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Spin dynamics in the transition metal oxides $La_{2/3}A_{1/3}Mn_{1-x}Co_xO_3$, A = Ca, Sr ($0.5 \leq x \leq 1$)

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We present a detailed study of the polycrystalline perovskite system $La_{2/3}A_{1/3}Mn_{1-x}Co_xO_3$ A = Ca, Sr ($0.5 \leq x \leq 1$) including electrical resistance, magnetization, ac susceptibility. The static magnetic susceptibility was also measured up to 1000 K. The phase and lattice parameters of the compounds were determined by X-ray powder diffraction. The variation of x will change the relative fraction of both Mn and Co ions spin states. The data suggest the presence of correlated magnetic clusters at low temperatures as confirmed from the frequency dependence of the ac susceptibility and from non-linear ac susceptibility measurements. The electrical resistivity has been measured in the temperature range from 4 K to 300 K in high magnetic fields up to 7 T. The data are analyzed in a in a phase separation scenario.

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1. Introduction

Stimulated in part by the discovery of high temperature superconductivity in 1986 and the associated rapid progress in sample synthesis and crystal growth, there has been an enormous surge of interest in the properties of transition metal oxides. In these compounds the electronic configuration of the transition element can change with its valency and can take various spin states and this generates strongly correlated electron interactions. These interactions lead to complex magnetic and metal-insulator transitions. The fascinating physics of these materials is driving by the close coupling between magnetic, electronic and lattice degrees of freedom that seems to be responsible for some very intriguing phenomena, such as high-temperature superconductivity in cuprates, an anomalously large negative magnetoresistance, the so-called "giant or colossal magnetoresistance" (GMR and CMR), high spin polarization of conduction electrons, ferromagnetism in diluted semiconductors, etc. [1-8].

The discovery of the colossal magnetoresistance in manganese oxides stimulated a great effort for the research of these materials with a view to be integrated in device applications for read sensors or for spintronics. The compounds belonging to the perovskite systems $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ were probably the most investigated manganites due to their special properties among the others. For a broad range of doping, these compounds show a paramagnetic to ferromagnetic transition upon cooling, accompanied by an insulator-metal transition. The compounds show a very large negative magnetoresistance, and thus the system can be tuned between the low and high conductivity phases by applying a magnetic field. The occurrence of ferromagnetism and metallic behavior had been attributed to the double-exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions. When the core electrons of 3d shells of two Mn^{3+} and Mn^{4+} neighbors are ferromagnetically aligned, the e_g electron of the Mn^{3+} can easily hop onto the empty e_g orbital of its neighbor. Unfortunately, the CMR effect cannot be explained by only considering models involving DE. Several studies take also into account the Jahn-Teller character of Mn^{3+} ions (the lattice distortion of oxygen octahedra around Mn^{3+} ions that lifts the degenerancy of e_g electronic states), the charge-ordering (CO) of Mn^{3+}/Mn^{4+} ions on the manganese sites, the orbital-ordering (OO), the phase separation scenario (coexistence of nanoscale regions representing ferromagnetic (FM) metallic phase and antiferromagnetic (AFM) charge ordered (CO) phase). The optimum doping (when the conductivity is the highest) was found to be around $x = 0.33$ when the transition temperatures are $T_C \approx 260$ K for $La_{2/3}Ca_{1/3}MnO_3$ and $T_C \approx 360$ K for $La_{2/3}Sr_{1/3}MnO_3$. The magnetoresistance is really colossal for these compounds as much as 100000% in thin films [1]. Much effort has also been devoted to the manganites $La_{1-y}A_yM_{1-x}Mn_xO_3$ substituted at the Mn site, where A = Ca, Sr, Ba and M = Al, Co, Cr, Cu, Fe, Ni [9-12]. The substitutions lead to a decrease of T_C, an increase of resistivity and an enhancement of the magnetoresistance, for low M content. The electronic phase separation in manganites results in spin glass-like behavior, for these compounds.

The discovery of CMR effect in manganites, attracted the interest to the new perovskite-type materials such as cobaltites [1,7,8,13]. These compounds are of industrial interest due to their high electrical and ionic conductivities, their use as cathode materials in solid oxide fuel-cells, oxygen permeable membranes, in ferroelectric thin film capacitors, and active catalysts [4,7,13].

