

Origin of the Glassy Magnetic Behavior of the Phase Segregated State of the Perovskites

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In this Letter we demonstrate that the phase segregated state observed in many rare-earth perovskites constitutes a sort of self-generated assembly of magnetic clusters in which magnetic interaction introduces collectivity among them. We show that the observed glassy behavior (memory, aging, etc.) can be perfectly understood taking into account only the intercluster interactions. We address the fundamental question about whether this state constitutes classical spin glass or if, on the other hand, a new universality class must be defined.

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The phase segregated state (PSS) that develops in many systems close to a first-order electronic phase transition is being intensively studied, mainly because of its potential relevance to colossal magnetoresistance and high temperature superconductivity [1,2].

For the particular case of manganites, there are plenty of examples in the literature of unusual relaxation dynamics and frequency dependent phenomena in the PSS which denote a certain degree of glassiness (see Chap. 13 in [2], and references therein). Among the most representative examples of this behavior, Freitas *et al.* [3] and Levy *et al.* [4] reported aging or rejuvenation and memory effects on the resistivity and magnetization of different manganites in the PSS. The occurrence of these time-dependent phenomena, many of them similar to those reported in classical spin glasses [5], made it usual to refer to the PSS as *cluster-glass* or *spin-glass-like* phase. Moreover, there is a total consensus at the time to ascribe the origin of the spin-glass-like characteristics of the PSS to the frustration introduced by the competition between ferromagnetic-double exchange (FM-DE) and antiferromagnetic-superexchange (AF-SE). However, these experiments only prove the existence of a sort of collective relaxation behavior, but do not provide any definitive evidence of a true spin glass. Instead, a detailed scaling analysis must be performed at the critical region, close to the transition temperature. So, at this moment, the fundamental question of whether the PSS of manganites can be described as a classical spin glass, or if on the other hand, it constitutes a new class of glass, remains still open.

In this Letter we address this issue by an analysis of the critical behavior of the nonlinear susceptibility, χ_{nl} , which is proportional to the divergent spin-glass order parameter susceptibility ($\chi_{SG} \propto \varepsilon^{-\gamma}$) [6]. The main conclusions of this work are that the system in the PSS regime must be considered as an assembly of interacting magnetic clusters; intercluster interactions introduces the collectivity and glassiness observed in the relaxation experiments. The terms “cluster” and “particle” will be

used in a similar way, to refer to ferromagnetic entities in a nonferromagnetic matrix, whether or not a physical limit for these entities exists.

For simplicity, only experiments performed on a ceramic sample of $(\text{La}_{0.25}\text{Nd}_{0.75})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ will be discussed, although similar effects were observed in other compositions in the PSS (manganites, and also rare-earth cobaltates [7]). The proximity of this composition to the metal-insulator transition [8] makes it an optimal choice for studies of magnetic relaxation phenomena. Although $M(T)$ rises close to T^* in $(\text{La}_{0.25}\text{Nd}_{0.75})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (see Fig. 2), it does not constitute a true FM- T_C , as it was recently demonstrated [9]. Instead, a PSS (ferromagnetic clusters in a insulating matrix) develops below T^* due to the proximity to the localized-to-itinerant crossover, which restrains the magnetic correlation length ξ to the size of the FM-clusters, and prevents the $\xi \rightarrow \infty$ divergence at T^* .

The nonequilibrium dynamics and memory phenomena in the PSS are reported in Fig. 1. The sample was cooled at zero field down to a certain $T < T^*$, and after a waiting time t_w , a field was applied (typically between 5 and 50 Oe) and the time-dependent magnetization was recorded. The function $S = (1/H)(\partial M / \partial \ln t)$ vs $\log t$, is plotted in Fig. 1 for different waiting times, t_w . A spin glass left unperturbed by external fields at a constant T , rearranges its spin configuration through a very slow process to reduce the domain wall energy. Within the Fisher and Huse droplet model [10] the magnetic response to an applied field after a t_w is probing the polarization of domains with different characteristic length scales. A crossover at $t \approx t_w$ due to gradual excitation of larger droplets including domain walls is expected, and will show up as a maximum in $S(\log t)$ at $t \approx t_w$.

