Non-volatile magnetoresistive memory in phase separated La$_{0.325}$Pr$_{0.300}$Ca$_{0.375}$MnO$_3$.

P. Levy, F. Parisi, M. Quintero, L. Granja, J. Curiale, J. Sacanell, G. Levy, G. Polla

Departamento de Física, Comisión Nacional de Energía Atómica, Gral Paz 1499 (1650) San Martín, Buenos Aires, Argentina

R.S. Freitas and L. Ghivelder.

Instituto de Física, Universidade Federal do Rio de Janeiro, C.P. 68528, Rio de Janeiro, RJ 21945-970, Brazil

We have measured magnetic and transport response on the polycrystalline La$_{32/8-y}$Pr$_y$Ca$_{3/8}$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) which 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 manganate 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 non-volatile memory has multilevel capability associated with different applied low magnetic field values.

Accepted for publication in Phys. Rev. B: Rapid Comm. + corresponding author levy@cnea.gov.ar

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 materials 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.

The PS scenario fully develops in the La$_{35/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ (LPCM(y)) family of compounds, whose end members exhibit homogeneous FM (y=0) and CO (y=1) states. Intense research activities in these compounds were developed by Moscow groups and by Cheong’s group. 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.

There are conclusive evidences, both theoretical and experimental, 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. Remarkably, it was also shown that this process is only achieved when field cooling (FC) the sample. 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%. 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$_3$: the low temperature zero-field resistivity of this compound display a strong dependence with 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 samples 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 one, 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 1000°C. Average grain size determined through Scanning Electron Micrographs was around 2 microns. Resistivity $\rho$ (standard four probe technique) and magnetization $M$ (extraction QD PPMS magnetometer) were measured as a function of temperature $T$ in the presence of an external low magnetic field ($LH$) $H < 1$ 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 $\rho$ and the peak in $M$. Some degrees 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%). 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 insulating 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. The MR $= (\rho(0) - \rho(H))/\rho(0)$ obtained on cooling (FC procedure) is depicted in Fig. 1c for different $LH$ 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 LH. The increase of the FM fraction occurring on cooling down through $T_{C2}$ is concomitant with the decrease of the MR curve. This fact can be also understood within the fraction enlargement mechanism: low MR values are obtained as soon as the FM fraction departs from the percolation threshold. Below $T_f$ the fraction of the coexisting phases is no longer controlled by the external field: the low temperature MR figures (30 % at $H = 0.6$ T) are consistent with those expected for an homogeneous polycrystalline system. So, no changes in the relative fraction of the coexisting phases are induced by $LH$ below the freezing temperature.

The unusual inhomogeneous state that develops in the $T$ range between $T_{C1}$ and $T_{C2}$ was previously shown to be characterized by interesting time dependent effects, as cooling rate dependence, relaxation in transport and magnetic properties, giant 1/f noise, non equilibrium fluctuations, etc. The microscopic origin of the dynamics observed in manganites with coexisting FM and CO regions (either short or long ranged) could be related to the strain accommodation, which is induced as a result of martensitic nucleation of the child phase within the parent matrix.

Time relaxation of both $\rho$ 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. The slope of the relaxations (positive for $M$ measurements, negative for the $\rho$ 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 shown the effect of $LH$ applied after zero field cooling the sample to a temperature close below $T_{C2}$, while the system is relaxing towards equilibrium. Fig. 2a displays $\rho$ 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 $\rho$ 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. $\rho$ when $H=0$) value. As it is suggested by the staircase structure displayed in Fig. 2a, the combination of the mentioned MR effects determines a response which 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. 2a due to the time scale used). The inset of Fig. 2a compares the normalized $\rho_{H=0}$ values extracted from Fig. 2 as a function of the elapsed time after the $LH$ 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 $LH$ 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 over-enlarged metastable state. This fact also unambiguously that the equilibrium state of the system between $T_{C2}$ and $T_J$ 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 $H < H_{MAX}$. Fig. 2b 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 instantaneous response producing a decrease of $\rho$ is observed, which vanishes when $H$ is switched off. The staircase structure of Fig. 2a is now replaced by deeps at the intervals when the field is turned on, their depth being determined by the $LH$ 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 non-trivial 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. 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 $\mu H_{MAX}$ (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 can not be reversed, and the system keeps memory of its magnetic history in the FM phase fraction. Within this framework, no additional FM enlargement is produced by the latter 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. 2b). 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 memory of $H_{MAX}$ encoded in its resistivity in a state which 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. 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 $LH$ 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 perovskite-like structure. In our case, the system keeps 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 non-volatile magnetoresistive memories.

