Novel Dynamical Effects and Persistent Memory in Phase Separated Manganites

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The time dependent response of the magnetic and transport properties of Fe-doped phase separated (PS) manganite $La_{0.5}Ca_{0.5}MnO_3$ is reported. The nontrivial coexistence of ferromagnetic (FM) and non-FM regions induces a slow dynamics which leads to time relaxation and cooling rate dependence within the PS regime. This dynamics influences physical properties drastically. On one hand, metalliclike behavior, assumed to be a fingerprint of percolation, can be also observed before the FM phase percolates as a result of dynamical contributions. On the other hand, two novel effects for the manganites are reported, namely, the rejuvenation of the resistivity after aging and a persistent memory of low magnetic fields (< 1 T), imprinted in the amount of the FM phase.

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Phase separation (PS), namely, the simultaneous presence of submicrometer ferromagnetic (FM) and charge ordered (CO) regions, is emerging as the most important issue in the physics of the manganese-oxide-based compounds [1]. The PS scenario appears as particularly favorable for the existence of out-of-equilibrium features. The competition between the coexisting phases opens the possibility for the appearance of locally metastable states, giving rise to interesting time dependent effects, as cooling rate dependence [2], relaxation [3–5], giant $1/f$ noise [6], two-level fluctuations [7], nonequilibrium fluctuations [8], noise [9], and relaxor ferroelectriclike behavior [10]. The similarity between PS manganites and glassy systems coming from the frustration of the FM and the CO states at the phase boundary was also suggested [11].

Most of the relaxation experiments were performed after the induction of metastable states by, for instance, application of magnetic fields H after zero field cooling [9–11], removal of H after field cooling [5], x-ray illumination [12], electron beam irradiation [8], etc. Such an external perturbation can also be an abrupt change of the temperature, as observed in the prototypical PS compounds $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y = 0.35$) and $La_{0.5}Ca_{0.5}MnO_3$ [2]. The extremely slow relaxation observed in all the mentioned experiments opens an interesting question not previously addressed about the path followed towards equilibrium in the PS state of manganites.

In this Letter, we present a detailed study of time dependent effects in the PS compound $La_{0.5}Ca_{0.5}Mn_{0.95}Fe_{0.05}O_3$ (LCMFO). The parent compound $La_{0.5}Ca_{0.5}MnO_3$ exhibits PS with the temperature of charge ordering T_{co} lower than that of the ferromagnetic order T_C [13]. From a microscopic point of view, the inclusion of Fe in the Mn site of $La_{0.5}Ca_{0.5}MnO_3$ yields the same overwhelming effect on the CO state as Cr doping does on other half doped manganites as $Nd_{0.5}Ca_{0.5}MnO_3$ [10] and $Pr_{0.5}Ca_{0.5}MnO_3$ [14], a feature ascribed to the presence of a random field quenched by the impurities [15]. But, unlike what happens with Cr doping, Fe atoms also disrupt the double exchange interaction, due to its filled e_g orbitals. Moreover, Fe-O-Mn superexchange interactions are likely to be antiferromagnetic [16]. All these facts are reflected in the decrease of T_C as a function of Fe doping [17].

We use transport and magnetization measurements to study the dynamics of the coexisting phases, which is observed close below $T_C \approx 90$ K. We find cooling rate dependence and slow relaxation effects in the temperature range between T_C and 50 K, indicating the enlargement of the FM phase as the PS state evolves with time. Within this scenario, our main results are two novel effects. One is the rejuvenation in the resistivity curve when cooling is resumed after aging, which resembles the behavior of glassy systems [18,19] and disorder ferromagnets [20]. The other one is the effect produced by the application of a low $H < 1$ T while aging, which, instead of inducing metastable states, can drive the system towards its zero field equilibrium point. As this process is irreversible, the effects of H on the resistivity remain even after it is removed, and the system keeps a memory of its magnetic history, acting as a magnetic field recorder.

