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Novel collective magnetic relaxation phenomena in manganites: a spin-glass behavior?

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Abstract

Here we address many of the fundamental open questions regarding the glassy behavior of the magnetic/electronic phase segregated state in rare earth perovskites. Magnetic relaxation (AC/DC) support a scenario in which collective effects (memory, ageing, etc.) can be understood as due to intercluster interactions. We propose that the phase segregated state (PSS) constitutes a sort of self-generated assembly of magnetic clusters in which the magnetic interaction introduces collectivity among them. The strength of the interactions can be tuned by composition and/or magnetic field, through the control of the size and concentration of the magnetic clusters. These results are general, applicable to other systems close to a localized to itinerant transition, like cobaltates, cuprates, etc.

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Keywords: Manganites; Phase separation; Nanoparticles; Spin-glass

It is now clear that the phase-segregated state (PSS) that develops in many systems close to a first-order electronic phase transition plays a fundamental role in colossal magnetoresistance phenomena [1,2]. Unusual relaxation dynamics and time/frequency-dependent phenomena (ageing, rejuvenation, memory, etc.) are common features of this magnetically inhomogeneous phase [3–6], which is normally quoted as a *cluster-glass-* or *spin-glass-like* phase [7]. These effects are normally associated to the competition between two exchange interactions of opposite sign (FM–DE vs. AF–SE) that frustrates the long-range order. However, a scaling analysis at the critical region has not been performed to date and hence those experiments only prove the existence of a sort of collective relaxation behavior, but do not provide any definitive evidence of a true spin-glass. The fundamental question of whether the PSS of manganites constitutes a new class of glass

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or if it can be considered a classical spin-glass, remains still open.

Here, we try to address this issue through an analysis of the critical behavior of the non-linear susceptibility, χ_{nl}, which is proportional to the divergent spin-glass order parameter susceptibility ($\chi_{SG} \propto \varepsilon^{-\gamma}$) [8]. We demonstrate that the system in the PSS regime behaves as an assembly of interacting magnetic particles and that the glassiness of the PSS can be explained taking into account the intercluster interactions that introduce the collectivity observed in the relaxation experiments. We want to make clear at this point that by "particle" we refer to the ferromagnetic clusters that develop below T^* in the PSS.

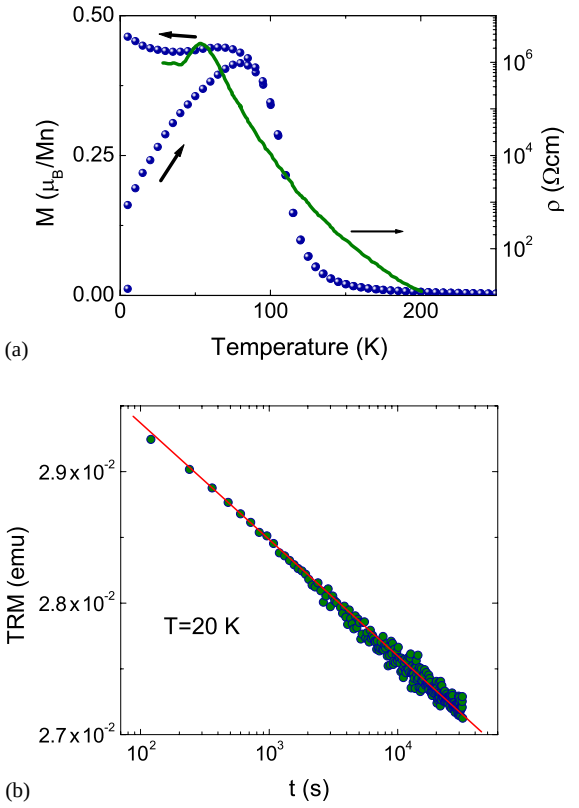

Fig. 1. (a) Temperature dependence of the magnetization (at 250 Oe) and resistivity. The irreversibility between the ZFC–FC magnetization curves and the strong variation in the ZFC, points to a magnetically inhomogeneous state (FM clusters in a non-metallic matrix). (b) Relaxation of the thermoremanence.