However, this behavior is not exclusive of conventional spin glasses and has been reported in systems of concentrated magnetic particles [11], and other nanostructure magnetic materials [12], where dipolar interactions introduce a collective state and magnetic relaxation depen-

dence like that of spin glasses at low temperatures. So, the existence of aging is only a proof of the existence of a collective relaxation, but not of a thermodynamic spin-glass phase.

In fact, many of these effects can be perfectly qualitatively understood on the basis of a system composed by noninteracting particles with a temperature dependent distribution of relaxation times [13]. To discard this possibility and to confirm proper spin-glass dynamics, a zero-field cooling (ZFC) magnetization experiment with stops during cooling at zero field must be performed. In a spin glass or a system of interacting magnetic particles (but not in noninteracting particles), a dip appears on reheating at the temperature at which the sample was stopped under zero field. This is exactly what we observed after stopping the ZFC process at 40 and 20 K (Fig. 1, inset). This constitutes a very important experiment as it confirms that the memory effects observed in the PSS reflect spin-glass dynamics, whether it constitutes a classical spin glass or the behavior is introduced by intercluster interactions. To discern between these two possibilities is the main goal of this Letter, and with this aim the field dependence of the magnetization and the nonlinear susceptibility at the critical region were carefully studied.

In Fig. 2 we show $M(T, H)$ in ac/dc conditions. The unusually strong dependence of T^* on the magnetic field is a consequence of finite size effects introduced by the limitation of ξ to the size of the FM clusters stabilized below T^* , and can be described by [14]

$$\frac{T^\infty - T^*}{T^\infty} = \varepsilon = \left(\frac{\xi}{\xi_0}\right)^{-1/\nu}, \quad (1)$$

where $T^\infty \approx 198$ K is the T_C of the infinite cluster ($\xi \rightarrow \infty$) obtained from extrapolation of the fitting of the T^* vs H curve (Fig. 2, upper inset) assuming a $T^*(H)$ dependence given by a function of the form $T^* = T^\infty (1 - A/H)$.

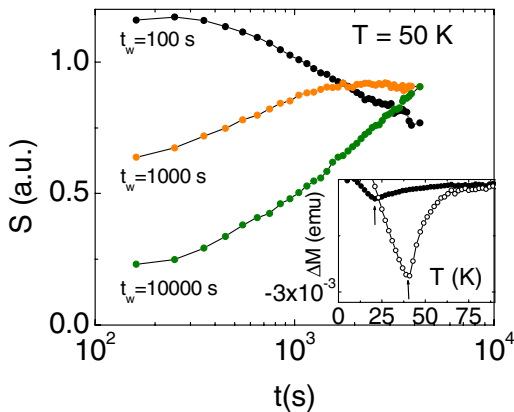


FIG. 1 (color online). Relaxation function $S = (1/H) \times \{\partial M / \partial \ln t\}$ vs $\log t$ at 50 K for different waiting times t_w . The displacement of the maximum respect to t_w , is due to an extra time to stabilize the temperature. Inset: Memory effect in the zero-field cooling magnetization.

From the field dependence of ξ observed in small angle neutron scattering experiments in the PSS [15], a phenomenological dependence $\xi \propto (H^\infty - H)^{-x}$ can be anticipated. In this case H^∞ is the field at which $\xi \rightarrow \infty$. The critical exponent for the correlation length obtained in this way is $\nu = 1.0(1)$ (Fig. 2, inset), using a value of $x \approx 1.7$, consistent with neutron scattering experiments. Numerical calculations and experimental results in fine particle systems reported a similar dependence of the T_C with particle size, governed by the finite-scaling law of Eq. (1) [16]. This is a strong argument in favor of a PSS composed of magnetic clusters whose size can be tuned by a magnetic field.