Polycrystalline samples of LCMFO were synthesized by the sol-gel technique; their average grain size was around 0.5 microns. dc resistivity was measured using the four probe technique, both in a home assembled equipment and in a Quantum Design one. Magnetization was measured using a commercial SQUID magnetometer. Figure 1 displays magnetization M and resistivity ρ as a function of temperature on cooling. $M(T)$ increases continuously between 100 and 50 K, reaching a low temperature plateau which reveals a mostly FM state. M vs H loops at 5 K show a saturation magnetization of $\approx 3\mu_B/\mathrm{Mn}$ at 5 T. The resistivity curve shows a pronounced maximum at $T_p \approx 80$ K. Both T_p and the resistivity below $T_D \approx 85$ K were found to be very sensitive to the cooling rate v_c (inset, Fig. 1). The dependence of the peak resistivity with v_c confirms that this cooling rate effect is not an experimental artifact.

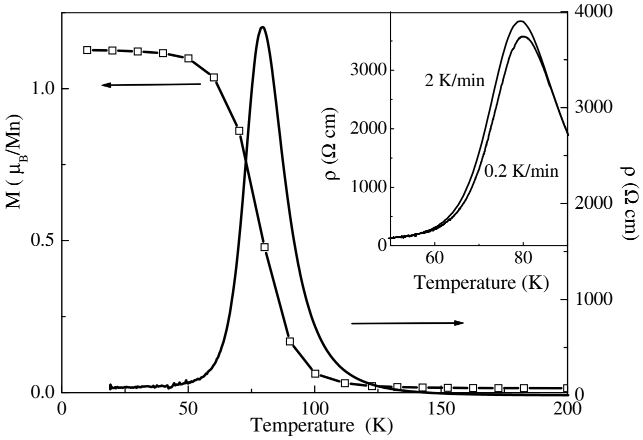

FIG. 1. Temperature dependence of M ($H = 0.1$ T) and ρ ($H = 0$) on cooling for LCMFO. Inset: $\rho(T)$ when cooling at $v_c = 2$ and 0.2 K/min.

We studied the time relaxation of ρ at several $T < T_D$ using $v_c = 0.2$ K/min as the cooling rate to approach and depart from the values at which T was stabilized for 1 h (Fig. 2). The relaxations are characterized by the decrease of ρ following a logarithmic time dependence and are as high as 18% in 1 h at 73.8 K. A related behavior (inset of Fig. 2) was observed in the relaxation of M. Both relaxations are consistent with the isothermal growth of FM regions embedded in a non-FM host.

A noteworthy fact is that, when the cooling process is resumed with $v_c = 0.2$ K/min after relaxation, ρ merges smoothly with the curve obtained without T stabilization steps at that v_c. This effect is similar to that found in the dissipation of some disordered ferromagnets and spin glasses [18–20] and has been named rejuvenation. Another striking feature is that the slope of the $\rho(T)$ curve in this range is highly dependent on the previous history of the sample. For instance, while $\partial\rho/\partial T > 0$ is found when cooling continuously, suggesting metallic behavior, a typical insulator response is obtained if, after 1 h aging, cooling is resumed (Fig. 2).

In order to get a better description of this behavior, we have studied the time dependence of the resistivity slope $\partial\rho/\partial T$ by performing small thermal cycles ($\Delta T \approx 0.6$ K) around fixed T values while the system is relaxing (Fig. 3). We observed that, after a sudden initial change of $\partial\rho/\partial T$, from positive for the continuously cooling curve to negative after 1 h relaxation, the slope increases smoothly and slowly (see Fig. 3, inset) as the system evolves. The increase of the resistivity slope is consistent with the enlargement of the FM phase as a function of time; their negative values indicate that the FM phase does not percolate close below T_p. The positive slope obtained in the continuously cooling process is then to be ascribed to dynamical contributions arising from the evolution with temperature of the relative fraction of the coexisting phases, which, in turn, is influenced by the out-of-equilibrium features displayed by the system below T_D.

As the approach to equilibrium becomes slower as time goes by, it is not possible to reach it within laboratory times, so at this point we cannot give conclusive statements about the nature of the equilibrium state (homogeneous FM or PS). However, as the system evolves by increasing the FM phase, an external H may assist in the path towards equilibrium. Following this idea, we have studied the effect of low H applied for a short time while the system is relaxing after zero field cooling the sample to a T close below T_D.

