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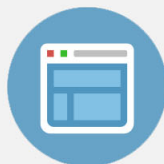
Temperature dependence of the magnetic properties in LaMnO$_{3+\delta}$

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Data are presented on the thermal dependence of the hysteretic properties of cationic vacancies including manganite samples of composition LaMnO$_{3+\delta}$ (δ=0.05 and 0.12). Our results evidence the presence in both samples of two magnetic phases having ferro- and antiferromagnetic orders, respectively. The temperature dependence of the coercivity and relaxational properties of the samples is closely linked to the connectivity of the magnetic moment bearing Mn^{3+}–Mn^{4+} ferromagnetic clusters that demagnetize independently in the case of the δ=0.05 sample and collectively in that of the δ=0.12 one, as evidenced from the activation volume results (δ=0.05) which yielded a size of the same order magnitude as that obtained in previous works for the Mn^{3+}–Mn^{4+} ferromagnetic cluster size. © *2006 American Institute of Physics.*
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I. INTRODUCTION

Perovskite materials of general formula LaMnO$_{3+\delta}$ have stimulated many research efforts due to their magnetotransport properties, which involve nanometric phase segregation and the simultaneous occurrence of different magnetic ordering mechanisms. More concretely, it has been shown that the introduction of cationic vacancies plays a role equivalent to that of the divalent cationic substitutions as a hole creation mechanism[1] and therefore originate the occurrence in the samples of Mn^{4+}. This point has been confirmed through both structural studies and the measurement of magnetic properties[1,2] but the analysis of its consequences on the extrinsic magnetic properties (hysteretic and relaxational behavior) still requires a substantial amount of research.[3] Our purpose here is to measure the temperature dependence of the low-field magnetization as well as those of the hysteretic and relaxational parameters in two La manganite samples including different amounts of oxygen. The results will be discussed in terms of the magnetic phase distribution of the samples.

II. EXPERIMENT

Two different samples were prepared. Sample A, with a composition of La$_{0.98}$(Mn$^{4+}_{0.12}$Mn$^{3+}_{0.88}$)$_{0.98}$O$_3$ (or LaMnO$_{3.05}$),

was prepared by heating stoichiometric amounts of La$_2$O$_3$ and MnO$_2$ to 1400 °C for 110 h and then quenching the powders in air down to room temperature. A second sample (sample B), with a composition of La$_{0.96}$(Mn$^{4+}_{0.24}$Mn$^{3+}_{0.76}$)$_{0.96}$O$_3$ (or LaMnO$_{3.12}$) was prepared using the same heating conditions and cooling the powders in oxygen inside the furnace at 2 °C/min down to room temperature. The cationic composition was determined by inductive coupling plasma and electron probe microanalysis. Oxygen content and, therefore, the Mn^{4+}/Mn^{3+} ratio was determined by thermogravimetric analysis in a CAHN-D200 electrobalance with an uncertainty of about 1 per thousand. X-ray diffractograms showed the occurrence in sample A of an orthorhombic phase (*Pnma* space group) and of a rhombohedral one ($R\bar{3}c$ space group) in sample B.

The magnetic characterization of pressed powder cylinders (2 mm height × 18 mm diameter) of both samples was carried out using a vibrating sample magnetometer at temperatures ranging from 4.2 to 300 K under applied fields of up to 4 T.

III. RESULTS

In Figs. 1(a) and 1(b) we present temperature dependence of the magnetization, obtained under different applied fields and after zero-field cooling (ZFC) and field cooling (FC) the samples (the samples were not submitted to any
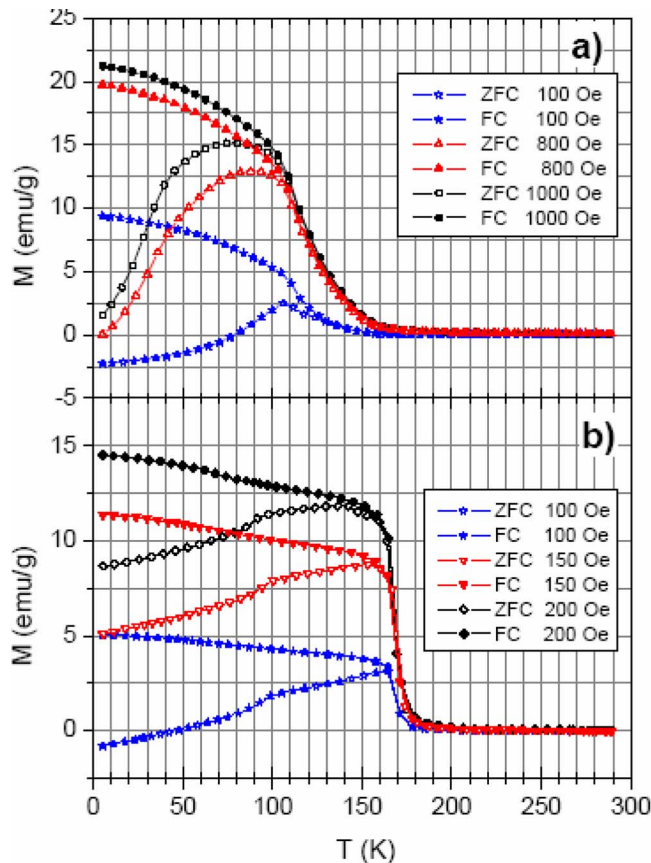
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FIG. 1. (Color online) Temperature dependence of the low-field magnetization measured for different applied fields in (a) sample A and (b) sample B.