However, the definitive way to confirm the existence of a true spin glass is to study the critical behavior of the spin-glass order parameter susceptibility and check the critical exponents through scaling. In the low field limit and in the critical region, the spin-glass order parameter susceptibility diverges of the form $\chi_{SG} \propto \varepsilon^{-\gamma}$ but it has been shown to be proportional to the H^2 term in the static scaling expansion of the nonlinear susceptibility [6],

$$\chi_{nl} = \chi_0 - M/H = \chi_3 H^2 + \chi_5 H^4 + \dots \quad (2)$$

Geschwind, Huse, and Devlin [17] proposed an static scaling equation for the nonlinear susceptibility of spin glasses of the form

$$\chi_{nl} = H^{2\beta/(\beta+\gamma)} F\left[\frac{\varepsilon}{H^{2/(\beta+\gamma)}}\right]. \quad (3)$$

A general scaling analysis according to Eq. (3) was performed for isotherms in the critical region above T^*

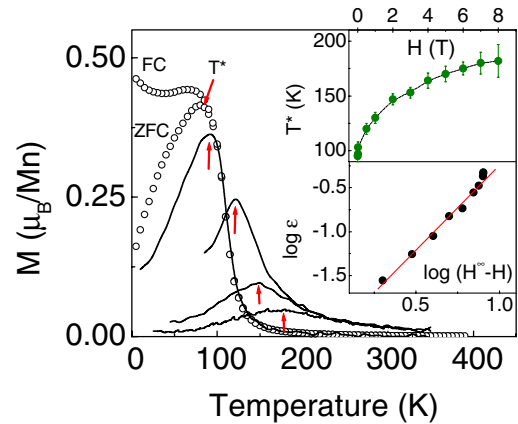


FIG. 2 (color online). Temperature dependence of the zero-field cooling-field cooling dc magnetization curves at 10 Oe (open symbols). The ac-zero-field cooling curves measured with different superimposed dc fields (solid lines) are also shown. Upper inset: The field dependence of T^* extracted from the peak in the ac-zero-field cooling susceptibility ($h = 1-10$ Oe, 10 Hz) with a superimposed dc field (up to 9 T). Lower inset: log-log plot of the reduced temperature vs $(H^\infty - H)$. The line is the linear fit from where the critical exponent ν for the correlation length was obtained.

(Fig. 3). Best data collapsing was obtained with $\beta = 0.30(3)$ and $T^* = 97$ K, using $\gamma = 2.4(2)$ obtained from the fit of the real component of the third harmonic of the ac susceptibility (Fig. 3, inset) [18].

To the best of our knowledge, this is the first time the divergent character of the nonlinear susceptibility is demonstrated in a PSS system. Applying the scaling relations between the critical exponents we got $\alpha = -1.1$ and $\nu = 1.03$. The latter one agrees reasonably well with the value obtained from finite size scaling of Eq. (1), supporting our analysis. Although the values of the critical exponents and the transition temperature were obtained independently and its consistency rechecked by the asymptotic behavior of the scaling function [19], a small dispersion is almost inevitable and we do not discard that slightly different values could be obtained for similar systems.

On the other hand, it is difficult to ascribe the critical exponents to an universality class, and then it could be tempting to conclude that the system behaves as an interacting assembly of magnetic clusters, where similar scaling collapse has been observed but with critical exponents also impossible to ascribe to an universality class [20]. However, the critical exponents we obtained experimentally are similar to these of $\text{Fe}_{10}\text{Ni}_{70}\text{P}_{20}$ amorphous material, considered as spin glass [21]. The problem is the enormous dispersion among the values of the critical exponents in the literature for different spin glasses, which makes it extremely difficult to decide to which universality class corresponds a particular spin-glass material. So in this case, scaling analysis of the critical nonlinear susceptibility is not enough to discern between a conventional spin glass and a system of interacting magnetic particles.

On the other hand, Ulrich *et al.* [22] demonstrated that in a frozen ferrofluid below its blocking temperature, dipolar interactions cause the relaxation rate, $W(t) = -(d/dt)\ln M(t)$, to decay following a power law, with an exponent n , which depends on the concentration and

hence on the strength of the magnetic interaction. The authors interpreted the scenario described by $n \geq 1$ as a clear signature of a spin-glass phase. These theoretical predictions were recently corroborated by magnetic relaxation measurements in granular magnetic films [23]. In Fig. 4 we show the decay of $W(t)$, and the values of n obtained for various fields and temperatures, always below T^* .