Figure 4(a) displays ρ as a function of elapsed time upon the application of several H values at $T = 72$ K,

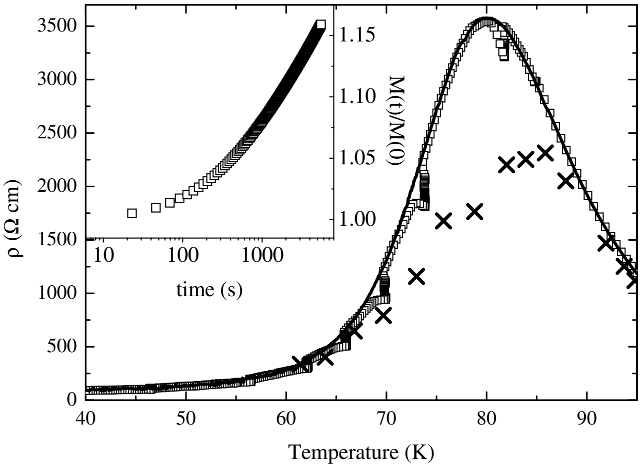

FIG. 2. Temperature dependence of ρ on cooling at 0.2 K/min continuously (solid line) and with intermediate stops of 1 h (open symbols). The crosses indicate the ρ values corresponding to the equilibrium state. Inset: time dependence of M after zero field cooling to 80 K and application of $H = 0.1$ T.

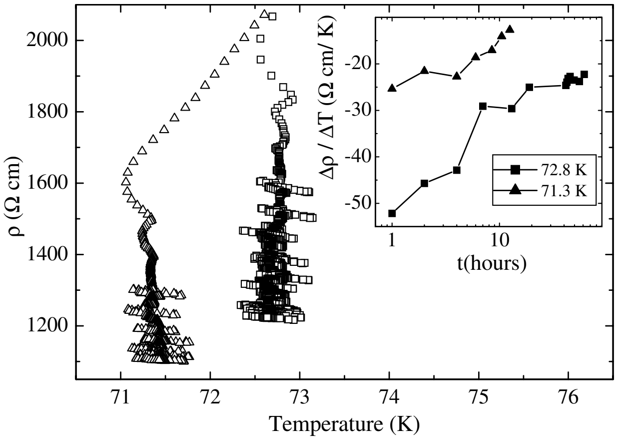

FIG. 3. Resistivity relaxation data obtained at 71.3 and 72.8 K; while the system was aging, small thermal cycles ($\Delta T \approx 0.6$ K) were performed at 0.2 K/min, to evaluate $\partial\rho/\partial T$. After these sweeps, cooling was resumed at 0.2 K/min confirming that the data rejoins the dynamic curve. Inset: time dependence of $\partial\rho/\partial T$ at 71.3 and 72.8 K.

