Critical exponents of the ferromagnetic-paramagnetic phase transition of $La_{1-x}Sr_xCoO_3$ ($0.20 \leqslant x \leqslant 0.30$)

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The critical exponents of the second-order ferromagnetic-paramagnetic phase transition of $La_{1-x}Sr_xCoO_3$ ($0.20 \leqslant x \leqslant 0.30$) compounds are obtained. The results $0.43 \leqslant \beta \leqslant 0.46$, $1.39 \leqslant \gamma \leqslant 1.43$, and $4.02 \leqslant \delta \leqslant 4.38$ are qualitatively different than those reported in the literature for parent manganites, and are taken as the indication of the absence of long-range interactions below the Curie point. Electronic phase segregation in hole-rich ferromagnetic and hole-poor $LaCoO_3$-like regions is supposed to explain the observations. The hole-poor regions would dilute the magnetic lattice and prevent the occurrence of long-range order. Also, a spin transition of the Co^{3+} ions at T_C or the hole-poor regions (acting equivalently to missed spin clusters in amorphous ferromagnets) could be the reason for the high β value in the framework of a Heisenberg model.
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I. INTRODUCTION

Since the discovery of colossal magnetoresistance (CMR)[1] in manganese-based compounds $R_{1-x}B_xMnO_3$ (R = rare earth, B = alkaline ion), their ferromagnetic to paramagnetic (FM-PM) phase transition has been widely studied. Metal-insulator transitions,[2] anomalous lattice thermal expansion,[3] and temperature hysteresis in the resistivity around their Curie temperature T_C (Ref. 4) have been reported, and has been interpreted some times as evidence of a first-order transition.[4–6] The related perovskite system $La_{1-x}Sr_xCoO_3$, which does not show CMR,[7–9] has a similar magnetic behavior, with ferromagnetic interactions setting up with increasing x.[10–13] However, thermally and compositionally induced spin state changes in the Co ions[12,14] (from low-spin to intermediate- or high-spin states[15,16]) add some peculiarities to this system. The nonhomogeneity of the spin state of these ions might affect the cooperative behavior of the Co sublattice, and concretely, the FM-PM phase transition. The lack of a proper study of such a transition has led us to the determination of its critical exponents, in the search for differences between this system and manganites.

II. RESULTS

$La_{1-x}Sr_xCoO_3$ samples with $x = 0.20$, 0.25, and 0.30 were prepared by conventional ceramic methods. X-ray powder diffraction revealed that all the samples are single phase. The temperature dependence of resistivity was checked with a standard four probe technique. Magnetic data were taken by vibrating-sample magnetometry between 77 and 300 K up to 15 kOe maximum applied magnetic fields.

Zero field cooled (ZFC) and field cooled dc magnetization under magnetic fields of 1 kOe and 20 Oe were measured. Figure 1(a) shows ZFC data for $H = 20$ Oe. For $x = 0.25$ and 0.30 the increment in magnetization around $T = 240$ K (considered so far as the Curie temperature of the FM-PM phase transition) marks the onset of ferromagnetic interactions. For $x = 0.20$ this onset takes place at lower temperature. These results are basically in agreement with the previous literature, excepting the fact that in Ref. 13 a lower onset temperature for $x = 0.20$ is given. In this study, we pay particular attention to the behavior near the FM-PM phase transition. A first rough evaluation of the transition temperature was done using the determination of the maximum slope of the temperature dependence of the magnetization. Further measurements below and above the determined ordering temperature were performed. As a general example, Fig. 2 shows the magnetization vs field isotherms for the particular case $x = 0.30$. Note that saturation magnetization is not fully reached. The same was found for other compositions studied, in agreement with Itoh *et al.*,[13] who pointed out the absence of true long-range order (LRO) ferromagnetism in these compounds. From these types of measurements the initial susceptibility χ_0 was also evaluated. Corrections of the demagnetizing field were taken into account.

First of all, in order to discard the possibility of a first-order phase transition we have used the criterion given by Banerjee,[17] who detected the essential similarity between the Landau-Lifshitz[18] and Bean-Rodbell[19] approaches to the problem to give a simple criterion for the identification of first- and second-order magnetic transitions. The criterion