Compared to the very well studied CMR manganites, the cobaltites exhibit an additional degree of freedom due to the cobalt spin state in these compounds. $LaCoO_3$ is a diamagnetic insulator, at low temperatures with a low spin state (LS) of Co^{3+} (S = 0) and it does not contain Co^{4+}. The substitution of Ca^{2+} or Sr^{2+} for La^{3+} in this compound converts a certain number of Co^{3+} to Co^{4+} ions. Co^{3+} ions ($3d^6$) can be in low-spin (LS, S = 0), intermediate-spin (IS, S = 1) or high-spin (HS, S =2) states. Co^{4+} ions have a $3d^5$ configuration with LS (S = 1/2), IS (S = 3/2) and HS (S =5/2). The energy separation between LS and HS configuration is less than 0.1 eV and the higher spin states seems to stabilize in the range from 110 K to 310 K [1] because of their greater entropy. In the mixed valence doped compounds $La_{1-x}A_xCoO_3$, the Co^{4+}- Co^{3+} pairs can interact ferromagnetically due to the double-exchange interaction, while the Co^{3+}- Co^{3+} and Co^{4+}- Co^{4+} pairs can be coupled antiferromagnetically due to the superexchange interaction [18]. When manganese is also present in the system, some other interactions enter into the competition: the positive Mn^{3+}- Mn^{4+}, Mn^{3+}- Mn^{3+}, Co^{2+}- Mn^{4+} and negative Mn^{4+}- Mn^{4+}, Co^{2+}- Co^{2+}, Mn^{4+}- Co^{3+} superexchange interactions [19]. The competition of antiferromagnetic and ferromagnetic interactions can lead to the frustration, which is responsible for spin glass-like (cluster glass) behavior observed in some perovskite manganites and cobaltites.

In the case of low doping it is assumed that the system separates into isolated hole-rich FM clusters and hole-poor $LaCoO_3$-like matrix [14,18]. The substitution of Ca or Sr for La can maintain the Co ions in the IS state, even at low temperatures [15,16]. With increasing doping, the interaction between hole-rich regions occurs and a cluster glass phase can appear. The transition temperature to the cluster glass phase was found to be strongly dependent on the preparation conditions [15]. It is expected a different behavior of cobaltites doped with Ca, and doped with Sr due to the difference between the ionic radii of Ca^{2+} (1.35 Å) and Sr^{2+} (1.44 Å) and that of La^{3+}(1.32 Å) [15,16,18]. Some reports indicate that electrical and magnetic behavior of these cobaltites do not only depend on the chemical pressure but also on the disorder created in the system by doping [19].

When Mn is also present in the system $La_{1-y}A_yMn_{1-x}Co_xO_3$, where A is a divalent element (Ca, Sr, Ba), the complexity of the behavior is associated with the presence of the two transition metal ions and the multitude of their 3d electron configuration.

It is interesting to introduce Co in the optimum doped manganite $La_{2/3}A_{1/3}MnO_3$ to see how the transport, structural and magnetic properties change when it becomes a cobaltite $La_{2/3}A_{1/3}CoO_3$.

Troyanchuk et al. analyzed the electrical and magnetic properties of the system $La_{2/3}Ba_{1/3}(Mn_{1-x}Co_x)O_3$ in terms of Mn and Co ions interactions (as already mentioned) and concluded that for $x \ge 0.5$ the compounds are phase separated and the samples can be seen as mixtures of microdomains with different cobalt and manganese content [19].

In this paper we present the effect of Mn substitution by Co on the properties of $La_{2/3}A_{1/3}(Mn_{1-x}Co_x)O_3$ (A = Ca, Sr) for $0.5 \le x \le 1$.

2. Experimental

The $La_{2/3}A_{1/3}Mn_{1-x}Co_xO_3$, A=Ca, Sr ($x$= 0.5, 0.6, 0.7, 0.8, 0.9, 1) compounds were prepared by conventional solid state reactions at high temperatures. The mixtures of the respective oxides were calcined at 1200^0C and then they were pressed and sintered in air at 1300^0C, with intermediate grindings for both of the series. The powder x-ray diffraction patterns were recorded by using a Bruker D8 Advance AXS diffractometer with Cu Ka radiation. A multipurpose Oxford Instruments MagLab System 2000 was used for magnetization and ac susceptibility measurements. We used a Weiss-Forrer equipment to measure the dc susceptibility in the range from 300 to 1000 K. The resistivities were measured in a cryogen free magnet cryostat CFM-7 T (Cryogenic Ltd.) by the four-probe technique in the temperature range from 5 to 300 K and magnetic fields up to 7 T.

