Alternating current magnetic susceptibility measurements in $La_{1-x}Sr_xCoO_3$ ($x \leqslant 0.30$) below 300 K

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A dynamical magnetic susceptibility study on $La_{1-x}Sr_xCoO_3$ samples obtained by a coprecipitation method is reported for $x \leqslant 0.30$. For $x < 0.20$ differences between zero field cooled and field cooled dc magnetic susceptibility appear at a temperature T_a below the Curie point, $T_C \approx 240$ K, as well as a magnetic freezing point at a temperature $T_b < T_a$. Alternating current magnetic susceptibility shows two maxima at these temperatures, which is interpreted as the evidence of different interaction processes between ferromagnetic clusters mediated by a matrix of changing spin-state Co^{3+} ions. For $x \geqslant 0.20$ an unique blocking process seems to take place due to the percolation of the ferromagnetic clusters, making unimportant the contribution of the matrix. © *1997 American Institute of Physics.* [S0021-8979(97)74008-8]

I. INTRODUCTION

The interplay between magnetism and electrical conductivity in perovskite type oxides has been matter of study for several years, and with renewed interest since the discovery of a colossal magnetoresitance (CMR) in doped manganese-based compounds.[1] Specifically, the dependence on the thermal-history of the dc magnetization in these manganese oxides has been related to similar effects on their magnetoresistive properties, in the search for correlations between electronic conductivity and spin structure.[2] Their magnetization is basically determined by the spin moment of the Mn ions, coexisting Mn^{3+}–Mn^{3+} interactions with Mn^{3+}–Mn^{4+} double exchange ones.[3] Competition or frustration between antiferromagnetic and ferromagnetic interactions might be responsible for the magnetic irreversibilities in dc magnetization.

A search over other transition metal oxides with the perovskite structure, like $LaCoO_3$ has been object of interest, due to the possibility of finding similar CMR properties. Nevertheless, $LaCoO_3$ is a more complicated system. In addition to the peculiarities of similar perovskites the spin state of the Co^{3+} ions depends on the temperature range, presenting a $t_2^6e^0$ low-spin ($S=0$) configuration at low temperatures, which changes above 35 K to a $t_2^4e^2$ high-spin ($S=2$) state. Near 100 K both populations are stabilized in a ratio 50:50 in a dynamical equilibrium.[4] Substitution of La^{3+} with divalent ions, like Sr^{2+}, creates intermediate-spin metallic ferromagnetic clusters, the ferromagnetic interactions taking place between Co^{3+}/Co^{4+}, supposed to arise from a double exchange mechanism like in other related materials.[5] In the $La_{1-x}Sr_xCoO_3$ series these clusters are in a superparamagnetic state if $x<0.20$. At $x=0.20$, the coupling between the intermediate-spin metallic ferromagnetic clusters within an interpenetrating Co^{3+} matrix reaches a percolation threshold that orders the clusters ferromagnetically below $T_C \approx 240$ K.[6] Also at this point the dynamical behavior of the magnetization changes from a spin-glass to a cluster-glass regime.[7] In order to gain a deeper insight in the dynamical behavior of $La_{1-x}Sr_xCoO_3$ in the vicinity of $x=0.20$, we have performed ac susceptibility measurements at different frequencies.

II. EXPERIMENTAL DETAILS

$La_{1-x}Sr_xCoO_3$ samples were prepared by a coprecipitation method described elsewhere[6] from La_2O_3, $Co(NO_3)_2$ and $SrCoO_3$ as starting materials. The cobalt nitrate was first dissolved in water; the cobalt content in the solution was determined gravimetrically with anthranilic acid as the precipitating agent. Known volumes of this cobalt solution were then mixed with the corresponding lanthanum and strontium nitrate solutions obtained by dissolving in nitric acid weighted amounts of dry La_2O_3 and $SrCoO_3$. Coprecipitation at pH 11 was achieved by adding aqueous solutions of KOH and K_2CO_3 as precipitating agents. The precipitates were carefully washed, dried, and then decomposed at 750 °C. The obtained precursor powders were subsequently pressed into pellets, heated in air at 1000 °C for 77 h and cooled slowly to room temperature (1°/min).

