Magnetic and Transport Properties of La$_{0.7}$Sr$_{0.3}$Co$_{1-y}$Mn$_y$O$_3$

D.N.H. Nam$^★$ and N.X. Phuc

Lab of Magnetism and Superconductivity, Institute of Materials Science, NCST, Nghia Do - Caugiay - Hanoi, Vietnam

L.V. Bat$□$ and N.V. Khiem

Department of Science and Technology, Hongduc University, Thanhhoa, Vietnam

L.H. Son

International Training Institute for Materials Science, 1A Dai-Co-Viet, Hanoi, Vietnam

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While both La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$CoO$_3$ are ferromagnets with metallic conductivity below $T_c$ (360K and 220K, respectively), partial substitutions of Co by Mn in La$_{0.7}$Sr$_{0.3}$Co$_{1-y}$Mn$_y$O$_3$ ($y < 0.1$) drastically suppress the ferromagnetic long-range order pre-established by Co-O-Co double exchange and tune the conductivity towards insulating behavior. Since Mn-O-Mn double-exchange interactions are avoidable at low Mn-substitution levels, the deterioration of ferromagnetism and conductivity thus provides evidence for no Mn-O-Co double exchange (but antiferromagnetic superexchange) in the present system. At $y = 0.1$, the ferromagnetism is no longer observed; the system becomes an insulating spin-glass with $T_c \approx 62$K as estimated from the ac-susceptibility data using the conventional critical slowing-down scaling law. With further substitution ($y \geq 0.3$), the ferromagnetism is recovered ($T_c = 165$K for $y = 0.3$ and 200K for $y = 0.5$) while the resistivity continues increasing and exhibits insulating behavior. These results indicate that the substitution is not simply a mixture of La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$CoO$_3$, but produces a more complicated scenario of spin states, interactions and disorder.

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I. INTRODUCTION

In recent years, the hole-doped manganites $Ln_{1-x}A_xMnO_3$ ($Ln$: Lanthanides, $A$: Alkaline earth elements) are one of the most intensively studied topics, being strongly attractive to both basic research and technology due to their rich physics and potential prospects of application. Most of the undoped compounds, $Ln$MnO$_3$, are insulators with an antiferromagnetic (AF) order established by Mn$^{3+}$ ($t_{2g}^3 e_g^1$, $S = 2$) ions via AF superexchange (SE) interactions below $T_N$. The substitution of $Ln^{3+}$ by $A^{2+}$ converts an adapted number of Mn$^{3+}$ to Mn$^{4+}$ ($t_{2g}^2 g_{z}^1$, $S = 3/2$) giving rise to ferromagnetic (FM) Mn$^{3+}$-O$^{2-}$-Mn$^{4+}$ double-exchange (DE) interactions$\dagger$ where the transfer of the $e_y$ electron from Mn$^{3+}$ to Mn$^{4+}$ is favored by a parallel spin configuration. In pertinent substitution ranges, where the DE interactions dominate, some compounds could be metallic ferromagnets and exhibit a colossal magneto-resistance (CMR) phenomenon at $T_c$. The DE mechanism is also usually invoked to explain the magnetic and transport properties of the hole-doped cobaltites, $Ln_{1-x}A_x$CoO$_3$, where the double exchange is supposed to occur between Co$^{4+}$ and Co$^{3+}$.$\ddagger$ Since the heart of the DE mechanism is the mixed-valence state, it is then curious to know whether double-exchange occurs between different transition-metal ions, specially between Co and Mn ions. Furthermore, doping at B-sites in manganites or cobaltites is also a good probe to study the DE mechanism.

The magnetic and transport properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$Co$_{1-y}$Mn$_y$O$_3$ have been largely documented; both of them are double-exchange systems. In this work, we study the magnetic and transport properties of La$_{0.7}$Sr$_{0.3}$Co$_{1-y}$Mn$_y$O$_3$ where Co is partially substituted by Mn. It is interesting that while the parent systems are metallic ferromagnets ($T_c = 360$K for La$_{0.7}$Sr$_{0.3}$MnO$_3$, and 220K for La$_{0.7}$Sr$_{0.3}$CoO$_3$), the mixed products become insulating spin-glasses at certain substitution levels ($T_c \approx 62$K for $y = 0.1$). The results also provide a clear evidence for no DE interactions between Mn and Co ions.

