromagnetic. The Curie temperature of the bulk samples is 365 K while that of the films lays around 250 K.⁴ A metal-insulator transition is observed at T_p , near T_C for the bulk samples and thick films ($t_h > 100 \text{ nm}$). As the film thickness is decreased below 100 nm a decoupling between T_p and T_C becomes noticeable.⁴ These materials present important temperature-dependent magnetoresistive effects that are maximum below and in close proximity to T_p .

Our first evidence for magnetic relaxation in manganites was obtained from magnetoresistance curves as a time-dependent hysteresis between the magnetoresistance curves for increasing and decreasing fields (Fig. 1). This effect is more important for faster sweep times and has been observed

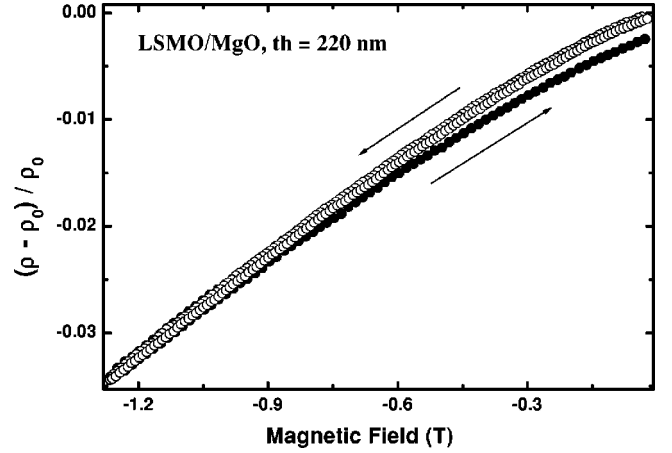


FIG. 1. Magnetoresistance curves of an LSMO/MgO film of $t_h = 220 \text{ nm}$ ($T_C = 250 \text{ K}$), measured at 280 K and at different sweep rates: (●) $R_{SW} = 0.3 \text{ T/min}$ and (○) $R_{SW} = 0.15 \text{ T/min}$.

in films even at room temperature, well above their Curie point of the sample (case shown in Fig. 1). These results show the existence of magnetic relaxation at temperatures where no or negligible magnetic coercivity is observed, and could be an indication of the presence of short-range ordered regions or magnetic polarons above T_C in the films. The existence of such states in similar systems has recently been reported by Soh *et al.*⁵ In their work Soh *et al.* present magnetic-force microscopy images measured above the Curie point in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films where mesoscopic regions of ferromagnetic order are observed.

In order to show the relation between the time effects observed in the transport measurements and the magnetism of the compounds, we have studied and compared the relaxation of the magnetization and the resistivity of the samples. For both cases, the measurements were performed following the same procedure, described in detail in the preceding section. The close relation between magnetic and transport properties is evident from Fig. 2, where the time dependence of the magnetization and resistivity of a LSMO/SrTiO₃ film ($t_h = 50 \text{ nm}$) measured at different temperatures is plotted. The decrease of the magnetization suggests an increase in magnetic disorder. Consequently an increase of resistivity is expected, as can be observed. A similar behavior is found in both magnetization and resistivity measurements.

We find that the magnetic relaxation varies between two different regimes, depending on the temperature of the measurement. At low temperatures ($T < 30 \text{ K}$) the change of magnetization with time in the intermediate time window ($100 \text{ s} < t < 3600 \text{ s}$) is well described by a logarithmic function. For shorter or longer time scales the magnetization change is smaller than that predicted by a logarithmic law, implying that some other contribution to the magnetization evolution must be considered. No saturation was observed in the time scale of our measurements (Fig. 2). As the temperature increases the logarithmic like behavior changes progressively towards an exponential decay character. For $100 \text{ K} < T < 0.8T_C$ the magnetization is described by an exponential law in the whole time scale.