In $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ the magnetization increases approximately below 100 K (Fig. 1), but it does not constitute a true FM–T_C, as it was recently demonstrated [9]. Instead, the PSS (metallic ferromagnetic clusters in a non-metallic matrix) develops below T^* due to the proximity to the localized-to-itinerant crossover in this material. In Fig. 2 we show the $\chi_{AC}(T, H_{DC})$ curves for $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$. $\chi_{AC}(T)$ increases sharply at the temperature T^*. In Fig. 3a we can see how the isotherms in the Arrott plots never reach the M^2 axis from a low-field extrapolation, it being impossible to define the spontaneous magnetization and hence a phase transition to a long-range FM state below T^* [10]. This is a direct consequence of the limitation of the magnetic correlation length ξ to the finite-size of the clusters (ξ does not diverge at the critical point).

All these effects make $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ an ideal system to study the relaxation of FM regions, because it is composed by large FM–metallic clusters immersed in an insulating matrix (approaches the metal-insulator transition from the localized side).

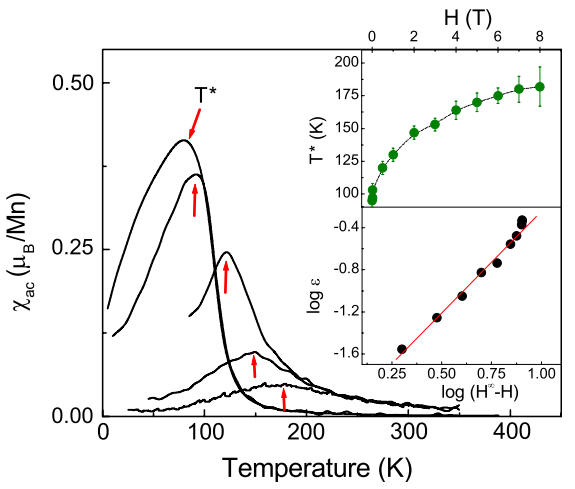

Fig. 2. The ZFC-χ_{AC} ($h = 10$ Oe, 10 Hz) magnetization curves measured with different superimposed H_{DC} (up to 9 T). Upper inset: The field dependence of T^* extracted from the peak in $\chi_{AC}(T)$ with H_{DC} (up to 9 T). Lower inset: log-log plot of ε vs. $(H^{\infty} - H)$ to obtain the critical exponent ν for the correlation length. $H^{\infty} \geqslant 13\,T$ for $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$.

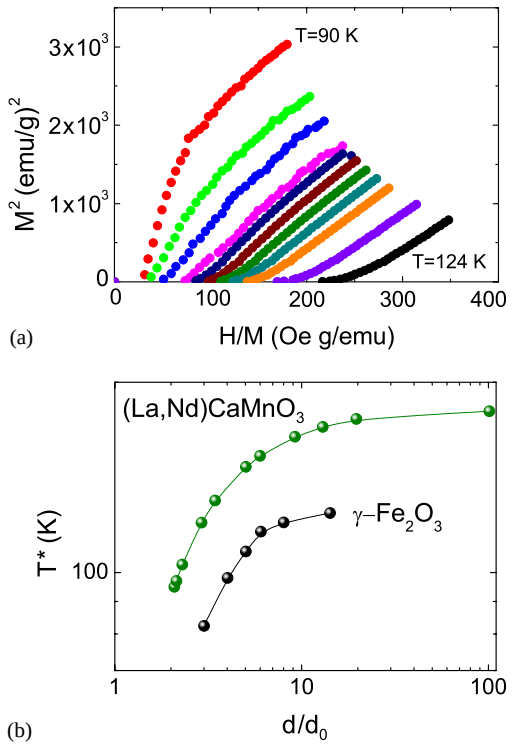

Fig. 3. (a) The Arrott plots for $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ around $T^* = 97$ K. Note how the isotherms never reach the M^2 axis from a low-field extrapolation. (b) Size dependence of the transition temperature to the PSS. It is compared with the effect on the transition temperature of maghemite nanoparticles obtained from Monte Carlo simulations [26]. d_0 is a characteristic microscopic dimension of the system, like in this case, to exchange length.

