Novel dynamical effects and persistent memory in phase separated manganites

P. Levy, F. Parisi, L. Granja, E. Indelicato and G. Polla.
Departamento de Física, Comisión Nacional de Energía Atómica,Gral Paz 1499 (1650) San Martín,Buenos Aires,Argentina
(29 October 2001)

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 drastically on physical properties. On one hand, metallic like 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 one, two novel effects for the manganites are reported, namely the rejuvenation of the resistivity after ageing, and a persistent memory of low magnetic fields (< 1 T), imprinted in the amount of the FM phase. As a distinctive fact, this memory can be recovered through transport measurements.

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. 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, relaxation, giant 1/f noise, two level fluctuations, noise and relaxor ferroelectric like behavior. The similarity between PS manganites and glassy systems, coming from the frustration of the FM and the CO states at the phases boundary was also suggested.

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, removal of $H$ after field cooling, x-ray illumination, electron beam irradiation, etc. Such external perturbation can also be an abrupt change of the temperature, as observed in the prototypical PS compounds La$_{5/8-y}$Pr$_y$Ca$_{3/8}$MnO$_3$ ($y = 0.35$) and La$_{0.5}$Ca$_{0.5}$MnO$_3$. The extremely slow relaxation observed in all the mentioned works opens an interesting question not previously addressed about the path followed towards equilibrium in the PS state of manganites.

In this work we present a detailed study of time dependent effects in the PS compound La$_{0.5}$Ca$_{0.5}$MnO$_{0.95}$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 $T_{C}$. 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$_3$ and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, a feature ascribed to the presence of a random field quenched by the impurities. But, unlike what happens with Cr doping, Fe doping also disrupts the double exchange interaction due to its filled $e_g$ orbitals. Moreover, Fe-O-Mn superexchange interactions are likely to be antiferromagnetic. All these facts are reflected by the decrease of $T_{C}$ as a function of Fe doping.

We use transport and magnetization measurements to study the dynamic of the coexisting phases, which is observed close below $T_{C} \approx 90$ K. We found 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, the rejuvenation in the resistivity curve when cooling is resumed after ageing, which resembles the behavior of glassy systems and disorder ferromagnets. The other is the effect produced by the application of a low $H < 1$ T while ageing 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 memory of the 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, magnetization was measured using a commercial SQUID magnetometer. Figure 1 displays magnetization $M$ and resistivity $\rho$ 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 $\approx 3 \mu_B$/Mn at 5 T. An insulator to metal transition is suggested 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 $v_c$ reassures that this cooling rate effect is not an experi-
ment artifact.

We studied the time relaxation of $\rho$ 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 one hour (Fig. 2). The relaxations are characterized by the decrease of $\rho$ following a logarithmic time dependence, and are as high as an 18% in one hour 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 noticeable fact is that, when the cooling process is resumed with $v_c = 0.2$ K/min after relaxation, $\rho$ merges smoothly with the curve obtained at that $v_c$ without $T$ stabilization steps. This effect is similar to that found in the dissipation of some disordered ferromagnets and spin glasses, 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 one hour ageing, cooling is resumed (Fig. 2).

This last result is opposite to that expected from a static vision of transport properties in PS systems, in which the change from metallic-like to insulator-like behavior is driven by a decrease in the amount of the metallic fraction. This fact points to the existence of dynamical contributions to the resistivity in the continuously cooling procedure. 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 a fixed $T$ value while the system is relaxing (Fig. 3). After a sudden initial change from positive to negative, the slope $\partial \rho / \partial T$ increases smoothly and slowly (see Fig. 3 inset) as the system evolves. The obtained ageing behavior of $\partial \rho / \partial T$ is now consistent with the static image for transport, the negative slope indicating that percolation of the FM phase has not been achieved close below $T_p$. As in this $T$ range the state of the system is characterized by the slow enlargement of the FM regions against the non FM host, the approach to equilibrium drives the system towards the percolation threshold, increasing the resistivity slope. The metallic-like behavior of the continuously cooling curve is then to be ascribed to the existence of non-static contributions to $\partial \rho / \partial T$ arising from the out-of-equilibrium dynamics of the coexisting phases. 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 can not 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 $T_p$.

Fig. 4-a displays $\rho$ as a function of elapsed time upon the application of several $H$ values at $T = 72$ K, showing jumps when the field was applied and removed. The sudden decrease of $\rho$ 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 $H$. It is worth noting the hysteretic behavior of $\rho$ after application and removal of $H$, indicating that the system keeps memory of the magnetic history imprinted in its zero field resistivity.

The slow 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 ultra-relaxation of \( \rho \) after the field is turned off reverses its sign: after \( H > H_{th} \) is applied and removed \( \rho \) slowly increases (instead of decreasing) indicating that the system is evolving by diminishing the amount of the FM phase (Fig. 4a inset). This fact signs unambiguously that the equilibrium state is of PS nature, characterized by the FM fraction \( f_0(T) \). The application of \( H_{th} \) while ageing drives the system towards its zero field equilibrium point, having an effect which is equivalent to a long relaxation process. The equilibrium points depicted in Fig. 2 provide a demonstration of the magnitude of the dynamical effects. By applying a \( H > H_{th} \) the amount of the FM phase overcomes the equilibrium volume, leading to a subsequent decrease of the FM fraction.