As was commented in the Introduction, a Richter-type

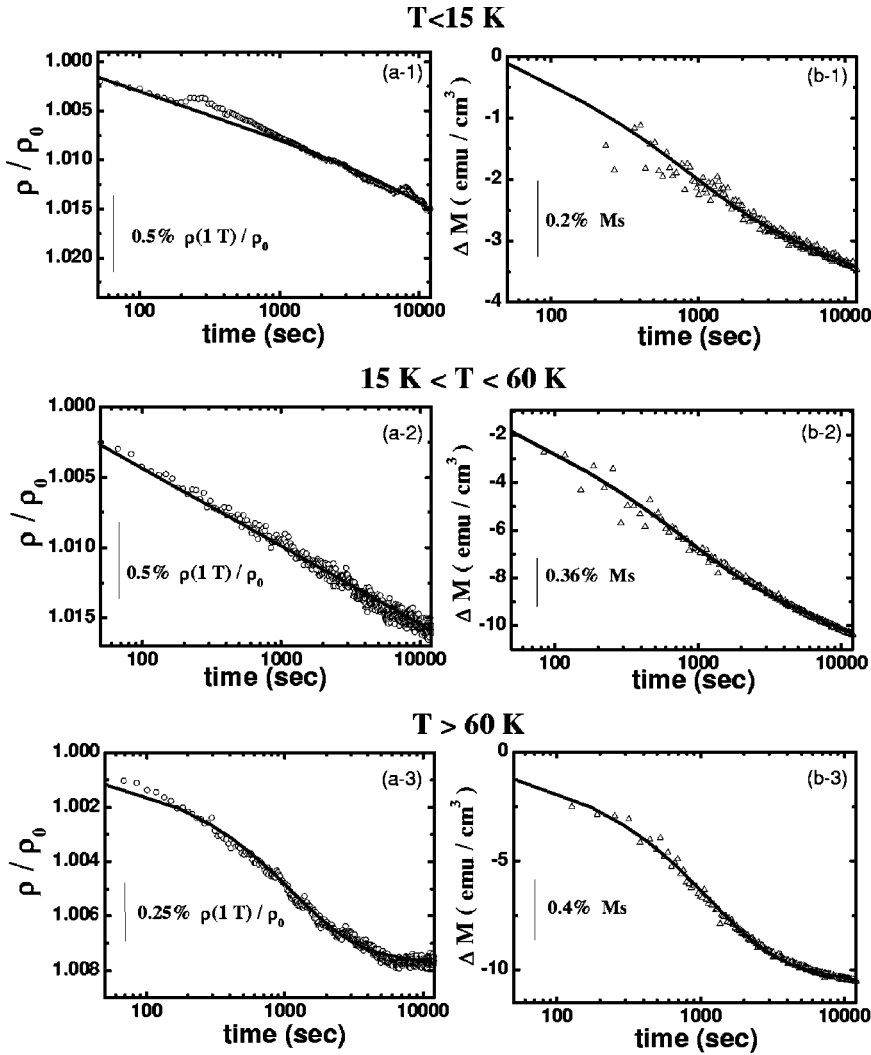


FIG. 2. Time dependence of the (a) resistivity and (b) magnetization of an LSMO/SrTiO₃ ($t_h = 50$ nm) film, measured at different temperatures. Solid lines are the best fits, obtained by the phenomenological model described in the text.

relaxation changes from a logarithmic to an exponential function depending on the time-measuring window with respect to the relaxation times. We have tried to fit our measurements with the Richter relaxation expressions. As expected, the pure logarithmic curves fit well with the model. However, as the temperature increases and the curves follow an exponential decrease the relaxation-time parameter obtained from the fits [expression (4)] does not agree with the condition of long-time limit ($t \gg \tau_2$). Thus, to describe the magnetization and transport results, it is necessary to introduce two relaxation terms. Both results can be described by a single phenomenological model consisting of a simple Debye relaxation with a slower logarithmic one,

$$M(t) = M_0 + a_2 e^{-t/\tau} - a_4 \ln(t), \quad (5)$$

$$\rho(t) = \rho_0 - b_2 e^{-t/\tau} + b_4 \ln(t), \quad (6)$$

where M_0 and ρ_0 are constants. The two terms of the magnetic relaxation may indicate the existence of two relaxation mechanisms that act in series. The first term is a Debye exponential function, $D = a_2(b_2)e^{-t/\tau}$, arisen from a single-barrier activation mechanism. The logarithmic term, $L = a_4(b_4)\ln(t)$, results from a relaxation mechanism that in-