II. EXPERIMENT

La$_{0.7}$Sr$_{0.3}$Co$_{1-y}$Mn$_y$O$_3$ samples with $y = 0$, 0.05, 0.1, 0.3, and 0.5 were prepared by conventional solid-state reaction method using La$_2$O$_3$, SrCO$_3$, Co$_3$O$_4$, and MnO$_2$ powders with purities of at least 99.9% as raw materials. The appropriate mixtures first underwent calcination at 1000°C for 24 hours. After being furnace at 1300°C for another 24 hours, the products were then sintered at 1350°C for 104 hours and slowly cooled to room temperature at 3°C/min rate. The heat treatment processes, always with very well pulverization and pelletization in between, had all taken place in air. X-ray powder diffraction measurements confirmed the single-phase property of all the samples. The temperature dependence of ac magnetic susceptibilities, $\chi'(T)$ and $\chi''(T)$, and resistivity, $\rho(T)$, were measured using a Closed Cycle Helium Refrigerator. The conventional four-probe method was
used for $\rho(T)$ measurements except for $y = 0.3$ and 0.5, which have rather high resistance, $\rho(T)$ data were read directly by a digital multimeter. Temperature dependent field-cooled (FC) and zero-field-cooled (ZFC) dc magnetizations, $M_{\text{FC}}(T)$ and $M_{\text{ZFC}}(T)$ respectively, were carried out by a noncommercial vibrating-sample and a Quantum Design MPMS5 magnetometer.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ curves measured in an applied field of $H_{\text{ex}} = 100$G. For all the samples except $y = 0.1$, which shows spin-glass behavior as shown in Fig. 4 and will be discussed later, there exists a cusp in the $M_{\text{ZFC}}(T)$ curves and a large separation of ZFC and FC magnetizations with lowering temperature in the FM phase. This behavior could be attributed to either (i) an appearance of frustration resulted from the competition of SE and DE interactions or (ii) a gradually freezing process of FM cluster moments caused by local anisotropy, or perhaps both. In general, this behavior is always expected if the measurements are carried out in an applied field smaller than the saturation field that develops faster than the increase of the saturation magnetization when the temperature is lowered. Quite similar behaviors have been observed for La$_{0.7}$Sr$_{0.3}$CoO$_3$ where the cusp of $M_{\text{ZFC}}(T)$ was explained by the competition between the energies of anisotropy and external fields acting on the ferromagnetic clusters existing in the system. In fact, La$_{0.7}$Sr$_{0.3}$CoO$_3$, and La$_{0.9}$Sr$_{0.2}$CoO$_3$ as well, was classified as ”cluster-glass” (CG) and we have also experienced that the magnetic and transport properties of the two compounds are qualitatively the same.

By fitting the susceptibility data, $\chi^{-1}(T) = H/M(T)$, at high temperatures in the paramagnetic region to the Curie-Weiss law, we find that the effective magnetic moment $\mu_{\text{eff}}$ per Co/Mn ion increases instantly with increasing $y$: $\mu_{\text{eff}} = 4.26, 4.49, 4.89$, and 5.09$\mu_B$ for $y = 0, 0.05, 0.1$, and 0.3, respectively. It is interesting that the variation of $\mu_{\text{eff}}$ does not incorporate with that of the phase transition temperature $T_c$. We attribute the increase of $\mu_{\text{eff}}$ to stronger cooperative Jahn-Teller distortions induced by the introduction of Mn$^{3+}$ ions that lift the degeneracy of $t_{2g}$ and $e_g$ orbits favoring them in higher-spin states.

