PHYSICAL REVIEW B, VOLUME 65, 140401(R)

Nonvolatile magnetoresistive memory in phase separated $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$

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(Received 28 December 2001; published 27 March 2002)

We have measured magnetic and transport response on the polycrystalline $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y=0.30$, average grain size 2 microns) compound. In the temperature range where ferromagnetic metallic and insulating regions coexist, we observed a persistent memory of low magnetic fields (<1 T) that is determined by the actual amount of the ferromagnetic phase. The possibility to manipulate this fraction with relatively small external perturbations is related to the phase-separated nature of these manganese-oxide-based compounds. The colossal magnetoresistance figures obtained (about 80%) are determined by the fraction enlargement mechanism. Self-shielding of the memory to external fields is found under certain described circumstances. We show that this nonvolatile memory has multilevel capability associated with different applied low magnetic-field values.

DOI: 10.1103/PhysRevB.65.140401 PACS number(s): 75.30.Vn, 75.50.Cc, 75.30.Kz, 75.60.Nt

The unusually large change of resistivity following application of magnetic field, the so-called colossal magnetoresistance (MR) effect observed in manganese-oxide-based compounds, is again being the focus of intense research due to the capability of small external forces to tailor the macroscopic material's response. This unique possibility is related to the simultaneous presence of submicrometer ferromagnetic metallic (FM) regions and charge ordered (CO) and/or paramagnetic insulating (PI) ones in some manganites, the phase-separation (PS) phenomena.[1]

The PS scenario fully develops in the $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ [LPCM(y)] family of compounds, whose end members exhibit homogeneous FM ($y=0$) and CO ($y=1$) states.[2] Intense research activities in these compounds were developed by Babushkina and co-workers[3–5] and by Cheong and co-workers.[6–12] In short, these works show the tendency of LPCM(y) to form inhomogeneous structures, which seems to be a generic property of strongly correlated systems.[2,13]

There are conclusive evidences, both theoretical[14,15] and experimental,[16,17] showing that the high values of MR achieved by PS manganites are due to the possibility of unbalancing the amount of the coexisting phases by the application of low magnetic fields. In $La_{0.5}Ca_{0.5}MnO_3$, a prototypical PS compound with its charge ordering temperature T_{co} lower than that of FM ordering T_C, the huge values of the low-field, low-temperature MR are related to the capability of the field to inhibit the formation of otherwise CO regions, leading to an effective increase of the FM fraction.[16] Remarkably, it was also shown that this process is only achieved when field cooling (FC) the sample.[16] Application of low H once the relative fractions of the coexisting phases were established has the only effect of domain alignment. At low temperature, this kind of MR affects mainly the intergrain tunneling in polycrystalline samples, with maximum values of the low-field MR around 30%.[18,19] The application of moderate magnetic fields in the FC mode plays also an unbalancing role in Cr-doped $Nd_{0.5}Sr_{0.5}MnO_3$:[20] the low-temperature zero-field resistivity of this compound displays a strong dependence on the cooling field. The reduction in the resistivity persists even after this annealing field is removed, meaning that the magnetic field remains imprinted in the sample's resistivity.

The possibility of producing technological applications with PS manganites, both for magnetic reading heads and magnetoresistive data storage, has been one of the aims in the investigation of these kind of systems. However, the mentioned features related to the way in which colossal values of MR can be achieved or the magnetic fields can be imprinted, seem to impose drastic restrictions to its actual implementation.

In this work, we show that low magnetic fields can be effectively written under isothermal conditions in the PS manganite $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$. This effect is achieved due to the confluence of two factors. On one hand, the fact that within a delimited temperature range the equilibrium state of the system is a true PS one with definite equilibrium fractions of the coexisting phases. On the other hand, the fact that in this temperature range the system displays out of equilibrium features governed by a slow dynamics, allowing different long-term metastable states to be tuned by a small external stimulus. We claim that the identification and understanding of these ingredients produces a breakthrough for technological uses of PS manganites.

Polycrystalline samples of LPCM(0.3) were synthesized by the sol-gel technique. Thermal treatments were performed at 1400 °C. Average grain size determined through scanning electron micrographs was around 2 microns. Resistivity ρ (standard four-probe technique) and magnetization M (extraction Quantum Design magnetometer) were measured as a function of temperature T in the presence of an external low magnetic field (LMF) $H<1$ T.