volves a distribution of energy barriers or time-dependent activation energies.²⁴ In order to analyze the weight of both contributions to the total magnetization change in the time window $t: [50 \text{ s}, 10\,000 \text{ s}]$, $\Delta D/(\Delta L + \Delta D)$ and $\Delta L/(\Delta L + \Delta D)$ ratios obtained from the fits have been plotted in Fig. 3. The fit parameters of both magnetization and resistivity curves show the same behavior as a function of temperature. At low temperatures the relaxation is driven mainly by the logarithmic term. At high temperatures, on the contrary, the relative weight of the exponential component increases abruptly to 1 while the logarithmic component tends rapidly to zero. Our phenomenological model fits the magnetic and transport results in the whole time scale and for temperatures below $0.8T_C$. In spite of this satisfactory result, we also analyzed the data in terms of a stretched exponential law. We observe that the curves are also well fitted to this complex law. It is important to outline that at low temperatures the exponent of the stretched exponential β tends to zero, leading to a pseudologarithmic function, while at high temperatures $\beta \rightarrow 1$, emulating a pure Debye function. In general, a stretched exponential law has been observed in the magnetic relaxation of strongly interacting materials and complex systems. The determination of the existence of one or two

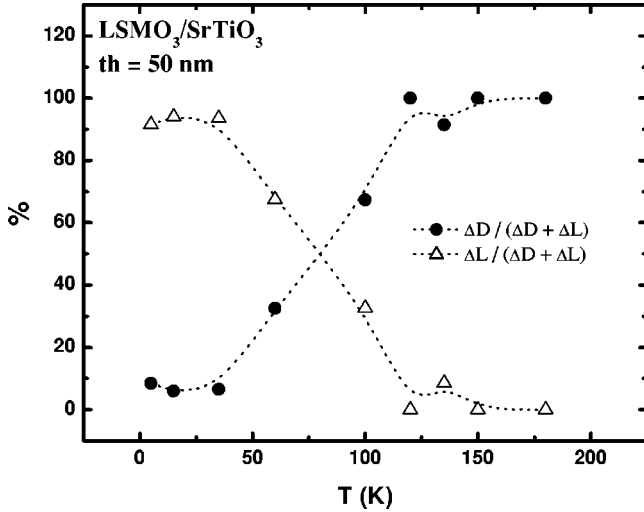


FIG. 3. Temperature dependence of the (Δ) logarithmic $\Delta L/\Delta D + \Delta L$ and (\bullet) exponential $\Delta D/\Delta D + \Delta L$ contributions to magnetic relaxation. These data are obtained from resistivity measurements.

mechanisms of magnetic relaxation cannot be ruled out only by these results. Direct observation of domain relaxation by magneto-optical techniques or studies of the dynamics of magnetic-force microscopy images could contribute to solve the origin of domain movement in these compounds. In a pioneering work in this area, Gupta *et al.*¹⁸ found that the change of magnetization with a magnetic field in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films is due mainly to rotation and domain-wall displacement. The existence of two relaxation mechanisms cannot be disregarded since there are several sources of domain-wall pinning in films, like strains, dislocations, and point defects, etc.,¹⁹ that could lead to these results.

The contribution of the logarithmic and exponential terms can also be analyzed in the magnetic viscosity S of the samples,

$$S_M = \frac{\partial(M/M_0)}{\partial \ln(t)} \quad \text{or} \quad S_\rho = \frac{\partial(\rho/\rho_0)}{\partial \ln(t)}, \quad (7)$$

depending on the time-dependent magnitude studied. It follows from the definition that a logarithmiclike relaxation would lead to a constant magnetic viscosity while an exponential one would result in a time-dependent one. For $t \ll \tau$ and $t \gg \tau$ a Debye law evolves more slowly than a logarithmic one. The derivative of the exponential law with respect to the $\ln(t)$ actually vanishes for short and long times and presents a maximum for $t = \tau$. As a consequence, the relaxation time τ of the exponential contribution can be obtained from the plot of the magnetic viscosity. In Fig. 4 we show the time dependence of the viscosity for a LSMO/MgO ($t_h = 220$ nm) film at different temperatures. A characteristic peak is observed in all the curves. However, it can be also noticed that the logarithmic constant contribution increases with decreasing temperature, indicating progressive increasing of its predominance.

