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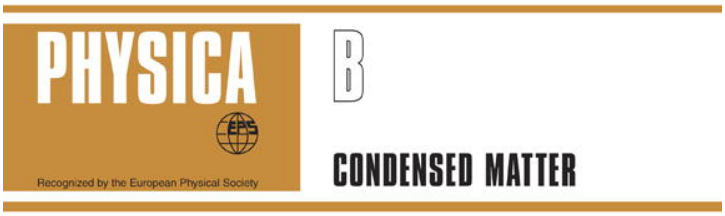

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Pressure effects on nanostructured manganites

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Abstract

We have measured the pressure sensitivity of magnetic properties on $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y = 0.3$) nanostructured powders. Samples were synthesized following a microwave assisted denitration process and a final heat treatment at different temperatures to control the grain size of the samples. A span in grain diameters from 40 nm to ~1000 nm was obtained. Magnetization curves as a function of temperature were measured following different thermomagnetic histories. AC susceptibility as a function of temperature was also measured at different hydrostatic pressures (up to 10 kbar) and for different frequencies. Our results indicate that the nanostructuration plays a role of an internal pressure, producing a structural deformation with similar effects to those obtained under an external hydrostatic pressure.

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Keywords: Manganites; Nanoparticles; Pressure effects; Magnetic properties

1. Introduction

Many efforts have been devoted to understand the influence of grain size (ϕ_G) down to nanometric dimensions in granular perovskite manganites of the form $L_{1-x}A_xMnO_3$ (where L is a trivalent rare-earth ion and A a divalent alkaline-earth ion). It was shown that ϕ_G has a clear influence in the magnetic and electrical properties of these materials. For example, it was earlier reported [1] that a reduction on ϕ_G from 110 to 20 nm in the $La_{2/3}Ca_{1/3}MnO_3$ compound decreases the magnetization (M) and increases the Curie temperature (T_c). The reduction of M was interpreted in terms of the increase of the surface to volume ratio of the grains, which increases the weight of the contribution to magnetization of the associated amorphous surface layer. The increase of T_c was related to a possible variation of the oxygen contents due to a different surface condition of the sample. On the other hand, studies reducing ϕ_G from 50 to 18 nm in $La_{0.875}Sr_{0.125}MnO_3$ showed an increase of both M and T_c, which correlates to structural measurements that indicate that the grain size modifies the relevant parameters that govern the double exchange mechanism (DE), like the Mn–O bond distance and the Mn–O–Mn bond angle [2]. Thus, the effects produced by nanostructuration are still an open question. In order to gain more information on the way ϕ_G affects the properties of manganites, and, in particular, to determine if ϕ_G has an influence on pressure effects, we report here on magnetization measurements and on hydrostatic pressure effects in $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ (LPCMO; $y = 0.30$) powder samples with ϕ_G values systematically reduced from the typical bulk value (~1000 nm) to tenth of nm, where monodomain features should dominate the magnetic properties of these samples, as was previously reported [3,4].

2. Experimental

Powder samples of LPCMO ($y = 0.30$) were synthesized following a microwave assisted denitration process described elsewhere [5]. In order to modify the final grain size

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of the powder samples, a final heat treatment at different temperatures was performed. Treatments during 2 h at 800, 1000, 1200 and 1400 °C were performed and the samples were labeled correspondingly. Samples were characterized by X-ray powder diffraction measurements and their average ϕ_G was estimated from the broadening of the strongest diffraction peak, using the well-known Scherrer formula.

DC magnetization measurements as a function of temperature in the 10–300 K range were performed using a SQUID magnetometer. AC susceptibility ($\chi_{AC}(T) = \chi' + j\chi''$) was measured as a function of temperature in the same temperature range applying high hydrostatic pressures up to 10 kbar. To apply pressure, a self-clamping cell was used with a 50–50 mixture of kerosene and transformer oil as the pressure transmitting medium. The applied AC magnetic field was ~1 Oe and the excitation frequency was varied from 130 Hz to 13 kHz.