At low temperature ($\approx 0.2T^*$) and at low fields, n is always of the order of 1, which indicates that the relaxation of the system is governed by interactions, reminding one of the behavior of a true spin glass. However, when the temperature is increased n is not constant, in opposition to a true spin glass or a system of strongly interacting particles with fixed diameter and concentration. In the PSS, n increases continuously as T^* is approached, reaching $n = 1.50(2)$ at $0.72T^*$. This experiment confirms that in the PSS an increase in the temperature towards T^* is equivalent to an increase in the concentration in a system of magnetic clusters. On the other hand, the increase of the magnetization as T^* is approached from below points to an increase in the number and/or the size of the clusters. So, the progressive increment of the exponent n reflects the increasing strength of the intercluster interactions as T^* is approached.

This result raises some serious doubts about the origin of the frustration and the glassy behavior of the PSS. If DE vs SE competition were the only cause of this frustration, as it is commonly accepted, we should in principle expect a constant value of n with T below T^* unless a variation of the strength of the DE/SE occurs with temperature. Although this cannot be ruled out completely, our experiment constitutes a definitive proof to demonstrate that the glassiness of the PSS in manganites can be perfectly explained considering only the coupling between

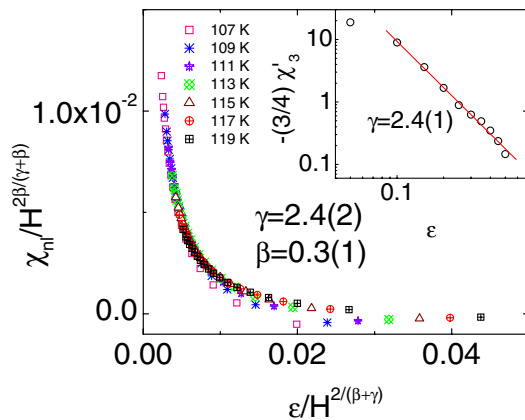


FIG. 3 (color online). Scaling plot of the nonlinear susceptibility above T^* . Inset: Critical exponent of the susceptibility derived from the nonlinear component of χ_{ac} .

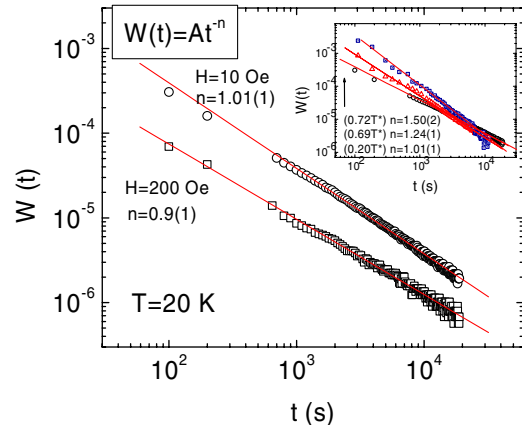


FIG. 4 (color online). Relaxation rate at constant temperature for different cooling fields ($n \approx 1$) for low fields. Inset: Relaxation rate as a function of T . As T^* is gradually approached from below n increases reflecting an increase in the magnetic interactions between cluster.

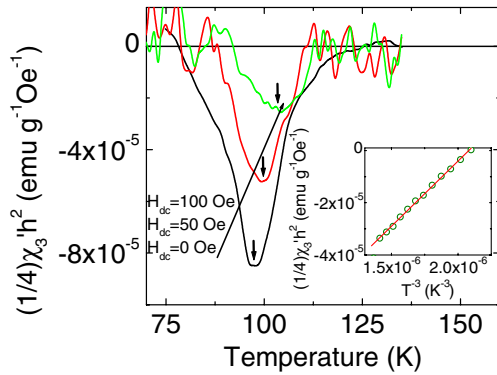


FIG. 5 (color online). Real part of the cubic susceptibility vs temperature for a field cooled sample (the cooling field is indicated). Inset: T^{-3} dependence of the cubic susceptibility above T^* .

an assembly of interacting magnetic clusters, independently of the microscopic interaction which mediates the FM on these clusters. It is the concentration of clusters, which could be controlled by composition and/or magnetic field, which introduces the frustration and the collectivity observed in the relaxation of the system.

Another important piece of information comes from the behavior of the nonlinear susceptibility measured from the ac susceptibility. The negative peak in χ_3' (Fig. 5) is very broad compared to that of a typical spin glass. Moreover, the Curie-Weiss dependence of the linear susceptibility and the T^{-3} dependence of the nonlinear term (Fig. 5, inset) is consistent with the Wohlfarth blocking model for an assembly of interacting magnetic particles [24]. The broadening and displacement of the curve to higher temperatures when a dc field is superimposed to the ac curve [18] is identical to the effect of an increase in the concentration of magnetic particles in a ferrofluid [25].