A noticeable narrowing of the viscosity peak together with an increase in intensity is observed as the temperature

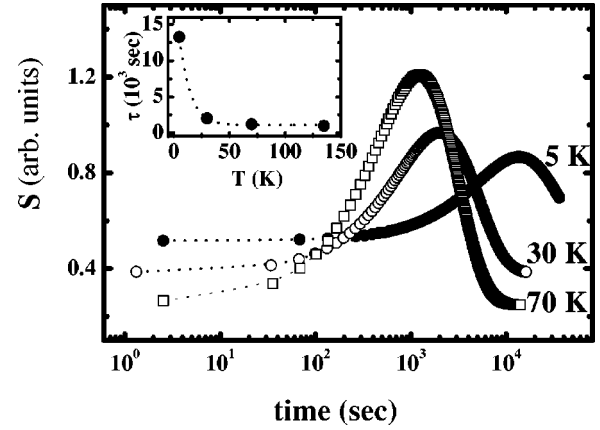


FIG. 4. Time dependence of the magnetic viscosity S calculated from resistivity-vs-time measurements at different temperatures in an LSMO/MgO ($t_h = 220$ nm) film. Inset: Temperature dependence of the Debye relaxation time for the same film.

risers above 100 K. In this temperature range not only thermally activated magnetization changes are measured, but also intrinsic temperature effects, due to the increasing number of magnons and changes of the magnetic anisotropy as the system approaches the Curie point.⁶

The shift of the viscosity maximum to shorter times as the temperature increases indicates a reduction of the relaxation time. τ falls following an exponential decay function.

The field dependence of the viscosity, plotted in Fig. 5 for a LSMO/MgO ($t_h = 39$ nm) film, was measured at 35 K. The viscosity presents a maximum close to the coercive field of the film ($H_C \sim 25$ mT), as can be seen in the figure. Previous theoretical and experimental studies^{11,20} showed that hysteretic magnetic materials exhibit a classical “bell-shaped” viscosity curve as a function of the applied field, peaked near the coercive field. Studies performed on assemblies of ferromagnetic nanoparticles found a very different behavior: the relaxation rate in these systems increases monotonically with the magnetic field.²¹ Moreover, Coey *et al.* showed that in yttrium-iron spin glasses the viscosity increases rapidly at low fields, tending to saturation above 1 T.²²

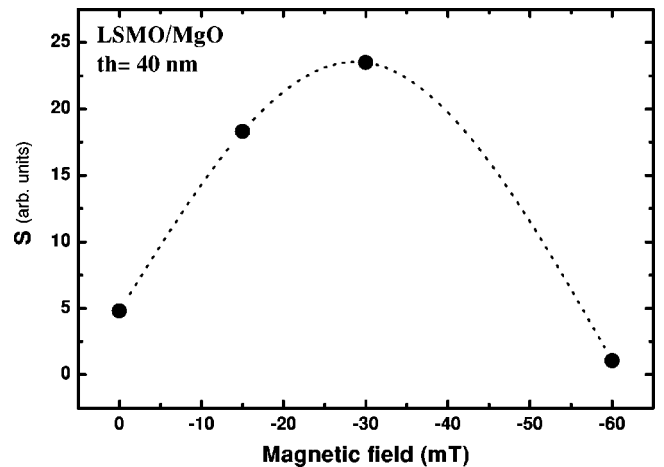


FIG. 5. Magnetic viscosity vs applied field, measured for an LSMO/MgO ($t_h = 40$ nm) thin film.

