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Complex dynamics of self-generated magnetic clusters in phase-separated perovskites

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Abstract

The linear and non-linear AC magnetic susceptibilities of the perovskite $La_{1-x}Sr_xCoO_3$, with $0.15 \leqslant x \leqslant 0.30$, are presented. It is observed that, for $x < 0.20$, a freezing temperature is defined by AC magnetic susceptibility, pointing to a glassy behaviour whose origin is the phase separation of ferromagnetic metallic-like clusters embedded in an insulating matrix. At this temperature, the non-linear magnetic susceptibility shows critical divergence, similar to spin-glasses, although the width of the diverging peak does not compare well with canonical spin-glasses.

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Keywords: Cobaltites; Non-linear magnetic susceptibility; Cluster-glass; Spin-glass

1. Introduction

The study of systems of magnetic nanoparticles has traditionally occupied a central place in the field of nanotechnology since its origins. The advances from both the basic scientific and the technological points of view have been linked to the practical realization of such systems. Nowadays, innovative works require the fabrication of nanoparticles by means of quite sophisticated physical experimental set-ups or, alternatively, the use of soft-chemistry synthesis routes, that in some cases are far from trivial [1].

Nevertheless, in recent years it has been found that nature generates, spontaneously in some solids, assemblies of magnetic regions [2] whose macroscopic behaviour resembles that of systems of magnetic nanoparticles with thermal irreversible magnetization and frequency-dependent dynamics [3–6].

Namely, perovskites with formula $R_{1-x}A_xMO_3$ ($R =$ lanthanide, $A =$ divalent alkali, $M =$ Co,

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Mn) exhibit at certain doping ranges a tendency towards phase separation [4,7], different from those ascribed to chemical inhomogeneities or to the existence of phases with different chemical composition. This phase separation, of electronic origin, leads in these perovskites to the formation of ferromagnetic metallic-like clusters embedded in an insulating $LaCoO_3$-like matrix [4].

Here, we show how these perovskites behave similar to systems of interacting magnetic nanoparticles. For this purpose we have analysed their complex dynamic behaviour inspecting their non-linear magnetic susceptibility, a powerful source of information to classify this kind of phenomena [8,9].

2. Experimental details

The materials studied were $La_{1-x}Sr_xCoO_3$ with $0.15 \leqslant x \leqslant 0.30$. Details on the synthesis and characterization are given elsewhere [10].

The linear and non-linear components of the AC magnetic susceptibility were measured as a function of temperature with a Lake Shore 7000 system using the mutual-inductance technique. Data were collected on warming from 13 to 300 K after zero-field cooling of the sample. The calibration was performed with a $Gd_2(SO_4)_3 8H_2O$ paramagnetic standard having the same shape and size as the investigated samples.

3. Results and discussion

In Fig. 1 we show the overall linear magnetic AC susceptibility of the series of $La_{1-x}Sr_xCoO_3$ samples. As expected, for $x \geqslant 0.20$, the curves show maxima that are associated with the already known onsets of ferromagnetic character [4,11]. Señarís Rodríguez and Goodenough explained this onset as the percolation of hole-rich ferromagnetic regions embedded in a hole-poor matrix, produced for $x > 0.18$ [4]. For $x = 0.15$ the macroscopic response of the system is not ferromagnetic. Instead, the data show glassy behaviour with a peak at a freezing temperature around 60 K, as is known [12]. The frequency dependence of both the real and imaginary parts, shown in Fig. 2, confirms the hypothesis of the cluster-glass-like interaction. In fact, the Arrhenius law, $f = f_0 \exp(-E/k_B T)$, holds to describe such frequency dependence. Extrapolation to the $\ln(1/f)$ axis in an Arrhenius plot, in order to obtain the pre-exponential factor $f_0 = 1/\tau_0$ (Fig. 3), leads to a non-physical relaxation time τ_0. This is a clear indication of the strong interaction established among the clusters. A similar macroscopic behaviour was also found in