3. Results and discussion

X-ray powder diffraction patterns indicate that the synthesized samples are crystalline single phases. Increasing the temperature of the final heat treatment produces a reduction of the linewidth that can be associated with an increase of ϕ_G, with estimated values ranging from 40 nm (sample 800) to ~1000 nm (sample 1400). Cell parameters are also influenced by ϕ_G. The reduction of ϕ_G down to 40 nm produces an increase of the *c* crystallographic axis (~0.2%) and a compression in the *ab* plane of the perovskite structure, without a significant change of the unit cell volume. The grain size sensitivity of the magnetization as a function of temperature can be observed in Fig. 1. Part of the rich phase diagram of this compound can be depicted in this FCC $M(T)$ curve: a charge order and antiferromagnetic (AF) transition at $T_{co} \simeq 225$ K and the two increasing steps that correspond to the ferromagnetic ordering of different domains (T_{c1} and T_{c2}). A more complex magnetic behavior was recently reported for this compound [6,7], related to the phase separation regime which includes cluster-glass-like properties at low temperature ($T = T_g$) and the possible existence of a consolute point at temperatures ~T_g [8].

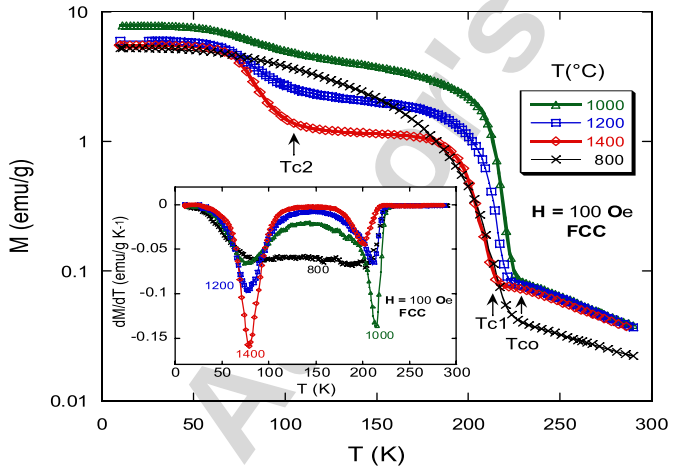

Fig. 1. Temperature dependence of the field-cooled-cooling (FCC) magnetization at 100 Oe of LPCMO ($y = 0.3$) powders with different final temperature treatment. The inset shows the temperature derivative of the magnetization as a function of temperature. The reduction of ϕ_G clearly affects the distribution of ferromagnetic phases (with transition temperatures T_{c1} and T_{c2}, indicated for sample 1400). A decrease of the contribution to magnetization of the low-temperature ferromagnetic phase can be observed with a concomitant increase of the one developed at T_{c1}.

It is clear, from the temperature derivative dM/dT, shown in Fig. 1 , that the reduction of ϕ_G favors the high temperature FM transition (T_{c1}) at expenses of the low temperature one (T_{c2}). It also increases the value of T_{c1} and the low temperature saturation magnetization. While this effect is systematic for samples 1000–1400, the behavior for the sample 800 is quite different, as was previously reported for samples with nanometric grain size. For temperatures below T_c a nearly constant dM/dT can be observed.

The temperature dependence of χ' for sample 1000 at different hydrostatic pressures is shown in Fig. 2. Similar results are obtained for samples 1200 and 1400. Pressure increases T_c and the magnitude of χ' while it reduces the irreversibility associated with the PS regime. This behavior is similar to that obtained for bulk samples, where $dT_c/dP \sim 2$ K/kbar. The anomalous behavior is, again, observed for sample 800, as a frequency and pressure-independent χ' peak, shown in Fig. 3. This behavior does not obey to the expected superparamagnetic properties, where usually the blocking temperature increases with increasing frequency. Pressure modifies the onset of T_{c1} (also with the same slope of bulk samples) and depresses the CO–AF ordering at a −35 K/kbar rate, as shown in Fig. 4. Only when $T_{CO-AF}(P) \leqslant T_{c1}$, pressure broadens the high temperature side of the peak at a 7 K/kbar rate (dT_{cp}/dP).

These results indicate that pressure effects on magnetic ordering are not influenced by nanostructuration, as the dTc/dP obtained for all the samples (even for sample 800)