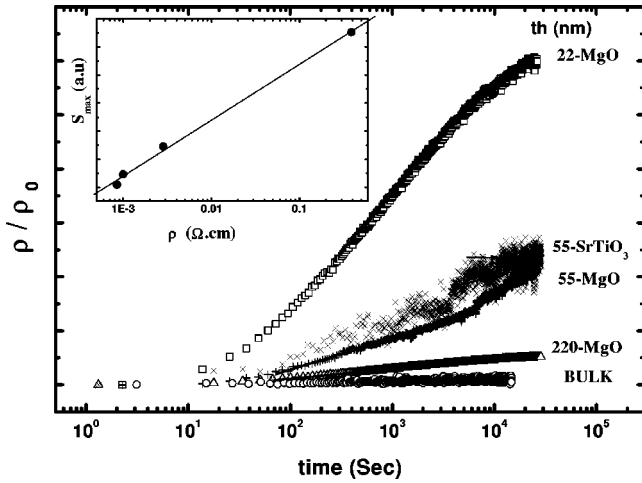


FIG. 6. Resistivity as a function of time for bulk samples and film of different thicknesses. The inset shows the magnetic viscosity as a function of the low-temperature resistivity for the same films.

The increase of structural disorder as the film thickness is decreased affects the resistivity of these samples^{4,17} and enhances their magnetic hardness.²³ Measurements performed on sputtered films show that both the H_C and the resistivity increase as the film thickness decreases. The density of defects in a solid reduces the mean-free path of the current carriers, leading to an increase in resistivity. Gupta *et al.* found a linear relation between the resistivity of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.75}\text{MnO}_3$ films and the inverse of the grain size.¹⁸ In Fig. 6 the resistivity relaxation of films and bulk samples is graphed for comparison. A large resistivity relaxation with high magnetic-viscosity ratios is measured for the thinner films. As the film thickness is increased these effects are strongly reduced reaching the bulk values asymptotically for $t_h > 300$ nm. These results can be attributed to the relatively more disordered structure of the thinner films due to lattice mismatch. Dislocation planes, point defects and strains contribute to the domain-wall pinning, reducing domain-wall movements. In the inset of Fig. 6, the magnetic viscosity of different films has been plotted as a function of its low-temperature resistivity. A systematic increase of the viscosity with increasing resistivity is observed. The magnetic viscosity for ferromagnetic materials has been shown to be²⁴

$$S = \frac{k_b T}{avM_S}, \quad (8)$$

where M_S is the spontaneous magnetization, a is a constant that depends on the thermal activation process involved in

the magnetization change, and v is the activation volume. In the frame of this model, an increase of the viscosity at a fixed temperature and M_S leads to a decrease of the activation volume in the sample. Our results suggest that there is a progressive decrease of the activation volume in relation to the decrease in the scattering mean-free path as the film thickness is reduced.

IV. CONCLUSIONS

We have studied the magnetic relaxation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ samples by performing magnetization and resistivity relaxation measurements. Due to the close relation between transport properties and the magnetization in manganese compounds, resistivity measurements provide an excellent indirect method to characterize the magnetic relaxation of these systems. An important magnetic aftereffect has been observed in all the samples. Even for $T > T_C$ a non-negligible magnetic relaxation observed in the magnetoresistance curves in a large time window. These results may indicate the existence of important short-range ordered regions above the Curie temperature.

Magnetic relaxation presents different regimes as a function of time and temperature. At low temperatures ($T < 30$ K) the magnetic relaxation is described by a logarithmic decrease and is attributed mainly to domain-wall movement and domain rotation. As the temperature rises a Debye contribution must be added to the logarithmic one in order to describe the measured results. Above 100 K the relaxation is purely Debye-like. The high temperature regime is assigned not only to thermal-activated mechanisms of domain movements but also to intrinsic temperature variations of the magnetization. We have found that the field dependence of the magnetic viscosity has a bell shape, characteristic of ferromagnetic systems.

The dependence of the magnetic aftereffect as a function of the film thickness reveals the influence of structural defects and strains on the magnetic relaxation. When the number of structural defects rises (i.e., increase of sample resistivity) the relaxation becomes more important and the magnetic viscosity increases (i.e., decrease of domain activation volume).

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