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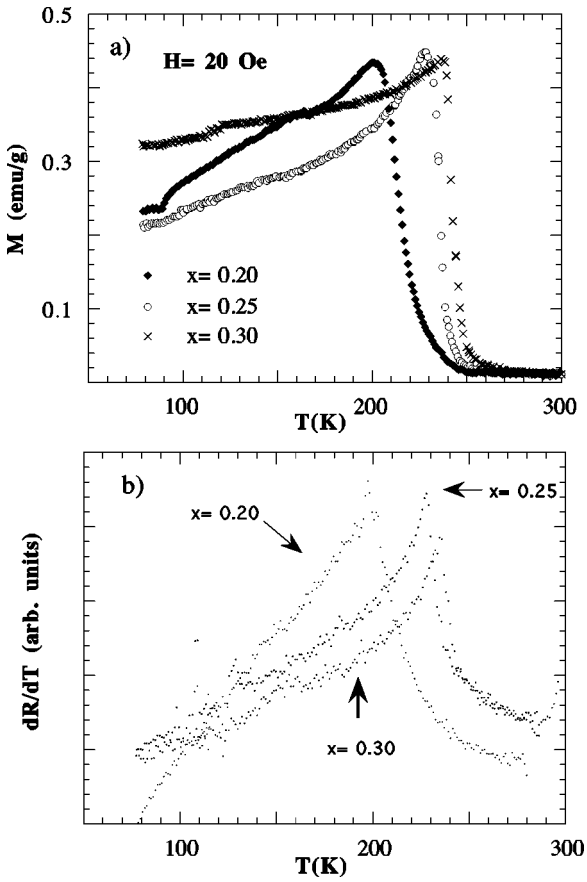

FIG. 1. (a) ZFC magnetization vs temperature under a field of 20 Oe and (b) derivative of the resistivity vs temperature curves for the studied samples (the temperatures at which they display the maxima are taken as T_C^*).

consists in inspecting the slope of isotherm plots of H/M vs M^2. In our case the slope is positive, so following Banerjee's criterion we assume that the FM-PM phase transition in these cobaltites is basically of second order. In the region around the phase transition, the following expressions hold for the spontaneous magnetization M_S and the initial susceptibility χ_0:

$$(\chi_0)^{-1}(T) \propto (T - T_C)^{1/\gamma} \quad \text{for} \quad T_C < T, \tag{1}$$

$$M_S(H) \propto H^{\delta} \quad \text{for} \quad T = T_C, \tag{2}$$

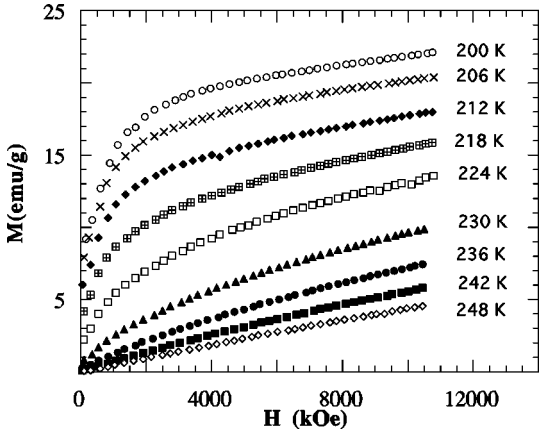

FIG. 2. M vs H curves at several temperatures for $La_{0.7}Sr_{0.3}CoO_3$.

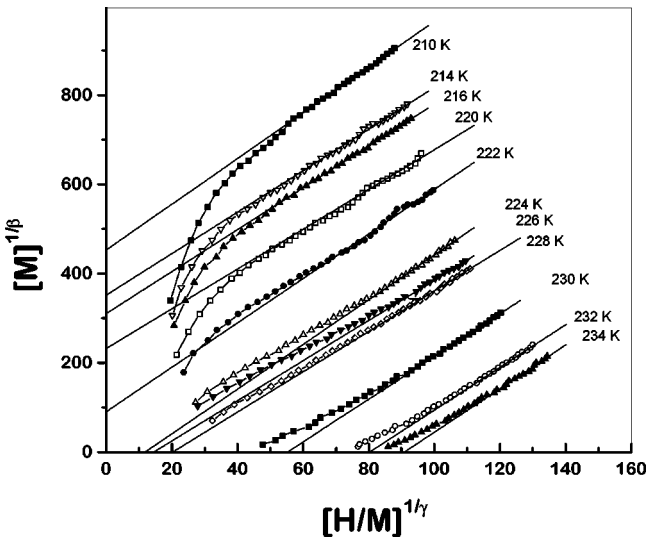

FIG. 3. Modified Arrott plot isotherms on $La_{0.75}Sr_{0.25}CoO_3$ for the optimum fitting ($\beta = 0.46$, $\gamma = 1.39$).