3. Results and discussion

The X-ray diffraction patterns of $La_{0.67}A_{0.33}Mn_{1-x}Co_xO_3$ showed that the compounds are mainly clean single phase, within the limit of experimental errors. The lattice parameters were obtained by Rietveld analysis, using the FULLPROF program. The analysis indicates that the samples are pseudo-cubic perovskites with slight rhombohedral distortions (space group $R\bar{3}c$). As an example, if we refer to the hexagonal system, we found: a_h = 5.5088(8) Å and c_h = 13.2229(3) Å, for x = 0.5 and a_h = 5.5441(7) Å and c_h = 13.1010(3) Å, for x = 1, when A = Ca. For A = Sr, a_h = 5.5547(8) Å and c_h = 13.3191(2) Å, for x = 0.5 and a_h = 5.4571(3) Å and c_h = 13.15562(0) Å for x = 1. The monotonic decrease of the unit cell volume with increasing Co content, for the two series, indicate a random distribution of the Mn and Co ions in the lattice, i.e. not long range Mn/Co order [17].

The magnetization measurements do not show saturation for none of the measured samples even at 5 K and 9 T. As shown in Fig. 1a, for A = Ca, and Fig. 1b for A = Sr, *M(H)* curves exhibit clear hysteresis at 5 K suggesting a ferromagnetic behavior but with any sign of saturation. It can be seen that the hysteresis loop is much narrower for the system with A = Sr.

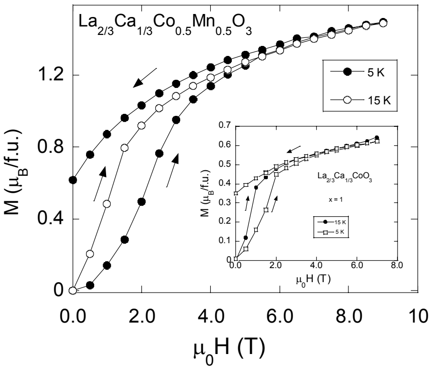

Fig. 1a. 5 K and 15 K M(H) curves for two samples for the case A = Ca.

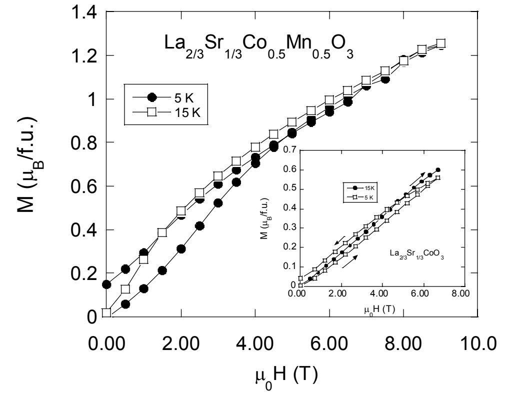

Fig. 1b. 5 K and 15 K M(H) curves for two samples for the case A = Sr.

The difficulty of approaching a magnetic saturation state has been attributed to the absence of true long-range order [14,20]. When the field was ramping up, the magnetization was even higher at 15 K than at 5 K, indicated that the system is phase separated containing FM and AFM clusters [7]. The coexistence of these two states leads to frustration, and thus to a spin glass-like behavior (cluster glass) [5,21,22,23]. To explain this situation, some hypotheses have been launched, like the presence of diamagnetic S = 0 ions, that can dilute the magnetic lattice [24].

The phase separation scenario was also confirmed by the frequency dependence of the cusp in ac susceptibility $\chi'(T)$ at the freezing temperature T_f, as can be seen in Figs. 2a and 2b, for the two systems. The presence of ferromagnetic clusters was also indicated by the negative peak of the nonlinear ac susceptibility of $\chi'_3(T)$ in the close vicinity of this temperature. $T_{\rm cusp}$, at 1 kHz and $H_{\rm ac}$ = 1 Oe, decreases from 166 K for x = 0.5 to 120 K for x = 1, when A = Ca. For the Sr doped system, $T_{\rm cusp}$ decreases from 220 K when x = 0.5 to 135 K for x = 1.