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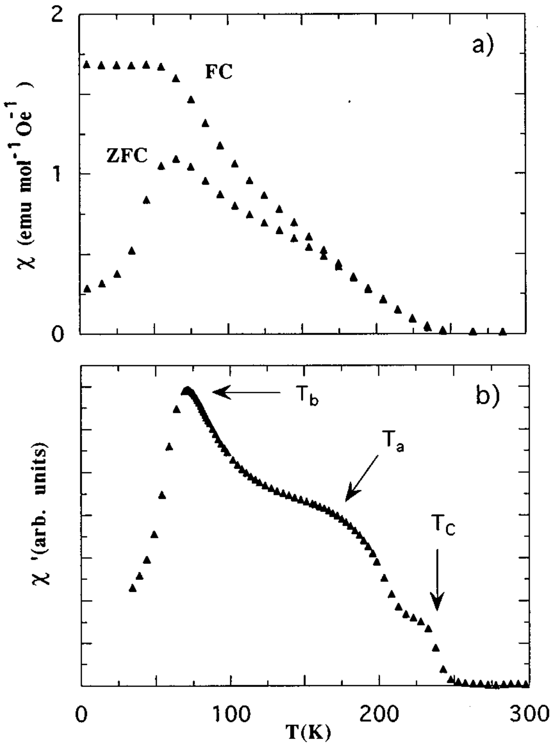

FIG. 1. (a) ZFC and FC dc magnetic susceptibility for $La_{0.85}Sr_{0.15}CoO_3$, (b) real part (χ') of the complex ac susceptibility vs temperature for the same sample. See the text for the definition of T_a, T_b and T_C.

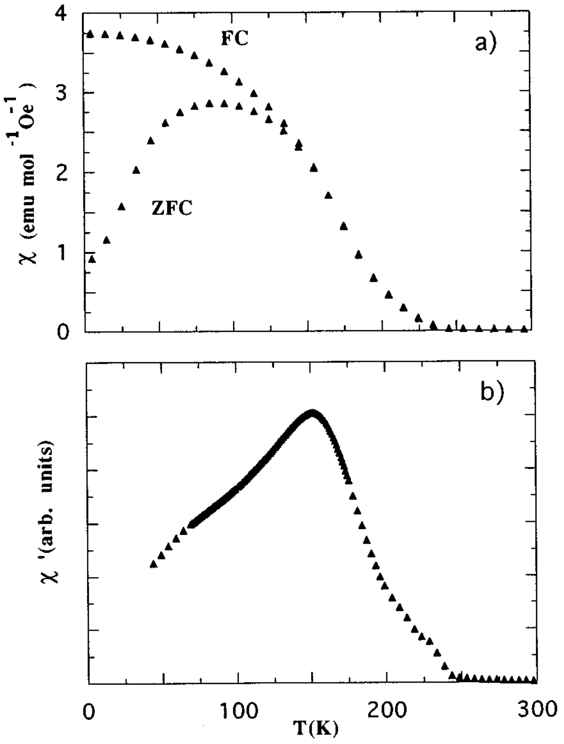

FIG. 2. (a) ZFC and FC magnetic susceptibility and (b) χ' vs temperature for $La_{0.8}Sr_{0.2}CoO_3$.

The product materials were examined by x-ray powder diffraction with a Philips PW 1729 diffractometer and Cu $K\alpha$=1.5418 Å radiation. NaCl was used as an internal standard. All the samples were single-phase materials. The lattice parameters calculated from the x-ray patterns were in agreement with those reported in literature.[8] The thermal stability of all the materials was checked by differential thermal analysis (DTA) and thermogravimetric analysis (TCA) with a Perkin-Elmer Thermal Analysis system. Iodometric titration were carried out to analyze the oxygen content of the materials: the samples were dissolved in acidified KI solutions, and the I_2 generated was titrated against a thiosulphate solution; the whole process was carried out under a nitrogen atmosphere. The iodometric titrations revealed that the samples are stoichiometric in oxygen. Particle size and morphology were studied with a JEOL 6400 scanning electron microscope. The coprecipitated samples showed individual particles with quite perfect spherical shapes with sizes between 700 and 900 nm.