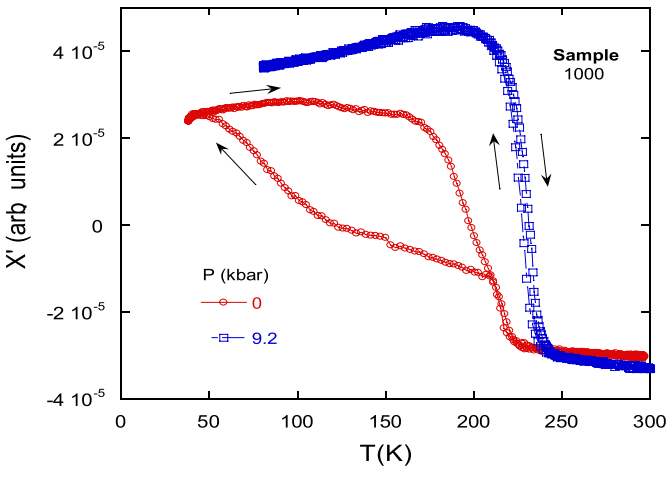

Fig. 2. χ' as a function of temperature of the LPCMO powder (sample 1000, $y = 0.3$).

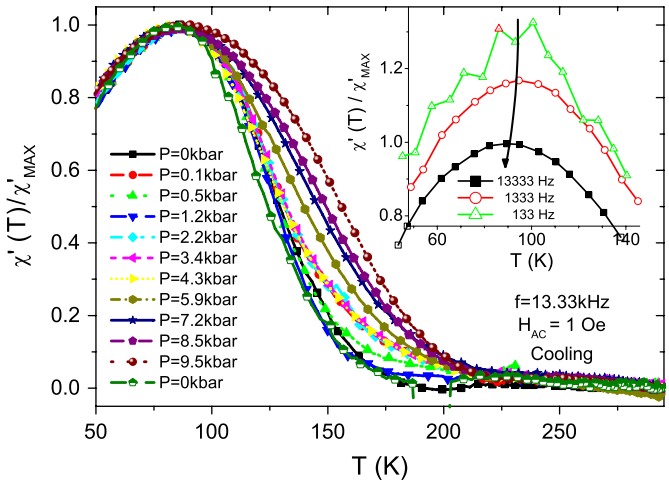

Fig. 3. Pressure sensitivity of χ' as a function of temperature for the LPCMO powder (800, $y = 0.3$). The inset shows a nearly frequency-independent peak.

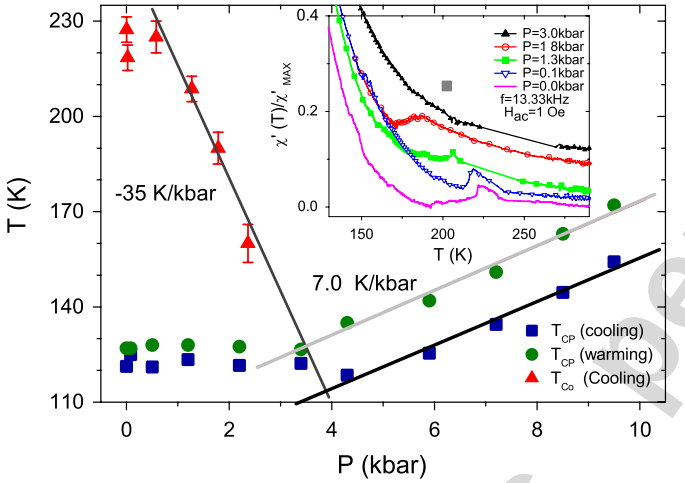

Fig. 4. Phase diagram for the LPCMO powder (800, $y = 0.3$). The inset shows a detail of the pressure sensitivity of the CO–AF transition. The pressure dependence of T_{c1}, not shown for clarity, is similar to that obtained for bulk samples. T_{cp} were determined from the peak of the temperature derivative of χ'.

are nearly the same as for bulk material. The increase of T_{c1} and the changes detected in the cell parameters as ϕ_G is reduced are consistent with an internal pressure developed by the constrains imposed by ϕ_G. The increase in T_{c1} observed as a consequence of the reduction of ϕ_G down to 40 nm represents an equivalent internal hydrostatic pressure of ~6 kbar.

4. Conclusions

We have presented in this paper the sensitivity to grain size of the magnetization and of pressure effects on LPCMO powders. We have shown that the reduction of ϕ_G modifies the structural and magnetic properties as an internal pressure. External pressure effects on ferromagnetic ordering remains unchanged by ϕ_G, although sample 800 (ϕ_G~40 nm) has a particular magnetic behavior. For this sample, $\chi'(T)$ seems to be closely influenced by the presence of the CO–AF phase and presents a pressure and a frequency independent peak, which is not the typical behavior expected for a superparamagnetic sample. Further work is needed to understand the behavior of the $\chi'(T)$ signal.

Acknowledgments

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