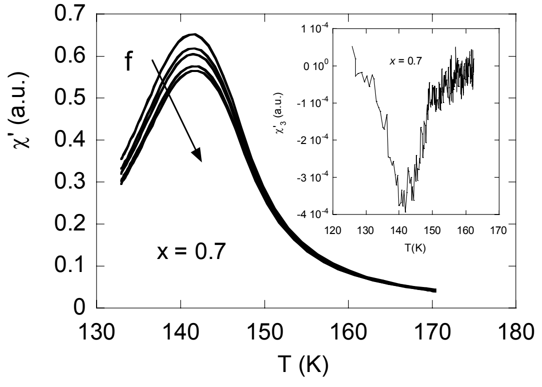

Fig. 2a. Frequency dependence of $\chi'(T)$ for the sample with x = 0.7. H_{ac} = 1 Oe, f = 100, 500, 1000, 5000, 10000 Hz. In the inset, $\chi'_3(T)$ for f = 1000 Hz ; A =Ca.

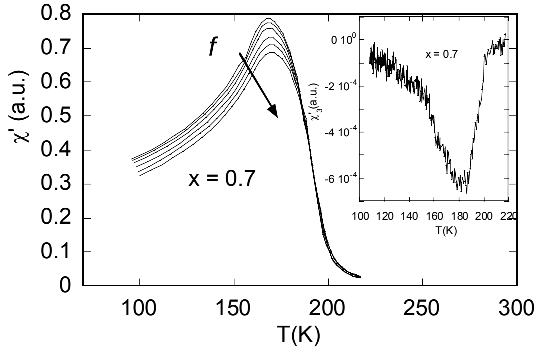

Fig. 2b. Frequency dependence of $\chi'(T)$ for the sample with x = 0.7. H_{ac} = 1 Oe, f = 100, 500, 1000, 5000, 10000 Hz. In the inset $\chi'_3(T)$ for, f = 1000 Hz. A =Sr.

The occurrence of FM clusters in the systems is also indicated by a curvature in the behavior of the temperature dependence of the inverse static magnetic susceptibility $1/\chi$ (not shown) at lower temperatures. In the high temperature range, 300 – 900 K, $1/\chi(T)$ has almost a linear behavior and this allow us to estimate the paramagnetic Curie temperatures, Θ, and the Curie constants (or the effective magnetic moments $\mu_{\rm eff}$).

When A = Ca, for low Co content Θ is positive, and for x = 0.5 we have Θ = 185 K (and the slope corresponds to $\mu_{\rm eff}$ ~ 4.40 μ_B) and it turns to be negative for higher concentrations and for x = 1, we get Θ = -50 K (and the slope corresponds to $\mu_{\rm eff}$ ~ 3.9 μ_B). When A = Sr, for x =0.5 we have Θ = 236 K (and the slope corresponds to $\mu_{\rm eff}$ ~ 4.80 μ_B) and it turns to be negative for $x \geq 0.8$, and for x = 1, we get Θ = -75 K (and the slope corresponds to $\mu_{\rm eff}$ ~ 3.9 μ_B). The data indicate the presence of Co^{3+} in all the three states LS, IS and HS in the x = 1 compounds.

Temperature dependences of electrical resistivity $\rho(T)$ in zero and 7 T are shown in Fig. 3a and 3b.

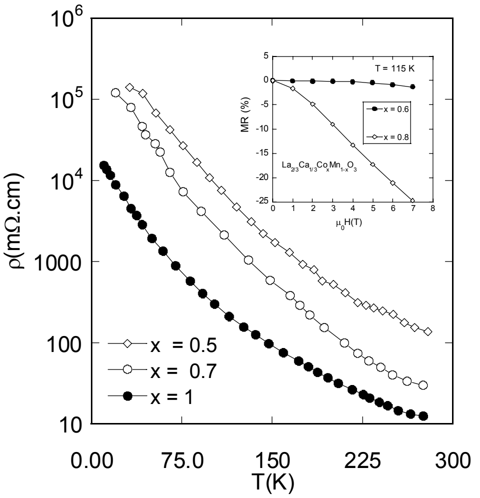

Fig. 3a. $\rho(T)$ curve for the samples with x =0.5, 0.7, 1 in 0 T. In inset $\rho(T)$ for x = 0.6 and 0.8 measured in 0 and 7 T. A = Ca.