A. The undoped compound, $y = 0$

The parent compound La$_{0.7}$Sr$_{0.3}$CoO$_3$ exhibits a paramagnetic (PM) - ferromagnetic phase transition at $T_c = 220$K in agreement with previously reported data. For ferromagnetic manganites, the conductivity is metallic below $T_c$ but insulating above $T_c$, showing a metallic-insulating (MI) transition at $T_c$, in consistence with the DE mechanism. However, as displayed in Fig. 2, the $\rho(T)$ curve of La$_{0.7}$Sr$_{0.3}$CoO$_3$ merely changes the slope at $T_c$ and still exhibits metallic behavior in the paramagnetic state. This feature is not expected for a typical DE system but can be understood considering the fact that the electronic configuration of the Co ions do not strictly obey Hund’s rule, an ingredient of the DE mechanism. That makes the $e_g$ electron of the Co ions quite mobile in the sense that it can hop between Co sites without strict requirement of a parallel localized-$t_{2g}$-spin configuration or a high applied field. By the way, this is one of the reasons for the magnetoresistance in cobaltites usually small compared to the manganites.

Another remarkable feature in the $\rho(T)$ curve is an upward ”tail” at low temperature, showing an MI-like transition. In the $\chi'(T)$ curve (not shown), we also observed a small ”hump" at $T_1 \sim 80$K signaling a transition to cluster-glass state, a feature very similar to that observed for La$_{0.5}$Sr$_{0.4}$CoO$_3$. We assume that this low-temperature resistance upturn is closely linked to the transition to cluster-glass state, where the cluster moments are randomly frozen since the metallicity according to DE mechanism is not expected in such glassy
states. This assumption is in conformity with the fact that $T_f$ is very close to the temperature where the upturn begins. The formation of the clusters is probably a consequence of an inhomogeneous distribution of Sr$^{2+}$ ions. The bigger the clusters, the higher the freezing temperature $T_f$. In order to check the influence of the inhomogeneity, we prepared a series of samples with varying the sintering time $t_s$. The longer $t_s$ would mean the better homogeneity and therefore the finer clusters and lower $T_f$. As expected, the samples sintered by short times show a huge low-temperature upturn with an increase of resistance by an order while metallic behavior is still observed at high temperature. For an example, Figure 3 displays the $\rho(T)$ and $\chi''(T)$ curves of a $y = 0$ sample after being sintered for 5 h at 1350°C. Note from this figure that $T_f$ and the resistance upturn temperature are still close to each other and both shift to higher temperatures (~150K) as a result of stronger inhomogeneity (i.e., larger cluster size) compared to those of the 104h-sintered sample. The upturn is fading out in the longer time sintered samples reducing to a minor tail (below ~70K) with $t_s = 104$h as shown in Fig. 2.

However, because of the weak intra-atomic Hund’s rule coupling of the Co ions, the freezing of magnetic moments is unlikely the only cause of the low-temperature resistance upturn although that certainly mainly contributes. The same effect would be observed if the sample contains insulating or semiconducting grain boundaries where disorder and spin frustration are strong and a Coulomb gap between small grains opens at low temperature. Because the grain boundaries are improved and so is the grain size by lasting $t_s$, the two effects caused by grain boundaries and cluster freezing are then mixed and indistinguishable in the polycrystalline samples.