$$M_S(T) \propto (T_C - T)^{1/\beta} \quad \text{for} \quad T_C > T. \tag{3}$$

In order to properly determine the Curie temperature as well as the critical exponents β, γ, and δ for the spontaneous magnetization and the inverse initial susceptibility, respectively, the modified Arrott plot technique was used[20] considering the temperature interval $\epsilon = |T_C - T|/T_C < 0.05$. A self-consistent method to obtain the best fitting was considered. Starting from an initial estimation of the values of the critical exponents, modified Arrott plots are constructed. The spontaneous magnetization as a function of the temperature is determined from the intersection of the linear extrapolation of the straight line in the modified Arrott plots with the $M^{1/\beta}$ axis, while the inverse of the susceptibility corresponds to the intersection of these lines with the $(H/M)^{1/\gamma}$ axis. These data are fitted to the exponential behavior of Eqs. (1) and (3). New values for the critical exponents are thus obtained, and reintroduced in the scaling of the modified Arrott plot axis. The process is repeated until the iteration converges, leading to the optimum fitting values. Figure 3 shows the behavior for $x = 0.25$ of $M^{1/\beta}$ and $(H/M)^{1/\gamma}$ for the β and γ values corresponding to the optimum fitting. δ is calculated from the Widom scaling relation $\delta = 1 + \gamma/\beta$. Direct fits of δ taking into account that near T_C $M_s \approx H^{\delta}$ give values close to those obtained from the scaling relation ($\delta = 3.96$ for $x = 0.20$ and 4.07 for $x = 0.30$). The data for the critical temperature T_C and the critical exponents are collected in Table I. It must be emphasized that a quite careful study has to be done in order to properly achieve the critical exponents and

TABLE I. Transition temperatures obtained from modified Arrott plots (T_C), peak temperature of the temperature derivative of resistance (T_C^*), and critical exponents of the magnetic phase transition for $La_{1-x}Sr_xCoO_3$ compounds with $x = 0.20$, 0.25, 0.30.

x	T_C (K)	T_C^* (K)	β	γ	δ
0.20	198.5	198	0.46	1.39	4.02
0.25	222.3	228	0.46	1.39	4.02
0.30	223.4	235	0.43	1.43	4.38

T_C. Special care must be paid to the search for optimum fittings. The roughness of many of the fits found in the literature for the manganites explains the important differences found from author to author for the critical exponents in similar systems. Also, to fully describe the behavior at the phase transition not only the ferromagnetic phase, but also the paramagnetic one must be analyzed, in order to calculate a complete set of critical exponents.

The temperature dependence of resistivity was also checked. The results, shown in Fig. 1(b), are in agreement with previous reports.[8,9] The samples are metallic and a decrease in temperature within the ferromagnetic region affects only the thermal dependence of the metallic behavior under a temperature T_C^*, due to magnon scattering,[21] but not the metallic regime, that continues above T_C^*. The values of T_C^* are shown in Table I. From this table, the first remarkable result is the discrepancy between the values of the transition temperatures and the temperatures of the change of the thermal dependence of resistivity T_C^* for samples $x=0.25$ and 0.30. Provided that magnon dispersion is responsible for the change in the resistivity evolution, bulk ferromagnetism should be necessary for the variation of slope in resistivity, therefore we expected T_C^* to be equal to T_C, and, in fact, in the past it has been interpreted so. This means that authors willing to study critical phenomena through observations of the electrical conductivity should proceed with caution and be aware of the absence of a critical point at T_C^*.

III. DISCUSSION

After Fisher, Ma, and Nickel,[22] who used a renormalization group analysis of systems with exchange interaction of the form $J(r)=1/r^{d+\sigma}$ (d=dimension of the system, σ =range of the interaction), mean field critical exponents correspond to LRO ($\sigma>2$). Theoretical predictions give $\beta=0.5$, $\gamma=1$, $\delta=3$ for such a case. This was found by Mohan *et al.* in $La_{0.8}Sr_{0.2}MnO_3$,[23] who reported values of $\beta=0.5$, $\gamma=1.08$, $\delta=3.13$. It is plausible if the metallicity induced in these materials by ferromagnetic interactions is considered. Also, Lofland *et al.*[24] use $\beta=0.5$, $\gamma=1$ to fit the Curie point with Arrott plots in the same compound. It must be noted that in the manganites, for slightly higher doping ranges ($x>0.25$) some authors[4,5] have signaled the incompatibilities of a smooth second-order transition with their results and have pointed out the existence of a first-order transition attending to thermal irreversibilities in the resistance, abrupt variations in the double exchange coupling energy,[4] and a discontinuous change in the mean kinetic energy of the Mn $3d$ electrons.[6] In recent neutron diffraction studies[25] an anomalous change of the Co-O bond length has been observed in $La_{0.7}Sr_{0.3}CoO_3$ above $\sim$220 K (at a value similar to the one extracted for T_c from our fits), associated to a transition from itinerant to polaronic regime. This might be an argument to suspect a first-order transition; however, we have concluded before that this transition is of second order.

