Phase separation as origin of the magnetic anomalies in La_{0.85}Sr_{0.15}CoO₃

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The dependence of the ac-magnetic susceptibility of $La_{0.85}Sr_{0.15}CoO_3$ on the annealing temperature used during synthesis is addressed. Such dependence has been previously attributed to compositional inhomogeneities. Nevertheless, the presence of distinct phases with different chemical compositions is excluded after explorations by several techniques. Instead it is proposed that an electronic phase separation takes place in the material, whose state is changed after charge-carrier redistributions due to the thermal history of the samples, analogously to parent manganese-based perovskites. (© 2001 American Institute of Physics. [DOI: 10.1063/1.1365060]

I. INTRODUCTION

The renewal of interest on transition metal perovskites, triggered first by the discovery of high- T_C superconductors¹ and in a more decisive way by the reports on colossal magnetoresistive (CMR) effects,^{2,3} has contributed different points of view to understanding their behavior. The most recent is the realization of the important role of phase separation, evidenced recently in mixed-valence manganites by both electron microscopy⁴ and scanning tunneling spectroscopy,⁵ although it had been previously highlighted by Señarís-Rodríguez and Goodenough⁶ to explain the magnetic and electrical properties of Sr-doped cobalt perovskites. It is now well established that this phase separation is not due to chemical inhomogeneities or to the existence of phases with a different chemical composition.⁷ Many reports are appearing on the electronic phase-separated nature of such perovskites, both from direct^{4,5} or indirect results like conductivity fluctuations,^{8,9} electrical noise,¹⁰ and others,^{11–15} including theoretical analysis.^{16–18}

Concerning cobalt perovskites $La_{1-x}Sr_xCoO_3$, the idea was already proposed in the commented Ref. 6 and further discussed in several works.^{19–26} Among them, Mira *et al.*¹⁹ analyzed the ac-magnetic susceptibility of $La_{0.85}Sr_{0.15}CoO_3$ in the framework of interactions between hole-rich clusters imbedded in a hole-poor matrix. This work was criticized by Anil Kumar *et al.*,²⁷ who argued that only in the framework of a compositionally inhomogeneous sample could the magnetic behavior of the above-mentioned sample be explained. Nowadays, with numerous works reporting on the subject, it is becoming clearer and clearer that this is an obsolete argument but, despite this, we have estimated convenient to revisit the dependence on synthesis temperature of the acmagnetic susceptibilities of $La_{0.85}Sr_{0.15}CoO_3$.

II. EXPERIMENTAL DETAILS

La_{0.85}Sr_{0.15}CoO₃ samples were prepared by a coprecipitation method from La₂O₃, Co(NO₃)₂· 6H₂O, and SrCO₃ as starting materials.⁶ The cobalt nitrate was first dissolved in water; the cobalt content in the solution was determined gravimetrically with anthranilic acid as a precipitating agent. Known volumes of the cobalt solution were then mixed with corresponding lanthanum and strontium nitrate solutions, obtained by dissolving in nitric acid weighted amounts of dry La_2O_3 and SrCO₃. Coprecipitation at pH 11 was achieved by adding aqueous solutions of KOH and K₂CO₃ as precipitating agents. The precipitates were carefully washed, dried, and then decomposed at 1023 K. The obtained precursor powders were pressed into pellets, heated in air for 24 h at different temperatures (T_{an} = 1273, 1373, 1473, and 1573 K), and then cooled very slowly to room temperature (at 0.3 K/min down to 973 K and at 0.7 K/min thereafter).

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 are single-phase materials. The thermal stability of all the materials was checked by differential thermal analysis and thermogravimetric analysis with a Perkin–Elmer system. Iodometric titrations were carried out to analyze the oxygen content of the materials: the samples were dissolved in acidified KI solutions and the I₂ generated was titrated against a thiosulphate solution; the whole process was carried out under a nitrogen atmosphere. The iodo-

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FIG. 1. Variation, with synthesis temperature (T_{an}) , of the real part of the linear ac-magnetic susceptibility vs temperature of La_{0.85}Sr_{0.15}CoO₃. Increases of T_{an} lead to the elimination of the anomalies at 170 and 240 K and to the increase of the cusp at $T_g = 70$ K, although for the highest T_{an} the value at T_g is slightly reduced with respect to $T_{an} = 1473$ K.

metric titrations reveal that the samples are stoichiometric in oxygen, nevertheless, as the samples annealed at higher temperatures only dissolved in more acidic conditions, in which the experimental error increases, we cannot discard a slight oxygen-deficiency in these samples with respect to those annealed at lower temperatures. Particle size and morphology of the samples annealed at 1273 K 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.

High-resolution transmission electron microscopy observations were carried out with a Philips CM200 microscope offering a point to point resolution of 0.27 nm. The samples were prepared by depositing the powder material on a carbon-coated copper grid.

Real and imaginary components of the external complex ac-magnetic susceptibility were measured as a function of temperature with a Lake Shore 7000 system, using a mutual inductance technique. 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 with a driving field of amplitude $H_0=3.75$ Oe, oscillating at a frequency of 1 kHz. The temperature of the sample was controlled with an accuracy of about 0.1 K.