In summary, we have demonstrated that the PSS observed in manganites close to a metal-to-insulator crossover must be considered as an assembly of interacting magnetic clusters, quite similar to a sort of *self-generated magnetic colloid*, at least from a magnetic point of view. Our experiments provide serious evidence to support a scenario in which the collective/glassy behavior observed experimentally can be explained considering the interaction among clusters. These interactions can be tuned by composition and/or magnetic field, through the control of the size and concentration of the magnetic clusters. The system, although it does not constitute a conventional spin glass in the sense that it cannot be associated to any of the existing universality classes, shares many of its features below T^* .

We hope our experimental results will attract the interest of future theoretical discussions in this direction.

We believe these results are general and should be applicable to other systems close to a first-order electronic transition similar to the one described here, like cobaltates, etc. Our work provides a link between the magnetic PSS and the systems of nanosize magnetic particles, which raised so much scientific and technological interest in the last 50 years.

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- [1] J.B. Goodenough and J.-S. Zhou, in *Structure and Bonding*, edited by J.B. Goodenough (Springer-Verlag, Berlin, 2001), Vol. 98.
- [2] E. Dagotto, in *Nanoscale Phase Separation and Colossal Magnetoresistance* (Springer-Verlag, Berlin, 2002).
- [3] R. S. Freitas *et al.*, Phys. Rev. B **64**, 144404 (2001).
- [4] P. Levy *et al.*, Phys. Rev. Lett. **89**, 137001 (2002).
- [5] J.A. Mydosh, in *Spin Glasses. An Experimental Introduction* (Taylor & Francis, London, 1993).
- [6] Masuo Suzuki, Prog. Theor. Phys. **58**, 1151 (1977).
- [7] M. A. Señarís-Rodríguez and J.B. Goodenough, J. Solid State Chem. **118**, 323 (1995).
- [8] J.-S. Zhou, W. Archibald, J.B. Goodenough, Nature (London) **381**, 770 (1996).
- [9] F. Rivadulla, J. Rivas, and J.B. Goodenough, cond-mat/0311476 [Phys. Rev. B (to be published)].
- [10] D.S. Fisher and D.A. Huse, Phys. Rev. B **38**, 373 (1988); **38**, 386 (1982).
- [11] T. Jonsson *et al.*, Phys. Rev. Lett. **75**, 4138 (1995).
- [12] S. Sahoo *et al.*, Phys. Rev. B **67**, 214422 (2003).
- [13] M. Sasaki, P.E. Jönsson, H. Takayama, and P. Nordblad, cond-mat/0311264.
- [14] M.N. Barber, in *Phase Transitions and Critical Phenomena*, edited by Domb and Lebowitz (Academic Press, London, 1983), Vol. 8.
- [15] J.M. De Teresa *et al.*, Phys. Rev. B **65**, 100403 (2002).
- [16] X. Balle and A. Labarta, J. Phys. D **35**, 15(R) (2002).
- [17] S. Geschwind, D.A. Huse, and G.E. Devlin, Phys. Rev. B **41**, 2650 (1990).
- [18] L.P. Lévy, Phys. Rev. B **38**, 4963 (1988).
- [19] K. Gunnarsson *et al.*, Phys. Rev. B **43**, 8199 (1991).
- [20] T. Jonsson, PhD thesis, University of Uppsala, Sweden, 1998.
- [21] T. Taniguchi, Y. Miyako, J.L. Tholence, J. Phys. Soc. Jpn. **54**, 220 (1985).
- [22] M. Ulrich, J. García-Otero, J. Rivas, and A. Bunde, Phys. Rev. B **67**, 24416 (2003).
- [23] X. Chen, W. Kleemann, O. Petravic, O. Sichelshmidt, S. Cardoso, and P.P. Freitas, Phys. Rev. B **68**, 54433 (2003).
- [24] T. Bitoh *et al.*, J. Magn. Magn. Mater. **154**, 59 (1996).
- [25] P. Jönsson, T. Jonsson, J.L. García-Palacios, and P. Svedlindh, J. Magn. Magn. Mater. **222**, 219 (2000).