Figure 1 displays magnetization, resistivity, and magnetoresistance as a function of temperature for a LPCM(0.3) sample. Around 220 K the CO state develops, as evidenced both by the increase in ρ and the peak in M. Some degrees

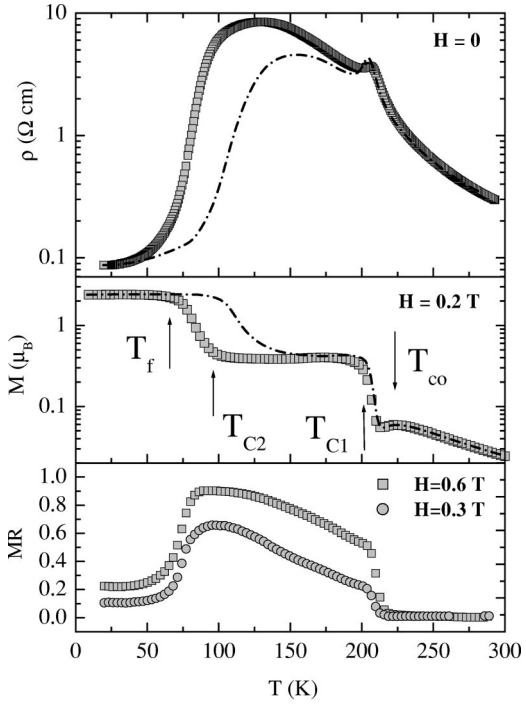

FIG. 1. Temperature dependence of (a) $\rho(H=0)$, (b) M ($H=0.2$ T), and (c) MR$=[\rho(0)-\rho(H)]/\rho(0)$ on cooling (filled symbols) and warming (dashed line) for polycrystalline LPCM(0.3); H values for the MR data are shown in the graph.

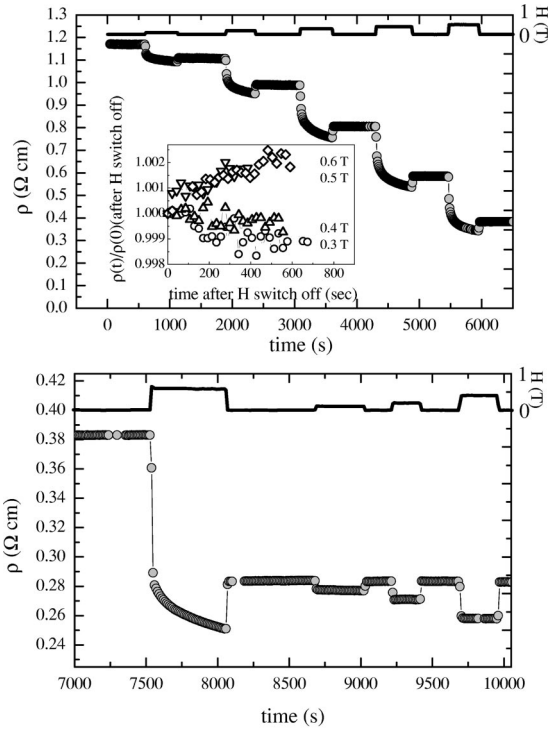

FIG. 2. (a) ρ(95.5 K) as a function of time upon application of $H=0.1$, 0.2, 0.3, 0.4, and 0.5 T. Inset: time dependence of ρ(95.5 K) in $H=0$ normalized to the ρ value after the field H was turned off; the labels are the H fields; (b) ρ(95.5 K) as a function of time upon application of $H=0.1$, 0.2, and 0.4 after $H_{MAX}=0.6$ T has been applied and turned off.

below, at $T_{C1}\approx 210$ K, FM clusters nucleate within the CO matrix, producing a peak in $\rho(T)$ and a steep increase in $M(T)$. The FM volume fraction of this state, which extends down to $T_{C2}\approx 100$ K, is nearly constant (about 14%) i.e., below the percolation threshold (17%).[8] In this temperature range, the state of the system is characterized by the coexistence of frozen isolated FM clusters within CO regions; these clusters start to grow at T_{C2}, and an insulator to metal transition develops when the fraction of the FM phase reaches the percolation threshold. Below the freezing temperature $T_f\approx 75$ K the $M(T)$ data exhibits a plateau, revealing that no further evolution in the fraction of the coexisting phases is produced on further cooling. The FM volume fraction in this low T region is about 90%. These results are in good agreement with previously reported data on the LPCM(0.3) compound.[6,8]

The MR$=[\rho(0)-\rho(H)]/\rho(0)$ obtained on cooling (FC procedure) is depicted in Fig. 1(c) for different LMF values. The high ($>60\%$) MR values obtained within the PS regime occurring between T_{C1} and T_{C2} can be understood as the result of the enlargement of the FM phase induced by the LMF.[16]