--- Project partially financed by CONICET, Fundaciones Antorchas, Balseiro and Vitae.

$^b$ Also at ECyT, Universidad Nacional de Gral. San Martin, San Martin, Argentina. * Also at CIC, CONICET, Argentina.
[1] E. Dagotto, T. Hotta and A. Moreo. Phys. Rep. 344(1-3), 1 (2001).
[2] D. Khomskii, Physica B: Condensed Matter, 280(1-4), 325 (2000).
[3] N. A. Babushkina, L. M. Belova, D. I. Khomskii, K. I. Kugel, O. Yu. Gorbenko and A. R. Kaul, Phys. Rev. B 59, 6994 (1999).
[4] A. M. Balagurov, V. Yu. Pomjakushin, D. V. Sheptyakov, V. L. Aksenov, N. A. Babushkina, L. M. Belova, O. Yu. Gorbenko and A. R. Kaul, Eur. Phys. J. B 19, 215 (2001).
[5] I. F. Voloshin, A. V. Kalinov, S. E. Savelev, L. M. Fisher, N. A. Babushkina, L. M. Belova, D. I. Khomskii and K. I. Kugel. JETP Letters 71, 106 (2000).
[6] M. Uehara, S. Mori, C. H. Chen and S-W. Cheong, Nature 399, 560 (1999).
[7] M. Uehara and S-W. Cheong, Europhys. Lett., 52 (6), 674 (2000).
[8] K. H. Kim, M. Uehara, C. Hess, P. A. Sharma and S-W. Cheong, Phys. Rev. Lett. 84, 2961 (2000).
[9] V. Podzorov, M. Uehara, M. E. Gershenson, T. Y. Koo and S-W. Cheong, Phys. Rev. B 61, R3784 (2000).
[10] V. Podzorov, C. H. Chen, M. E. Gershenson and S-W. Cheong, Europhys. Lett., 55(3), 411 (2001).
[11] V. Podzorov, B. G. Kim, V. Kiryukhin, M. E. Gershenson and S-W. Cheong, Phys.Rev.B 64, 140406(R)(2001).
[12] V. Kiryukhin, B. G. Kim, V. Podzorov, S-W. Cheong, T. Y. Koo, J. P. Hill, I. Moon and Y. H. Jeong, Phys. Rev. B 63, 024420 (2001).
[13] N. D. Mathur and P. B. Littlewood, Solid State Comm. 119, 271 (2001).
[14] A. Moreo, M. Mayr, A. Feiguin, S. Yunoki and E. Dagotto, Phys. Rev. Lett. 84, 5568 (2000).
[15] G. Varelogiannis, Phys. Rev. Lett. 85, 4172, (2000).
[16] F. Parisi, P. Levy, L. Ghivelder, G. Polla and D. Vega, Phys. Rev. B 63, 144419 (2001).
[17] R.S. Freitas, L. Ghivelder, P. Levy and F. Parisi, Phys. Rev. B 65, 104403 (2002).
[18] S. Lee, H.Y. Hwang, B. Shraiman, W. Ratcliff and S-W. Cheong, Phys. Rev. Lett. 82, 4508 (1999).
[19] H.Y. Hwang, S-W. Cheong, N.P. Ong and B. Batlogg, Phys. Rev. Lett. 77, 2041 (1996).
[20] T. Kimura, Y. Tomioka, R. Kumai, Y. Okimoto and Y. Yokura, Phys. Rev. Lett. 83, 3940 (1999).
[21] L. Granja, E. Indelicato, P. Levy, G. Polla, D. Vega and F. Parisi, Physica B, in press (2001).
[22] P. Levy, F. Parisi, L. Granja, E. Indelicato and G. Polla, submitted for publication (2001).
[23] A. Beck, J. G. Bednorz, Ch. Gergber, C. Rossel and D. Widmer, Appl. Phys. Lett 77, 139 (2000).