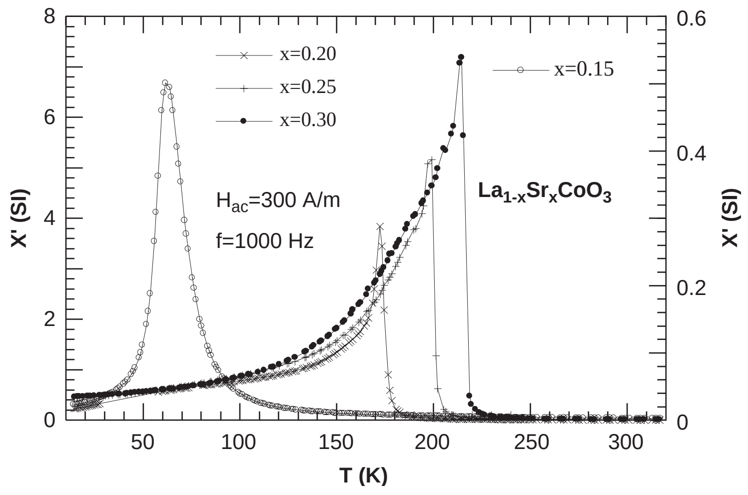

Fig. 1. Real part (χ') of the linear AC magnetic susceptibility of the studied $La_{1-x}Sr_xCoO_3$ series. The right axis scale corresponds to the $x = 0.15$ sample.

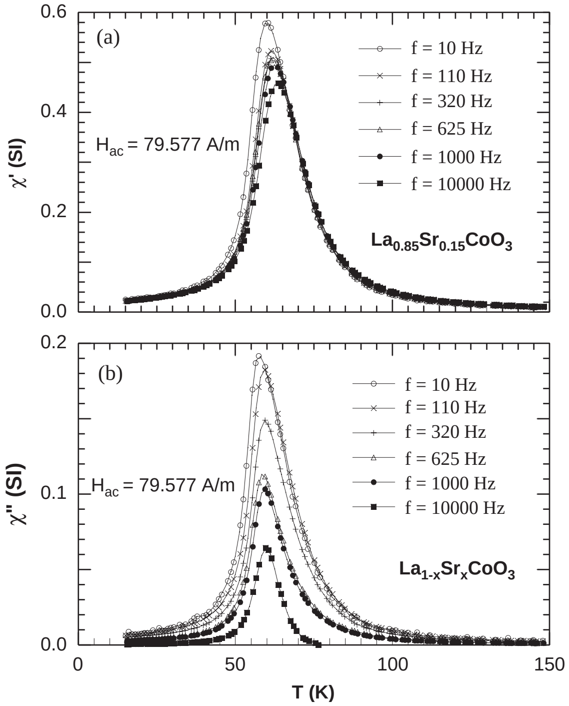

Fig. 2. Real (a) and imaginary part (b) of the linear AC magnetic susceptibility, versus frequency of $La_{0.85}Sr_{0.15}CoO_3$.

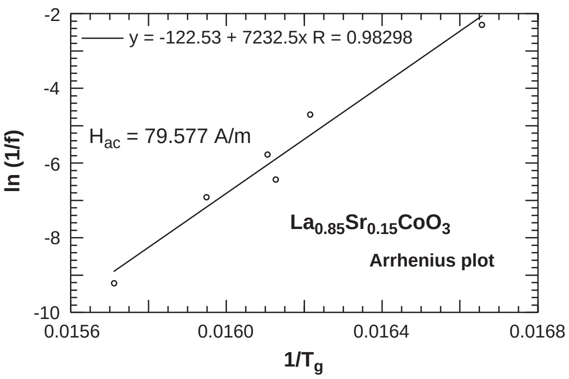

Fig. 3. Fit to the Arrhenius law of the variation of the freezing temperatures of $La_{0.85}Sr_{0.15}CoO_3$ versus the frequency of the exciting field.

Gd_2CuO_4 [13], where the interacting clusters are formed due to the lack of coherence of the lattice distortions, necessary for the creation of a weak ferromagnetic component in the system [14].