The dc magnetic measurements were carried out using a Quantum Design SQUID magnetometer in the temperature range $4<T(\mathrm{K})<350$. The real and imaginary part components χ' and χ'' of the external complex ac susceptibility were measured as a function of temperature using a mutual inductance technique described elsewhere.[9] The calibration was performed using a $Gd_2(SO_4)_3 \cdot 8H_2O$ paramagnetic standard with the same shape and size as the investigated samples. Demagnetizing effects have been taken into account in the calculation of the so called internal susceptibility. Data were collected on warming from 13 to 300 K, after zero field cooling of the sample. For each run of measurements, the ac field was applied in the same direction as the dc field with a fixed amplitude of H_{ac}=300 A/m (3.75 Oe) at fixed frequencies f, ranging from 5 to 1000 Hz. The temperature of the samples was controlled with an accuracy of about 0.1 K.

III. RESULTS

In Fig. 1(a) zero field cooled (ZFC) and field cooled (FC) susceptibility measured at 1 kOe for $La_{0.85}Sr_{0.15}CoO_3$ are shown. The rapid onset of dc magnetic susceptibility at T_C=240 K indicates the ferromagnetic ordering within the clusters. Below T_C, the susceptibility increases with a small shoulder at about 170 K, where irreversibility appear. At 70 K a plateau in the FC curve and a clear cusp in the ZFC one are observed. The real part of the ac susceptibility for the same sample [Fig. 1(b)] shows three features: a sharp decrease of signal near T_C, a wide shoulder near T_a=170 K and a sharp maximum at T_b=70 K. All of them are scarcely dependent on the frequency of the applied field: the largest variation is shown by T_b, which shifts from 69 to 72 K when the frequency changes from 33 to 1000 Hz.

For x=0.20 several variations with respect to the previous sample are seen. The material is a ferromagnet below T_C,[6] and for this reason the susceptibility is much higher [Fig. 2(a)]. The clear cusp has disappeared and only a broad hump persists in the ZFC curve near 100 K. Alternating current measurements confirm the variation [Fig. 2(b)], with χ' presenting a clear maximum at 150 K. Small humps are visible at 70 K and near T_C.

Samples with $x>0.20$ show basically a same qualitative behavior, with a cusp in the ZFC branch near T_C [Fig. 3(a)]

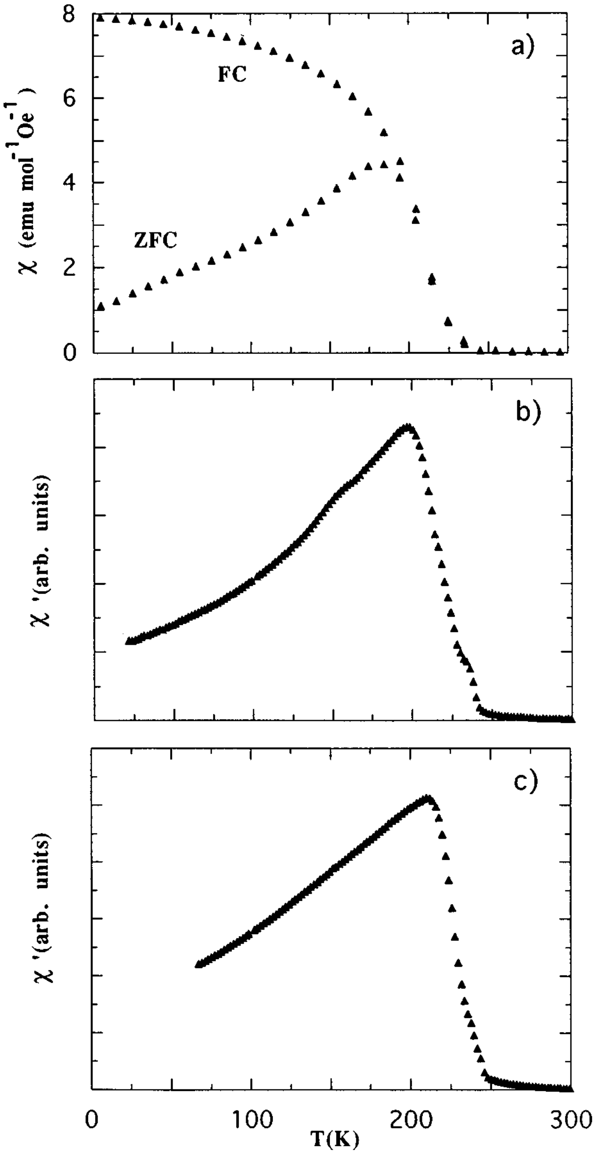

FIG. 3. (a) ZFC and FC magnetic susceptibility for $La_{0.75}Sr_{0.25}CoO_3$, (b) χ' vs temperature for the same sample, (c) χ' vs temperature for $La_{0.7}Sr_{0.3}CoO_3$.

and a sharp asymmetric frequency independent maximum in χ' at almost the same temperature [Figs. 3(b) and 3(c)]. T_C experiences a slight increase with the Sr content. The small anomaly in χ' near T_C is still present in these samples, although it appears hidden by the magnitude of the main peak.