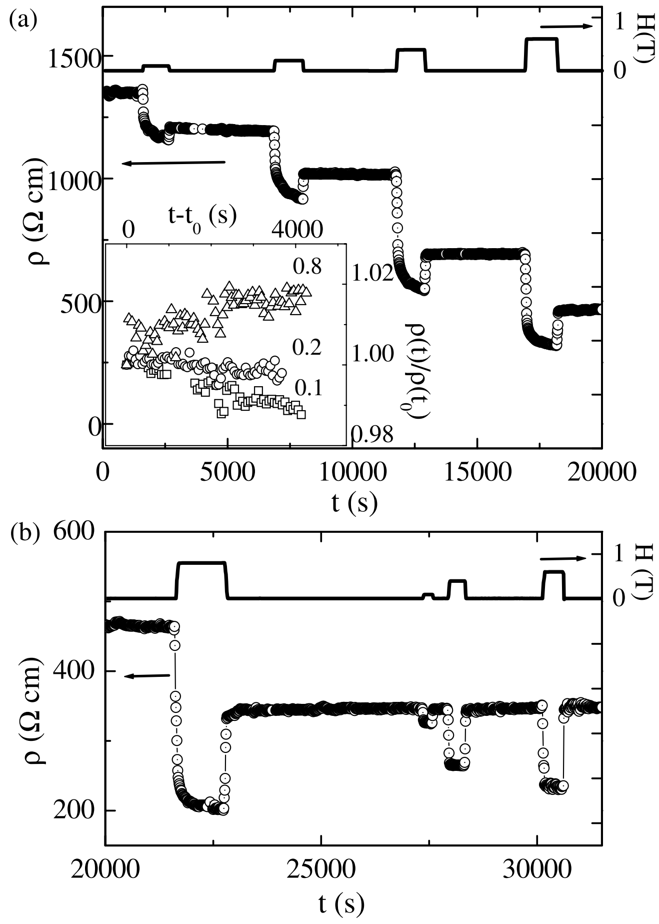

FIG. 4. (a) Resistivity (open circles) at $T = 72$ K as a function of time upon application of $H = 0.1$, 0.2, 0.4, and 0.6 T (solid line). Inset: time dependence of ρ (72 K) in $H = 0$ normalized to the ρ value after the field H was turned off; the labels are the H fields. (b) Resistivity at $T = 72$ K as a function of time upon application of $H = 0.1$, 0.4, and 0.6 T after $H = 0.8$ T was applied and removed.

showing jumps when the field was applied and removed. The sudden decrease of ρ when the field is turned on can be ascribed to two independent mechanisms, one originated in the alignment of spins and domains and the other due to the enlargement of the FM phase driven by H [21]. It is worth noting the hysteretic behavior of ρ after application and removal of H, indicating that the system is able to keep a memory of the magnetic history imprinted in its zero field resistivity.

The relaxation of the persistent resistivity value observed after H was removed indicates that, depending on the strength of the field, the FM phase may still be growing against the non-FM one [Fig. 4(a), inset]. Upon increasing H, we found a T-dependent threshold H_{th} value above which the ulterior relaxation of ρ reverses its sign: after $H > H_{\mathrm{th}}$ is applied and removed ρ slowly increases (instead of decreasing) indicating that the system is evolving by diminishing the amount of the FM phase [Fig. 4(a), inset]. This implies that the application of $H > H_{\mathrm{th}}$ produces an increase of the amount of the FM phase which overcomes the equilibrium volume, leading to the subsequent decrease of the FM fraction when H is turned off. This fact signs unambiguously that the equilibrium state is of PS nature, characterized by a FM fraction $f_0(T)$. The application of H_{th} while aging has thus an effect which is equivalent to a long relaxation process. The equilibrium points depicted in Fig. 2, obtained after application and removal of the appropriate H_{th}, provide a demonstration of the magnitude of the dynamical effects.

In what follows, we discuss the overall results. At T_C an inhomogeneous FM state appears, consisting in the coexistence of isolated FM clusters within a non-FM host. At $T_D = 85$ K, the onset temperature for the irreversibilities, the FM regions start to grow against the host material with the equilibrium size of the clusters increasing as T is lowered. The process followed by the clusters to reach their equilibrium size can be thought of as a stepwise movement of the phase boundaries through energy barriers. A qualitative understanding of the behavior of the system close below T_D can be obtained by describing the temperature and rate dependent resistivity $\rho(T, v_c)$ through a simple series circuit, i.e.,

$$\rho(T, v_c) = n(T, v_c)\rho_F(T) + [1 - n(T, v_c)]\rho_{nF}(T), \quad (1)$$

where $\rho_F(T)$ and $\rho_{nF}(T)$ are the resistivities of the FM and non-FM constitutive media, respectively, and $n(T, v_c)$ is a measure of the relative fraction $f(T, v_c)$ of the FM phase. As the system is rather close to the percolation limit, $n(T, v_c)$ can be a cumbersome functional of $f(T, v_c) - f_c$ (where f_c is the percolation threshold), but is always a monotonous increasing function of $f(T, v_c)$. That coefficient can be obtained, for instance, from conduction models of binary alloys [22] or, more sophistically, through a random-resistor network with a T-dependent FM fraction [23]. Within that frame, the slope of the resistivity curve has two components. On one hand, a contribution is given by $n(T, v_c)\frac{\partial \rho_F}{\partial T} + [1 - n(T, v_c)]\frac{\partial \rho_{nF}}{\partial T}$, corresponding to the response of a binary mixture with fixed constitutive fractions, which is typically less than zero in the nonpercolative regime. On the other hand, a "dynamical" term defined as $\frac{\partial n(T, v_c)}{\partial T}(\rho_F - \rho_{nF})$ is related to the change of the size of the FM clusters as T is varied. This term gives a positive contribution to $\partial\rho/\partial T$ in the whole range in which $f(T, v_c)$ increases as T is lowered. As the system is cooling down at a rate v_c, the appearance below T_D of energy barriers at the cluster surface prevent their free growth, and the FM fraction $f(T, v_c)$ no longer follows its equilibrium value $f_0(T)$, larger differences corresponding to higher v_c values. This fact accounts [Eq. (1)] for the overall increase of ρ as v_c is increased (Fig. 1, inset). Close below T_D, the kinetics of the phase boundary motion governs the growth of the FM phase, producing a retarded process. As a consequence, $f(T, v_c)$ increases slower than $f_0(T)$, yielding a low dynamical contribution, i.e., larger (negative) slopes are achieved with higher v_c. As the difference between $f_0(T)$ and $f(T, v_c)$ becomes larger, the rate at which the FM clusters grow increases, and the dynamical contribution approaches the static one. Both terms are of the same magnitude at T_p, and below, the dynamical contribution is even larger than the static one. A positive slope resembling "metalliclike" behavior is then obtained below T_p, although the FM clusters do not percolate.