In order to properly identify the processes involved in $La_{0.85}Sr_{0.15}CoO_3$ we measured some of the coefficients of the non-linear magnetic susceptibility, more exactly the χ_2 and χ_3 terms of the expansion of the magnetization measured in the presence of an exciting field Hac

$$M = \chi_1 H_{ac} + \chi_2 H_{ac}^2 + \chi_3 H_{ac}^3 + \cdots. \tag{1}$$

χ_2 and χ_3 contain plenty of useful information [8,9], but their magnitude is so small that they are seldom investigated. In our case, these non-linear terms were obtained from both the second and third harmonics of the voltage induced in the pickup coils by the time-varying sample magnetization. The primary coil was driven at a fundamental frequency f, while the reference input to the lock-in amplifier, set to a band-pass filter mode of operation, was driven at frequencies $2f$ and $3f$. The voltage response corresponding to those components was quite low and affected by noise. For this purpose a high driving field was applied. In Fig. 4 we show the second harmonic of the magnetic susceptibility, that arises due to the presence of a symmetry-breaking field and is observed only in the presence of a DC field or in materials with a large permanent magnetization [8]. Its shape indicates magnetic order within the clusters. In fact, the peak at about 65 K is associated with the onset of ferromagnetic order inside them.

As for the third-order magnetic susceptibility, χ_3, it has been used to identify spin-glass transitions [15] and its divergence is indeed a signature of spin-glass behaviour. This critical

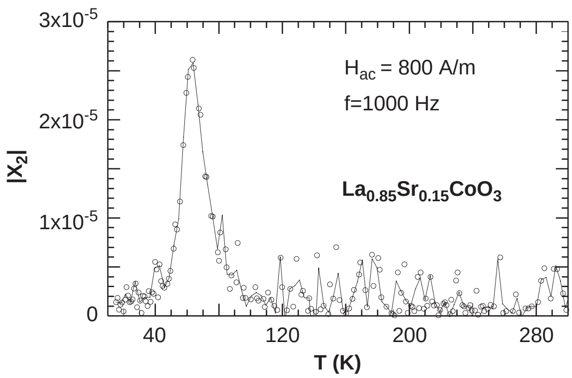

Fig. 4. χ_2 component of the non-linear AC magnetic susceptibility of $La_{0.85}Sr_{0.15}CoO_3$ under an exciting field of 800 A/m and frequency 1000 Hz.

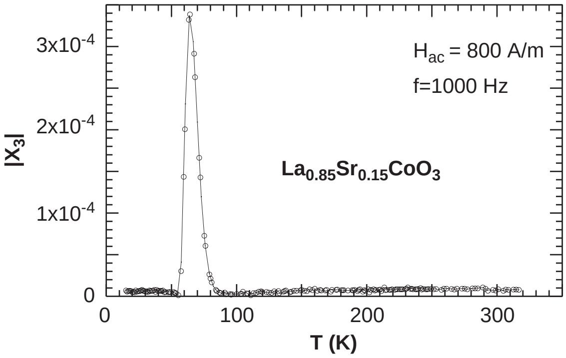

Fig. 5. χ_3 component of the non-linear AC magnetic susceptibility of $La_{0.85}Sr_{0.15}CoO_3$ under an exciting field of 800 A/m and frequency 1000 Hz.

divergence was first found in perovskites in $La_{0.95}Sr_{0.05}CoO_3$ by Caciuffo et al. [16] and this and other anomalies in AC susceptibility results attributed to phase separation [10,12]. The critical divergence of $La_{0.95}Sr_{0.05}CoO_3$ was fitted to the power law $[(T-T_f)/T_f]^{-\gamma}$, which yielded a critical exponent $\gamma = 1.1$, that compares favourably with the values of canonical spin glasses [15]. More recently, Rivadulla et al. [6] found in $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ a similar divergence in χ_3, and, from an analysis of the freezing temperatures with magnetic field, also reported a critical exponent similar to that expected for spin glasses. Concerning $La_{0.85}Sr_{0.15}CoO_3$, χ_3 also shows a clear divergence at 64 K (Fig. 5). Nevertheless, although all the hitherto mentioned clues would lead one to think of a spin-glass phase, the peak width is about 30 K, in contrast with the typical divergence of spin-glass systems [17]. Another clue in this line was given by previous studies of magnetic ageing [18], that failed to find a finite temperature of spin-glass transition. The checking of the divergence in χ_3 has not been possible in this case due to the noise that masks the signal when lowering the driving field.

4. Conclusions

We have shown that the phase separation produced in cobalt perovskites of formula $La_{1-x}Sr_xCoO_3$, with $x < 0.20$, leads to a collective behaviour similar to non-conventional spin glasses. This is deduced from a critical point marked by a wide divergence in non-linear-magnetic susceptibility vs. temperature data. Nevertheless, the width of the peak does not compare well with the typical divergence of canonical spin glasses.

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