Time relaxation of both ρ and M were observed between T_{C1} and T_f, indicating that, in this T range, the data shown in Fig. 1 does not correspond to the equilibrium state. This fact is in close agreement with previously reported cooling rate dependences.[7] The slope of the relaxations (positive for M measurements, negative for the ρ ones) signals that the system reaches the temperature T with a FM fraction lower than that corresponding to the equilibrium state. In Fig. 2, we have shown the effect of LMF applied after zero-field cooling the sample to a temperature close below T_{C2}, while the system is relaxing towards equilibrium. Figure 2(a) displays ρ at $T=95.5$ K as a function of elapsed time upon the application of magnetic fields of 0.1, 0.2, 0.3, 0.4, and 0.5 T with intermediate switching off. Sudden decreases are observed in ρ when the field is applied, followed by slow relaxations. These jumps are related to both the alignment of spins and domains with the field and to the enlargement of the FM phase driven by H. Remarkably, when the field is turned off the resistivity steeply increases, but without recovering its previous $\rho_{H=0}$ (i.e., ρ when $H=0$) value. As it is suggested by the staircase structure displayed in Fig. 2(a), the combination of the mentioned MR effects determines a response that is persistent after the magnetic field is removed.

An interesting fact is that the system still relaxes after the field is switched off [this is not apparent from Fig. 2(a) due to the time scale used]. The inset of Fig. 2(a) compares the normalized $\rho_{H=0}$ values extracted from Fig. 2 as a function of the elapsed time after the LMF was turned off. Also remarkably, there exists a threshold value H_{th} above which the relaxation of $\rho(t)$ reverses its sign, i.e., $\rho(t)$ slowly increases (instead of decreasing) upon increasing the value of the LMF applied. This result suggests that the amount of the FM phase decreases after $H>H_{th}$ is applied, as if the system was driven to an overenlarged metastable state. This fact signs unambiguously that the equilibrium state of the system be-

tween T_{C2} and T_f is of PS nature, characterized by an equilibrium fraction of the FM phase.

To further elucidate the contribution of each MR mechanism (alignment and enlargement) to the overall persistent MR effect, we studied the response of $\rho_{H=0}$ (determined by the previous application of some H_{MAX}) when further applying $H < H_{MAX}$. Figure 2(b) shows the effect of application and removal of 0.1, 0.2, and 0.4 T after $H_{MAX}=0.6$ T have been applied and removed at $T=95.5$ K. As seen, when H is turned on, an immediate response producing a decrease of ρ is observed, which vanishes when H is switched off. The staircase structure of Fig. 2(a) is now replaced by deeps at the intervals when the field is turned on, their depth being determined by the LMF strength, with a characteristic specific MR/H value of 22%/T.

By simple inspection of the above presented results the persistent effect on the resistivity can be unambiguously assigned to the FM enlargement process. The nontrivial relaxation of the system towards its equilibrium point by increasing the FM volume fraction indicates the existence of a distribution of energy barriers through which the FM phase grows against the non-FM one.[21] As soon as a field H_{MAX} is applied, the system is forced to increase its FM fraction overcoming the barriers of height less than μH_{MAX} (μ a characteristic parameter of the system relating the field and energy scales). Once the system is driven to a ''close to equilibrium'' state, the effect cannot be reversed, and the system keeps the memory of its magnetic history in the FM phase fraction. Within this framework, no additional FM enlargement is produced by the ulterior application of $H<H_{MAX}$, and the only effect achieved is due to the alignment mechanism. When $H=0$ this alignment MR vanishes, and the response associated with the same previously existing FM volume fraction (determined by H_{MAX}) is restored, i.e., the previous $\rho_{H=0}$ is obtained [Fig. 2(b)]. Thus, the electrical transport response $\rho_{H=0}$ is not altered by processes involving external H as long as $H<H_{MAX}$; the system keeps the memory of H_{MAX} encoded in its resistivity in a state that is shielded against external $H<H_{MAX}$.

The above described scenario seems to be characteristic of the so-called ''low T_C'' manganites exhibiting PS. We obtained very similar data to that shown in Fig. 2 on $La_{0.5}Ca_{0.5}Mn_{1-y}Fe_yO_3$ for $0.2<y<0.6$, another PS family of compounds with rather different hole doping level.[22] The key ingredients leading to the magnetoresistive memory are the existence of a true PS thermodynamic state joined to the possibility of tuning long-term metastable states by small external stimuli. As a distinctive fact, the strength of the persistent MR effect is directly related to the magnitude of the LMF applied, envisaging applications as a sort of ''analogical memory device.'' This multilevel memory associated with different applied magnetic fields below 1 T has similarities to that achieved using electric fields in thin oxide films with pervskitelike structure.[23] In our case, the system keeps the memory of its magnetic history in the FM phase fraction; it can be recovered by transport measurements, with a MR/H performance of $\approx 80\%$/T, opening a path for the design of nonvolatile magnetoresistive memories.

This project was partially financed by CONICET, Fundación Antorchas, Fundación Balseiro, and Fundación Vitae.

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