FIG. 2. Hysteresis loop (and associated differential susceptibility) measured in sample A at 10 K.

magnetic field before measuring the ZFC curves). Our data evidence the presence in both of them of two transition temperatures, taking place at 110 and 130 K in the case of sample A and at 100 and 170 K in that of sample B.

Interestingly, when measuring $M(T)$ under a 100 Oe field, after ZFC the samples, it was possible to observe that the 4.2 K magnetization was negative (antiparallel to the measuring field direction) in both samples. This effect was observed for different nonpolarized samples, ruling out a possible dependence of the previous history of the sample. When increasing the applied field up to ca. 800 Oe (still below the low-temperature coercivity), in the case of sample A, and up to 200 Oe, in that of sample B, the ZFC lower-temperature magnetization values became positive. These results suggest that the two phases present in the sample couple in an antiparallel way at close to zero fields and that the coupling is not very strong since it can be overcome by applying a moderate field.

As for the hysteresis loops measured at different temperatures both samples exhibited a completely different behavior. In Fig. 2 we have plotted the hysteresis loop (and the associated field dependence of the differential susceptibility) measured at 10 K and after FC in sample A. The field dependence of the magnetization evidenced the presence of two phases (one of them demagnetizing at low field and the second one at a field of the order of 2000 Oe) and confirmed the fact that they should be only weakly coupled since the differential susceptibility peaks were clearly independent. In
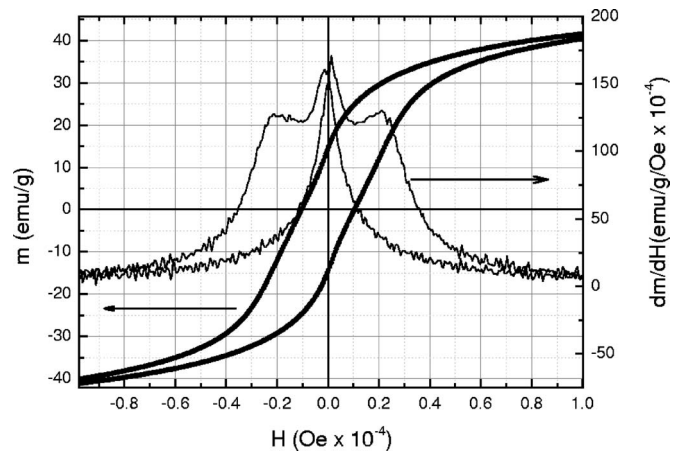
agreement with this, a very small loop shift (of the order of tens of oersteds) in the sense of the fields contrary to the saturation one was observed after FC the sample. The hysteretic behavior of sample A at higher temperatures was characterized by a rapid decrease of the coercivity and the observation of a single peak in the field dependence of the differential susceptibility at temperatures higher than 100 K.

In the case of sample B the loops measured at increasing temperatures (not shown here for the sake of brevity) evidenced both the occurrence of a soft magnetic behavior (with coercivities always below a few tens of oersteds) and the absence at low temperatures of any indication of independent reversal of the phases present in the sample.

The elevated coercivity of sample A allowed characterizing the thermally activated magnetization reversal (relaxation) processes taking place in that sample. That characterization was carried out by measuring the time evolution of the magnetization when keeping the sample under constant applied fields (in the range from zero up to above the coercivity) and temperature (three temperatures were considered: 10 and 75 K, both of them below the two observed transformation/blocking processes, and 110 K, above the low-temperature transformation/blocking process but below the high temperature one).

The relaxation results evidenced the occurrence at all the measuring fields and temperatures of time decays of the magnetization of logarithmic type, $M(t) = M(0)(1 - S \ln t)$, with t being time and $M(t)$ the temporal dependent magnetization [$M(0)$ is the magnetization at time $t=0$]. An example of the obtained data and their fit are shown in Fig. 3. From these decays it was possible to evaluate the field dependence of the magnetic viscosity coefficient (S);[4] the results measured at 10 K for sample A are shown in Fig. 3 as an inset. These data were used to calculate at different temperatures (T) the activation volume v_{ac} associated to the demagnetization of the harder phase through the relationship $v_{ac} = k_B T \chi_{irr} / S M_s$, where χ_{irr} is the irreversible susceptibility and M_s the saturation magnetization.[5] The results corresponding to the thermal dependence of the activation volume diameter are shown in Fig. 4.
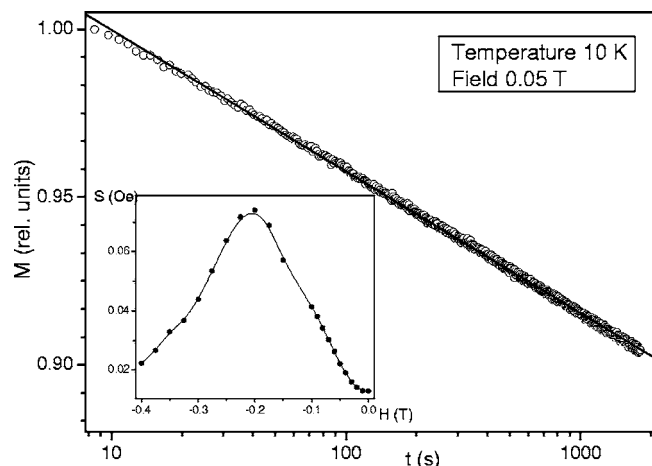
FIG. 3. Magnetic relaxation of sample A measured at 10 K under an applied field of 0.05 T. The experimental points (open circles) are fitted to a logarithmic law of the form $M(t) = M(0) - S \ln t$. The inset shows the values of the magnetic viscosity (S) obtained at different fields at a temperature of 10 K.