The unusually strong dependence of T^* on the magnetic field (Fig. 2, upper inset) is also 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 the following size scaling law [11]:

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

where $T^\infty \approx 198$ K is the T_C of the infinite cluster ($\xi \to \infty$) obtained from extrapolation of the fitting of $T^* = T^\infty\ (1 - A/H)$ relationship (Fig. 2, upper inset). From the field dependence of ξ observed in SANS experiments in the PSS [12], a phenomenological dependence $\xi \propto (H^\infty - H)^{-x}$ can be anticipated. In this case H^∞ ($\geqslant 13$ T) is the field at which $\xi \to \infty$. The critical exponent for the correlation length obtained in this way is $\nu = 1.0$ (Fig. 2, lower 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 (Fig. 3b), governed by the finite-scaling law of Eq. (1) [13,14]. This is a strong argument in favor of a PSS composed of magnetic particles whose size can be tuned by a magnetic field. This opens the possibility of using the magnetic field as a new variable for a precise control of the particle size/interactions, which opens a new path to investigate finite size and surface effects.

The non-equilibrium dynamics and memory phenomena in the PSS are reported in Fig. 4. The sample was cooled at zero field down to a certain $T < T^*$, and then a field of 10 Oe was applied or removed and the time-dependent magnetization $M(t)$ was recorded. The derivative of $M(t)$ shows a clear kink at a time corresponding to the time the sample spent below T^*, irrespective of whether the field was applied or removed. Conventional ageing was also recently reported in this system by Rivadulla et al. [15] and in other

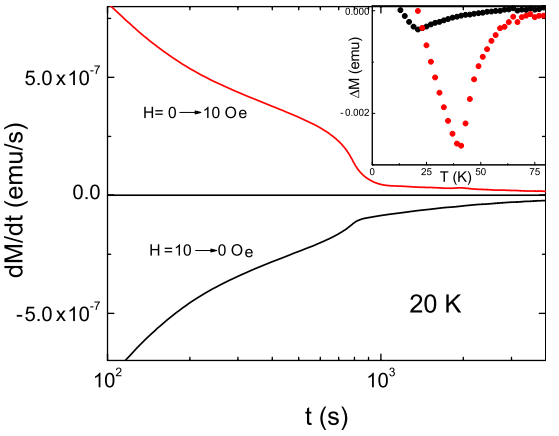

Fig. 4. Relaxation rate at 20 K after we applied or removed a field of 10 Oe. The absolute value of the derivative of $M(t)$ drops at a time corresponding to the time the system was left unperturbed below T^* (below the transition temperature for the PSS). Inset: Memory effect in the DC ZFC magnetization.

compositions close to a localized-to-itinerant behavior by Freitas et al. [3].

However, this behavior is not exclusive of conventional spin glasses and has been reported in systems of concentrated magnetic particles also [16], and other nanostructure magnetic materials [17], where dipolar interactions introduce a collective state and magnetic relaxation dependence like that of spin-glasses at low temperatures. So, the existence of ageing and memory effects is only a proof of the existence of a collective relaxation, but not of a thermodynamic spin-glass phase [18].

In fact, many of these effects can be perfectly and qualitatively understood on the basis of a system composed by non-interacting particles with a temperature-dependent distribution of relaxation times [19]. To discard this possibility and to confirm proper spin-glass dynamics, a 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 non-interacting 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 magnetization process at 40 and 20 K (Fig. 4, 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 interparticle interactions. To discern between these two possibilities the field dependence of the magnetization and the non-linear susceptibility at the critical region were carefully studied.