In what follows we discuss the overall results. At \( T_C \) an inhomogeneous FM state appears, consisting in the coexistence of isolated FM clusters of definite size within a non-FM host. At \( T_D= 85 \) K 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 as a stepwise movement of the phase boundaries through energy barriers. Before the FM clusters reach the percolation threshold, the temperature and rate dependent resistivity \( \rho(T, v_c) \) can be modeled as a series circuit, i.e.

\[
\rho(T, v_c) = n(T, v_c)\rho_F(T) + [1 - n(T, v_c)]\rho_n(T) \tag{1}
\]

where \( \rho_F(T) \) and \( \rho_n(T) \) 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 \( f(T, v_c) \), and can be obtained from conduction models through binary alloys. Within this frame, the slope of the resistivity curve has two components. On one hand, a static contribution given by \( n(T, v_c)\frac{\partial\rho_F}{\partial T} + (1 - n(T, v_c))\frac{\partial\rho_n}{\partial T} \), which is typically less than zero in the non-percolative regime. On the other hand, a "dynamical" term defined as \( \frac{\partial n(T, T_C)}{\partial T}(\rho_F - \rho_n) \) 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 of energy barriers at the clusters surface below \( T_D \) 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 \( \rho \) as \( v_c \) is increased (Fig. 1, inset). Close below \( T_D \), \( f(T, v_c) \) 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 “metallic-like” 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 ageing 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 non-stop process, because of the “clamping” of the interface. The main contribution to $\partial \rho / \partial T$ after ageing comes then from the static part, giving rise to the “insulator like” response. On further cooling, the frozen-in state is released, the system falls again in the dynamical regime mainly determined by $v_c$, and the resistivity curves (with and without ageing) merge into a single one.

This dynamical process produces ageing and rejuvenation effects which bear similarities with those found in glassy systems. Slow relaxations following stretched exponential or logarithmic dependences were accounted for with models based on a hierarchical constrained dynamics, in which the system evolves through a hierarchy of energy barriers, constrained to accomplish determined requisites after 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 ageing at a fixed $T$ showed 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 effect. In this context, once all the energy barriers of height up to some applied $H_{\text{MAX}}$ were overcome, the subsequent application of a $H < H_{\text{MAX}}$ 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 $H_{\text{MAX}} = 0.6 T$ has determined the relative phase fractions, higher application of $H < 0.6 T$ 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 $H_{\text{MAX}}$, the process can not be reversed and the system keeps 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 slight different Fe doping and in La$_{0.5}$Pr$_y$Ca$_{0.5}$MnO$_3$ ($y = 0.30$), 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) can not be directly inferred from metallic or insulator behavior. The rejuvenation found in the resistivity curve after ageing 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 sizeable and persistent change of the resistivity is a distinctive fact of the memory effect, and opens a route for applications. Memory effects in manganites have been previously reported, 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.

Project partially financed by CONICET, Fundación Antorchas and Balseiro.

[1] E. Dagotto, T. Hotta and A. Moreo, Phys. Rep. 344(1-3), 1 (2001).
[2] M. Uehara and S-W. Cheong, Europhys. Lett. 52(6), 674 (2000).
[3] I. F. Voloshin et al., JETP Letters 71, 106 (2000).
[4] N. A. Babushkina et al., Phys. Rev. B 59, 6994 (1999).
[5] V. N. Smolyaninova et al., available at cond-mat/9907087 (unpublished).
[6] V. Podzorov et al., Phys.Rev.B 61, R3784 (2000).
[7] R. D. Merithew et al., Phys. Rev. Lett. 84, 3442 (2000).
[8] V. Podzorov et al. to appear in Europhys. Lett. (2001).
[9] A. Anane et al., Phys.Rev.B 59, 77(1999).
[10] T. Kimura et al., Phys.Rev.Lett.83, 3940 (1999).
[11] M. Roy, J. F. Mitchell and P. Schiffer, J. Appl. Phys. 87, 5831 (2000).
[12] D. Casata et al., Europhys. Lett. 47, 90 (1999); D. Casata et al., Phys. Rev.B 64, 100404 (2001).
[13] P. Levy et al., Phys. Rev. B62, 6437 (2000); Q. Huang et al., ibid 61, 8895 (2000); R. S. Freitas et al., ibid 65, 104403 (2002).
[14] R. Mahendiran et al., Solid State Commun. 114, 429 (2000).
[15] T. Katsufuji, et al., J. Phys. Soc. Jpn. 68, 1090 (1999).
[16] L. K. Leung, A. H. Morrish and B. J. Evans, Phys. Rev. B 13, 4069 (1976).
[17] P. Levy et al. J. Magn. Magn. Mat. 226, 794 (2001).
[18] K. Jonason et al., Phys.Rev.Lett. 81, 3243, (1998).
[19] J. P. Bouchaud, in Soft and Fragile Matter, M. E. Cates and M. R. Evans, Eds., IOP Publishing (Bristol and Philadelphia) pp 285-304 (2000).
[20] E. Vincent et al. Europhys. Lett. 50 (5), 674 (2000).
[21] F. Parisi et al., Phys. Rev. B 63, 144419 (2001).
[22] D. S. Mc Lachlan, J.Phys.C 20, 865 (1987).
[23] R.G. Palmer et al., Phys. Rev. Lett. 53, 958 (1984).