In principle, mean field exponents, similar to those in the manganites, should be expected in the FM-PM transition in $La_{1-x}Sr_xCoO_3$, but our results (Table I) give a β coefficient that is not as high as expected (0.5). Furthermore, the γ value is very close to that corresponding to a Heisenberg model. In the only report to our knowledge on a related compound, Menyuk, Raccah, and Dwight[26] studied the critical exponents of the FM-PM phase transition of $La_{0.5}Sr_{0.5}CoO_3$. For this doping degree the material does not present a distortion of the perovskite cubic structure[27] and they expected $\gamma=1.4$, applying the high-temperature thermal expansion calculation of the classical Heisenberg model with nearest-neighbor interactions.[28] They got 1.27, and tried to justify the deviation invoking the role of more-distant-neighbor interactions. Difficulties in the achievement of the correct phase might also be involved. In fact, Señarís-Rodríguez and Goodenough[12] have recently noted the difficulty to achieve full oxygen stoichiometry in $La_{1-x}Sr_xCoO_3$ for $x\geqslant 0.30$.

According to our results γ corresponds to a Heisenberg model but β is more mean-field-like, which distorts a global composition. As β is calculated from fittings below T_C [Eq. (3)] and γ above that point [Eq. (1)] there could be room for other changes not considered until now. One of them might be changes in the spin state of the Co^{3+} ions due to the alterations of the Co-O bond length. In fact several authors[29,30] have already stressed the strong influence of such a bond length on the electronic state of $LaCoO_3$. As we have already mentioned, the abrupt increase in the Co-O bond length for the $x=0.30$ sample at T_C could cause a spin-state transition simultaneously with the FM-PM transition. This picture would indicate that different regimes are fitted above and below T_C.

At this point one concern must be addressed. Why does $La_{1-x}Sr_xCoO_3$ ($x\geqslant 0.20$) behave so differently compared to doped manganites? Or equivalently, why do the studied materials behave so much like a Heisenberg model, provided that it does not apply properly to metallic conductors such as these? The main reason should be searched for in the changing nature of the Co^{3+} spin state, which makes the difference with the unaltered Mn^{3+} spin state in the manganites (as has been remarked on in several papers,[9,12,31] especially by Gayathri *et al.*[32] in a study of $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ mixed compounds), and in the phase segregation taking place in these cobaltites.[12] According to Señarís-Rodríguez and Goodenough[12] the Sr content leads to hole-rich metallic ferromagnetic regions and a hole-poor matrix similar to $LaCoO_3$. These regions are isolated until $x=0.20$, where the ferromagnetic clusters reach a percolation threshold and order ferromagnetically below T_C. But despite the percolation, the hole-poor matrix still persists and within it the Co^{3+} spin state is in a ratio 50:50 high-spin/low-spin. Here the hole-poor portions of the material with diamagnetic $S=0$ ions will dilute the magnetic lattice and prevent global LRO. This could also be the reason for the high β in the framework of the Heisenberg model. Poon and Durand[33] studied in the 1970's the critical behavior of amorphous ferromagnets. They detected a trend of enhanced values of β in amorphous alloys that contained at least one nonmagnetic component, and explained it in terms of a dilution model. They supported their results with simulations done by Müller-Krumbhaar[34] on homogeneous Heisenberg spin systems with missed spin clusters. In these simulations it was found that the local value of β increased close to the missed clusters (increasing, therefore, the the bulk value as well). In our case, the hole-poor regions might act as missed spins.

The discrepancies between the Curie temperature and the temperature of the change of slope in resistivity are similar

to those reported by Lofland *et al.*[24] in $La_{0.8}Sr_{0.2}MnO_3$, and our reasoning will be in some aspects similar: T_C marks only the break of cluster ordering, but the clusters can persist above T_C, and short-range magnetic correlations could take place between them. If the lifetime of such magnetic correlations is larger than the transport time, from an electronic point of view the carriers see a global ferromagneticlike environment. These different time scales underlie the coexistence of a magnon dispersion without having global ferromagnetism from a static measurement point of view. From $x=0.25$ to $x=0.30$, T_C remains almost the same, but T_C^* increases from 227 to 235 K, indicating that the clusters have grown and enable a FM environment to carriers up to higher temperatures. On the other hand, the growth does not affect the ordering among clusters, so T_C is not altered.

In summary, through an analysis of the critical exponents at the second-order FM-PM phase transition on the title compounds we have obtained that the system is better described with a Heisenberg model than with a mean field one, suitable for manganese perovskites. This also means that the absence of long-range interactions are probably due to the presence of segregated $LaCoO_3$-like hole-poor regions that would hinder them. Also, the β value is larger than expected for a Heisenberg model, which could be understood if a spin-state transition takes place at T_C (yielding different magnetic species above and below T_C) or if such hole-poor regions act equivalently to missed spin clusters in amorphous ferromagnets.

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