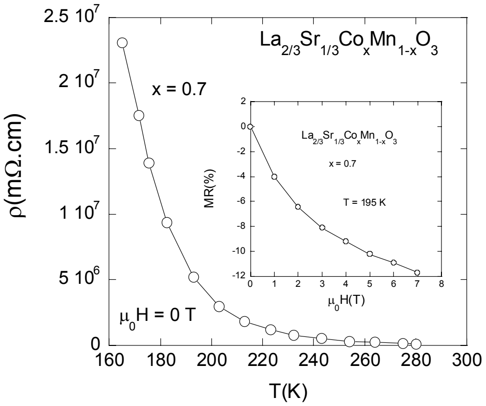

Fig. 3b. $\rho(T)$ curve for the samples with x =0.5, 0.7, 1 in 0 T. In inset $\rho(T)$ for x = 0.6 and 0.8 measured in 0 and 7 T. A = Sr.

The semiconducting behavior is observed for all the compositions in the whole temperature range for the both systems.

The magnetotransport properties do not seem to be linked to the occurrence of magnetic transition from paramagnetic state to the cluster glass state, as ac susceptibility measurements indicated. A negative magnetoresistance $[\rho(H)-\rho(0)]/\rho(0)$ of about 25 % was found for the samples with $x \geq 0.8$ in a magnetic field of 7 T and at 100 K, while for the other samples MR is only a few percents for the case when A = Ca.

For the other system, when A = Sr, the magnetoresitance does not exceed 18 % for the samples with $x \geq 0.7$ at 7 T while for the samples with a low Co content the magnetoresistance is only a few percent. The value of the resistivity decreases with increasing Co content and it reaches the lowest value for $x = 1$, for both the systems. The higher values of the resistivities and the low magnetoresistance, for the low Co content samples, probably, is a combined result of the high disorder created in the system and of the grain boundaries conduction. The doping with Ca^{2+} or Sr^{2+} will force some of Mn ions to be Mn^{4+} (more than in the absence of this doping). The charge excess can be compensated by Co^{2+} ions, supplying more hoping electrons for the Co^{3+} matrix [17]. This behavior suggests that the Co subsystem has the main role in electrical conduction. The low values of the resistivities in the high temperature region can be attributed to the disproportionation effect for Co^{3+} ions in Co^{2+} and Co^{4+} [17].

4. Conclusions

The solid solutions $La_{2/3}A_{1/3}Mn_{1-x}Co_xO_3$, A = Ca, Sr ($0.5 \le x \le 1$) form perovskite structure with rhombohedral symmetry. The lattice parameters do not change too much when Ca is replaced by Sr in the system.

These materials are very complex systems with a multitude of interactions between the magnetic ions (Mn^{3+}, Mn^{4+}, Co^{2+}, Co^{3+}, Co^{4+}).

The Co substitution for Mn for the both systems induced a glassy behavior. The presence of correlated magnetic clusters at low temperatures was confirmed from magnetization measurements, the frequency dependence of the ac susceptibility and from non-linear ac susceptibility measurements. This state can be seen as composed from FM clusters (hole rich regions) embedded in some AFM (or PM) regions. At low temperatures the FM clusters extend and interact each other and the cluster glass state occurs. The transition temperatures in the cluster glass state are sensible higher for the Sr doped system for the same Co and Mn content. This is probably a reminiscence from the behavior of the manganites $La_{2/3}A_{1/3}MnO_3$ with A = Ca and A = Sr.

The resistivity is higher, for low Co content in the samples and the magnetoresistance is only a few percents, probably due to the disorder created in the system and due to the grain boundary resistance. The resistance decreases and the magnetoresistance has higher values (25% for A = Ca, and 18% for A = Sr) for high Co content. This behavior suggests that the Co subsystem has the main role in electrical conduction. The electrical behavior can be explained by hopping of the carriers in a Co^{3+} matrix in the presence of a disproportionation effect in the high temperature region.

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