The history-dependent $\partial\rho/\partial T$ obtained after a relaxation process (Figs. 2 and 3) is consistent with this scenario. By relaxing at a given temperature, $f(T, v_c)$ slowly approaches its equilibrium value $f_0(T)$ and the growth dynamics becomes partially frozen. When cooling is resumed, a small dynamical contribution is obtained, compared with that of the nonstop process, because of the "clamping" of the interface. The main contribution to $\partial\rho/\partial T$ after relaxation comes then from the static part, giving rise to the "insulatorlike" response. On further cooling, the frozen-in state is released, the system falls again into the dynamical regime mainly determined by v_c, and the resistivity curves (with and without aging) merge into a single one.

This dynamical process produces aging and rejuvenation effects in $\rho(T)$ which bear similarities with those found in glassy systems [18–20]. Slow relaxations following stretched exponential or logarithmic dependences were accounted for with models based on a hierarchical constrained dynamics [24], in which the system evolves through a hierarchy of energy barriers, constrained to fulfill certain requisites before a process at time t can proceed. In our case, the existence of a hierarchy of energy barriers is revealed by the response of the system to H while relaxing at a fixed T, shown in Fig. 4(a). When H is applied, all the barriers of height $<H$ are overcome, yielding the sudden growth of the FM phase. As H is increased, higher barriers are crossed, giving rise to further enlargement effects. In this context, once all the energy barriers of height up to some applied H_{MAX} are overcome, the subsequent application of a $H < H_{\mathrm{MAX}}$ should have no immediate effect on the relative fractions of the coexisting phases. This picture is confirmed by the results shown in Fig. 4(b). As can be seen, once $H_{\mathrm{MAX}} = 0.8$ T has determined the relative phase fractions, ulterior application of $H < 0.8$ T produces only domain alignment, without inducing additional changes on the amount of the coexisting phases. Then, after the system was driven to a "close-to-equilibrium state" by some H_{MAX}, the process cannot be reversed and the system keeps a memory of the largest H applied in its magnetic history.

The above described scenario seems to be characteristic of the low T_C PS systems. We have obtained very similar data in other samples of LCMFO with slightly different Fe doping and in $\mathrm{La}_{5/8-y}\mathrm{Pr}_y\mathrm{Ca}_{3/8}\mathrm{MnO}_3$ ($y = 0.30$) [25], a PS compound with rather different hole doping but similar PS characteristics.

Summarizing, we have presented robust evidence of the importance of the coexisting phase dynamics in the behavior of the PS manganites. When dynamical effects are present, the amount and spatial distribution of the FM phase (percolative or not) cannot be directly inferred from metallic or insulator behavior. The rejuvenation found in the resistivity curve after aging and the persistent memory after the application of a low H are novel features in the physics of manganites. The possibility to record an external magnetic field as a sizable and persistent change of the resistivity is a distinctive fact of the memory effect. Memory effects in manganites have been previously reported [4,10–12], related to the field induction of metastable states. In our case, instead, the low field carries the system closer to its zero field equilibrium state. Since both the "virgin" state and the "H-enlarged" state are, in general, out of equilibrium, the memory could be erased after a very long time, but the effect is protected by the very slow dynamics displayed by the system.

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