IV. DISCUSSION

The $LaMnO_3$ phase is characterized by a long-range A-type antiferromagnetic order, linked to superexchange between the Mn^{+3} pairs and with a transition temperature of 140 K.[6] The modification of the cationic distribution of this phase to introduce Mn^{+4}, either through cationic substitution or through the introduction of vacancies, results on the observation at low temperature of ferromagnetic clusters associated to $Mn^{3+}-Mn^{4+}$ pairs embedded in the $Mn^{3+}-Mn^{3+}$ antiferromagnetic matrix. At the site of a Mn^{4+}, the double exchange interaction results on the formation of a "ferromagnetic cluster" linked to the parallelism between the moments of the Mn^{4+} and those of its first Mn^{3+} neighbors. The particular laminar structure of the antiferromagnetic phase originates from the fact that the $Mn^{3+}-Mn^{4+}$ ferromagnetic cluster acts like an exchange bridge between its neighboring top and down planes, whose moments point along the same direction than the net moment of the $Mn^{3+}-Mn^{4+}$ cluster does.

In our samples we have measured transition temperatures for the antiferromagnetic phase lower than that measured in a Mn^{4+} free sample. In the case of sample A the transition blocking temperature was 110 K, whereas in that of sample B was 95 K (slightly varying with the field applied during the measurement). These results are directly linked to the way in which the cationic distribution of our samples was modified, i.e., to the presence of different concentrations of vacancies. As it was possible to expect, we observed a lower transition temperature in the case of the sample having the larger concentration of vacancies (sample B, ca. 4%) which simply reflects the lower average number in this sample of $Mn^{3+}-Mn^{3+}$ pairs originated by the occurrence of broken bonds. It is also interesting to indicate the fact that the destabilization of the antiferromagnetic structure (measurable field variation of the transition temperature) is larger in the sample having the larger concentration of vacancies.

As for the $Mn^{3+}-Mn^{4+}$ ferromagnetic phase, the evaluation of the activation volume transverse dimension reveals that the thermally reversed regions have a typical dimension which, at temperatures below that of transition/blocking of the antiferromagnetic matrix, is lower than 1 nm and therefore comparable with that associated to the $Mn^{4+}-Mn^{3+}$ ferromagnetic clusters.[7] This datum allows us to explain the different behavior of our two samples as linked to the percolation of the $Mn^{3+}-Mn^{4+}$ clusters, in the case of sample B, and to the independent cluster demagnetization in that of sample A. In the latter case the hysteretic behavior is characterized by a large coercivity (typical of small size magnetic entities), whereas in the case of sample B the easy demagnetization is related to the propagation of the walls separating reversed and unreversed regions rendered possible by the percolation of the ferromagnetic sites (for this particular ferromagnetic phase configuration the global phase reversal can proceed from the sites exhibiting the lowest reversal field).
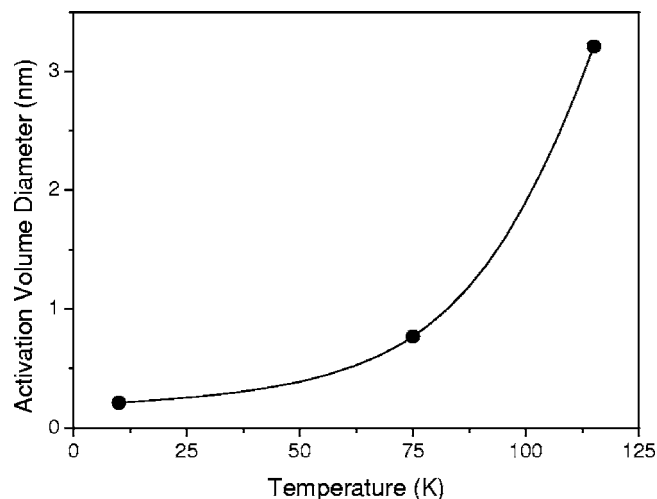
FIG. 4. Temperature dependence of the transverse dimension of the activation volume measured in sample A. The plotted data were evaluated at the maximum of the coefficient of magnetic viscosity, observed near the sample coercive force (demagnetization of the hard phase, see Fig. 2). The line is a guide for the eye.

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