III. RESULTS

As expected, the dynamic magnetic behavior of $La_{0.85}Sr_{0.15}CoO_3$ is strongly dependent on the annealing temperature T_{an} . Figure 1 shows how the real part of its linear magnetic susceptibility changes with such synthesis condition. The data of the sample annealed at 1273 K are coincident with the ones of Ref. 19 but not with those of Ref. 27 (following the same route as here). In any case, the general trend can be regarded as similar, in spite of the quantitative differences that might lie on variations from laboratory to



FIG. 2. (a) High-resolution electron microscopy image taken along the [0, -1, 1] zone axis for $T_{an} = 1273$ K. (b) The same for $T_{an} = 1573$ K. Observe how the fringes lessen their intensity.

laboratory. There is a main peak at around $T_g \approx 70$ K common to all the cases. For low T_{an} a broad hump is present at about $T_a \approx 170$ K, and the onset of the magnetic signal, marking a magnetic transition, begins at $T_b \approx 240$ K. Both disappear when increasing T_{an} , and the one at T_g increases its signal. The maximum at T_g for $T_{an} = 1573$ K is frequency dependent and behaves in a similar way as canonical spin glasses.

In order to investigate hypothetical structural changes, high-resolution electron micrographs were taken along the [0, -1, 1] zone axis (Miller indices referred to the rhombohedral crystallographic cell). In Fig. 2(a) the micrograph of the T_{an} =1273 K sample is shown, and the presence of a stripe structure can be observed that much resembles the structure found in La_{1-x}Ca_xMnO₃ attributed to charge stripes.²⁸ This structure has been observed for x up to 0.30 and for T_{an} until 1573 K, in regions with sizes between 8 and 40 nm.²⁹ The increase of T_{an} modifies their number and

makes the stripes more diffuse, although they are still present for the highest $T_{\rm an}$ [Fig. 2 (b)]. It is worth mentioning that no superstructure spots were detected in any of the various crystallites selected and oriented along different zone axes. The coexistence of distinct phases with different chemical compositions has also been excluded by high-resolution neutron diffraction,²⁹ on the basis of the expansion of the unit cell with the increase of Sr doping,²¹ which would cause variations in the neutron diffraction patterns if different chemical phases were present.

IV. DISCUSSION

The key point is to identify what is changing with T_{an} , that is originating, so important variations in the ac magnetic susceptibility results. Anil Kumar et al. invoked compositional inhomogeneity,²⁷ more concretely, they claimed that the compounds La_{0.85}Sr_{0.15}CoO₃ synthesized at low temperature contain sufficient amounts of x = 0.5 and x = 0.2 phases in order to explain both the onset of signal at 240 K [which is similar to the Curie temperature of $La_{0.50}Sr_{0.50}CoO_3$ (Ref. 30)] and the hump at 170 K [in the order of the Curie temperature of $La_{0.80}Sr_{0.20}CoO_3$ (Ref. 30)]. In this picture the variation with T_{an} would be simply the elimination of such undesired phases and, consequently, the elimination of the anomalies at 170 and 240 K (in other words, to the homogenization of the material). Nevertheless, from both highresolution electron microscopy and high-resolution neutron diffraction it is concluded that this is not the case. The question then is opened again, and in order to solve it a new perspective must be adopted. Compositional inhomogeneities were invoked a few years ago to justify the anomalous behavior of manganese perovskites until evidences in favor of a phase separation scheme were becoming clearer and clearer, especially after the finding of magnetic polarons in CMR perovskites³¹ that can be viewed as a manifestation of phase segregation on a small scale.³² In fact, electronic phase separation has been suggested to be responsible for CMR.³³ Nowadays it is accepted that, in materials in which magnetism is due to double-exchange interactions, $^{34-36}$ below T_C a phase separation takes place if the concentration of dopants is increased enough.^{37–39} Then, inhomogeneous structures of metallic and insulating zones coexist, so that the ferromagnetic transition at T_C is viewed as a percolation of metallic ferromagnetic regions.^{4,5} Although it sounds like a brand new idea, it had been already proposed five years ago by Señarís-Rodríguez and Goodenough⁶ for cobalt perovskites. After our results, the exclusion of chemical inhomogeneities (at least in our samples) leads again to this hypothesis to explain the variation of ac magnetic susceptibility with T_{an} . In a material with double-exchange interactions like cobalt perovskites, with mixed valence Co³⁺/Co⁴⁺ ions due to the introduction of Sr^{2+} , the ferromagnetic ordering is linked to the presence of mobile electrons of e-orbital parentage that are shared by core $\operatorname{Co}^{4+}-t^5e^0$ configurations. Given that $T_{\rm an}$ modifies the stripe structure and the amount of ferromagnetic material is found to vary, it appears that the thermal processing induces a charge-carrier redistribution. For x<0.20 the percolation threshold of ferromagnetic regions in La_{1-x}Sr_xCoO₃ is not already reached,⁶ but a small net magnetic moment is measured for low T_{an} samples, indicating that some hole-rich regions might be interconnected for those cases. This net magnetic moment is eliminated upon increase of T_{an} , which would happen if the interconnecting paths were supressed. Even if the stripe structure is still distinct for the T_{an} =1573 K sample, it seems that the charge redistribution is enough to eliminate the interconnection between hole-rich clusters and, subsequently, the net moment at T=240 K in the T_{an} =1273 K case. In this framework, the stripe structure could be interpreted as a charge pattern, similar to that reported for manganites,²⁹ for which a similar dependence of the amount of ferromagnetic material on the thermal history has been reported, and attributed to a charge-carrier redistribution (see Ref. 7).

In summary, the presence of chemical inhomogeneities is excluded in $La_{0.85}Sr_{0.15}CoO_3$, whatever the synthesis temperature between 1273 and 1573 K. We propose that the existence of an electronic phase separation is the origin of the observed dependence of its magnetic ac susceptibility with the synthesis temperature.

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