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 non-linear susceptibility [8],

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

Geschwind et al. [20] proposed a static scaling equation for the non-linear susceptibility of spin glasses of the form

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

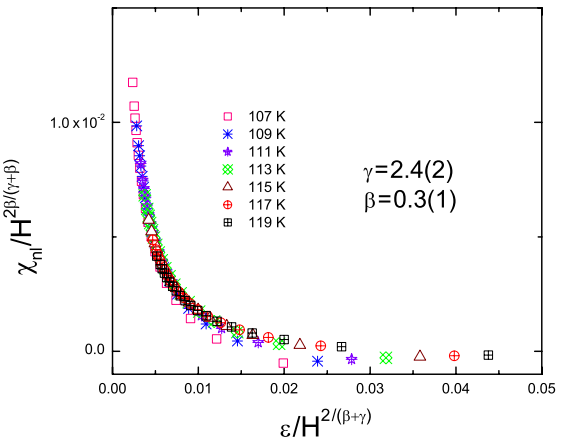

Fig. 5. Critical exponents ($\gamma = 2.4(2)$, $\beta = 0.3(1)$) derived from the scaling plots of the non-linear component of χ_{AC} data according to the equation-of-state given in Eq. (3).

A general scaling analysis according to Eq. (3) was performed for isotherms in the critical region above T^* (Fig. 5). 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 [21].

To the best of our knowledge, this is the first time the divergent character of the non-linear susceptibility is demonstrated in a PSS system. Applying the scaling relations between the critical exponents we get $\alpha = -1.1$ 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 re-checked by the asymptotic behavior of the scaling function [22], 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 particles, where similar scaling collapse has been observed

Table 1
Critical exponents from the scaling analysis of Fig. 5, compared with those of a interacting system of FeC nanoparticles and a classical spin-glass

$(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$	FeC particles Ref. [26]	$Fe_{10}Ni_{70}P_{20}$ Ref. [26]
$\alpha = -1.1$ (1)	−4.4	−1.3
$\beta = 0.3$ (1)	1.2	0.5
$\gamma = 2.5$ (1)	4.0	2.3
$\nu = 1.0$ (1)	2.1	1.1

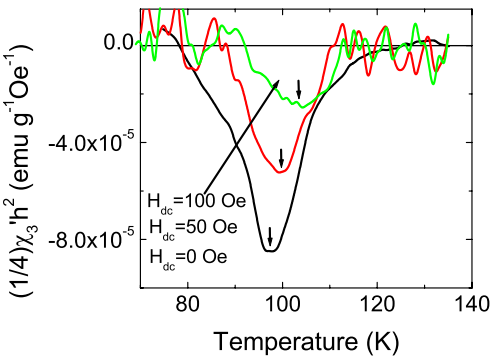

Fig. 6. The real part of the cubic term of the susceptibility vs. temperature for a field cooled sample (the superimposed DC field is indicated).

but with critical exponents also impossible to ascribe to an universality class [23]. However, the critical exponents we obtained experimentally are similar to those of $Fe_{10}Ni_{70}P_{20}$ amorphous material, considered as classic spin-glass [24] (see Table 1). The problem is that there is an enormous dispersion among the values of the critical exponents reported in the literature for different spin-glasses, which makes it extremely difficult to decide to which universality class a particular spin-glass material corresponds. So in this case, scaling analysis of the critical non-linear susceptibility is not enough to discern between a conventional spin-glass and a system of interacting magnetic particles.

Another important piece of information comes from the behavior of the non-linear susceptibility measured from the AC-susceptibility. The negative peak in χ_3' (Fig. 6) is very broad compared to that of a typical spin-glass. Moreover, a Curie–Weiss–like dependence of the linear susceptibility and a T^{-3} dependence of the non-linear term above T^* was found in Ref. [15], which is fully consistent with the Wohlfarth blocking model for an assembly of interacting magnetic particles [25].

The broadening and displacement of the curve to higher temperatures when a DC magnetic field is superimposed to the χ_{AC} curve [21] is identical to the effect of an increase in the concentration of magnetic particles in a quenched ferrofluid [26].

In conclusion, 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. The interactions among the clusters can be tuned by composition and/or magnetic field, through the control of the size and concentration of the magnetic clusters. The system, although 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^*. In a simple model, the origin of this magnetic relaxation in the glassy region can be interpreted as a consequence of the strong coupling of the magnetic moments of a dense assembly of clusters.

We believe these results should be applicable to other systems close to a first-order electronic transition similar to the one described here, like cobaltates, etc, and we hope it will attract the interest of future theoretical discussions in this direction.

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