IV. DISCUSSION

A first inspection of Fig. 1(a) could be interpreted as being a measurement taken in a conventional spin-glass, with a first splitting of FC and ZFC near T_a corresponding to the blocking of the larger clusters and a cusp at a temperature T_b in ZFC accompanied by a plateau in FC evidencing a final collective blocking of smaller clusters; and in fact it has been interpreted so.[7] But, in a conventional case a well defined maximum has to appear in the real part of ac susceptibility at the same temperature of the cusp in the ZFC curve.[10] This is not clearly the case here: the shoulder at T_a is telling us that the blocking process is not exactly the same as in T_b. What makes then the difference? As we said in Sec. I $La_{1-x}Sr_xCoO_3$ is somewhat more complex than other perovskites because of the changing nature of the Co spin state with composition and temperature. Upon small Sr doping the material segregates into hole-rich metallic ferromagnetic regions and a hole-poor matrix similar to $LaCoO_3$.[6] While the $S=0$ Co^{3+} ions are diamagnetic, the $S=2$ ones can indeed mediate the intercluster interactions. Thus, intercluster coupling through the matrix takes place at a relative high T (above 110 K). On the other hand, as below 110 K the Co^{3+} ions in the matrix tend to go low-spin, the matrix mediation weakens and the ferromagnetic clusters have more difficulties to couple, presenting for the new situation a second blocking point at T_b. The low temperature spin-glasslike characteristics, i.e., the sharp maximum in ZFC susceptibility and χ', and the plateau in FC susceptibility below T_b suggest a collective freezing of cluster moments.

The increase of Sr leads to a growing of cluster size and then to a decreasing role of the matrix in mediating intercluster interactions, reducing therefore the differences between the two aforementioned processes. For $x=0.20$, the large maxima observed in the ZFC susceptibility and χ', and the behavior of the FC susceptibility suggest a progressive blocking of cluster moments, not followed in this case by the collective freezing at lower temperature.

For higher Sr content ($x>0.20$) the ferromagnetic clusters reach a percolation threshold which orders them ferromagnetically below T_C. The matrix actually losses its role for so high Sr concentrations. The sharp maximum of χ' at a frequency independent temperature is due indeed to the ferromagnetic transition in the percolating cluster network.

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[1] R. Von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[2] R. Von Helmolt, J. Wecker, T. Lorentz, and K. Samwer, Appl. Phys. Lett. **67**, 2093 (1995).
[3] C. Zener, Phys. Rev. **81**, 440 (1951); P. G. de Gennes, *ibid.* **118**, 141 (1960).
[4] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967); K. Asai, P. Gehring, H. Chou, and G. Shirane, Phys. Rev. B **40**, 10982 (1989); M. A. Señarís-Rodríguez and J. B. Goodenough, J. Solid State Chem. **116**, 224 (1995).
[5] J. B. Goodenough and J. M. Longo, *Landolt-Börnstein*, edited by K. H. Hellwege (Springer, Berlin, 1970), New series, Group III, Vol. 4.
[6] M. A. Señarís-Rodríguez and J. B. Goodenough, J. Solid State Chem. **118**, 323 (1995).
[7] M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Jpn. **63**, 1486 (1994).
[8] P. M. Raccah and J. B. Goodenough, J. Appl. Phys. **39**, 1209 (1968).
[9] J. Mira, J. Castro, J. Rivas, D. Fiorani, R. Caciuffo, D. Rinaldi, C. Vázquez-Vázquez, J. Mahía, M. A. López-Quintela, T. E. Jones, and S. B. Oseroff, J. Appl. Phys. **76**, 7034 (1994).
[10] K. H. Fischer and J. A. Hertz, *Spin Glasses* (Cambridge University Press, New York, 1991).