**B. The lightly doped compounds, $y = 0.05$ and $0.1$**

The influence of the substitution is so strong. $T_c$ decreases from 220K for $y = 0$ to 192K for $y = 0.05$ and the ferromagnetic state is no longer observed in the $y = 0.1$ sample. Correspondingly, the resistivity increases strongly, and very pronounced is the upturn at low temperatures that develops with increasing Mn concentration and typical insulating behavior is obviously seen for $y = 0.1$. Since the Mn ions are very dilute in this substitution range, the substitution just creates new Mn-O-Co bonds at the expense of the existing Co-O-Co bonds, implying that there exists no Mn-O-Mn link. The severe deterioration of the ferromagnetism and conductivity by such a low doping level as $y = 0.05$ provides a strong evidence for no DE interactions via Mn-O-Co couplings. Moreover, these observations clearly indicate that the Mn-O-Co interactions are superexchange antiferromagnetic and much stronger than the DE Co-O-Co one. This conclusion is in agreement with other previously reported experiments, where it was found that a substitution of Co for Mn also severely suppresses the ferromagnetism and destroys the metallicity of La$_{0.7}$Sr$_{0.3}$MnO$_3$. Increasing Mn concentration results in an increase of the degree of frustration and disorder and, at $y = 0.1$, the system becomes an insulating spin-glass. Figure 4 presents the $M_{ZFC}(T)$ and $M_{FC}(T)$ curves and the inset the $\chi'(T)$ curves of the $y = 0.1$ sample measured at different frequencies $f = 0.037, 0.37, 3.7$, and 37 kHz. The results are very similar to those of a conventional spin glass. With lowering temperature from the paramagnetic phase, the spin relaxation of a spin-glass slows down and the maximum relaxation time $\tau$ diverges at $T_g$ when the system enters the spin-glass state. $\chi'$ attains a maximum at $T_f$ that shifts towards higher temperatures with higher frequencies. For the ac susceptibilities, $T_f$ defines the freezing temperature where the characteristic time of the measurement, $\tau_m = 1/2\pi f$, becomes smaller than $\tau$ when the temperature is lowered. An attempt at fitting the $T_f(f)$ data extracted from Fig. 4 to conventional slowing-down scaling law, $\tau/\tau_0 = [(T_f - T_g)/T_g]^{-2\nu}$, gives $\tau_0 = 1.1 \times 10^{-13}$ s, $2\nu = 8.2$, and $T_g = 61.8$ K, implying that the La$_{0.7}$Sr$_{0.3}$Co$_{0.8}$Mn$_{0.1}$O$_3$ compound is a conventional 3D spin-glass.

There is also a remarkable feature in the evolution towards insulating behavior of the system, as seen in Fig. 2, where the low-temperature resistance upturn develops with increasing $y$. The metallicity totally disappears once the system becomes a spin-glass in consensus with the DE mechanism. This indicates that the upturn in the Mn-doped compounds is closely related to the weakening of ferromagnetic correlation and the appearance of frustration and disorder, consolidating the above assumption that it has a tight relationship with the freezing of cluster moments.

The Mn ions are believed to always exist in high-spin states whereas, because of the comparable magnitude of the crystal field splitting and the Hund’s coupling en-
energy, the Co ions can exist in different spin states. The effective magnetic moment value of 4.26μB found for y = 0 does not allow us to extract qualitative information about the spin states of Co ions. However, qualitatively, μeff = 4.26μB implies that a part of Co ions, either of trivalence or tetravalence, or both, must exist in intermediate- and/or low-spin states. When increasing y from 0 to 0.05, the ferromagnetism is suppressed, however, μeff increases by an amount of 0.23μB, that is almost equal to the possible maximum contribution of 0.25 μB from the doped Mn ions in the case that all of them are Mn³⁺. This sounds as if (i) all Mn ions have replaced to only the low-spin state Co¹¹¹ sites or (ii) an amount of Co ions must have transferred to higher-spin states. Moreover, for the case of y = 0.1, the gain in μeff is 0.63μB while the possible maximum contribution from Mn ions (i.e., assuming they are all Mn³⁺) is only 0.49μB. This later case unambiguously indicates that, in this doping region, there are certainly significant amounts of Co ions converted to higher spin-states as a consequence of the substitution. Since Mn³⁺ are strong Jahn-Teller ions, it is possible that an introduction of Mn³⁺ into the system by the substitution induces stronger Jahn-Teller distortions lifting the degeneracy of t₂g and e_g orbits of Co ions, that favors a conversion of the Co ions to higher-spin states.

C. The heavily doped compounds, y = 0.3 and 0.5

With further substitution the ferromagnetism reappears at y = 0.3 with Tc = 165K, that increases to 200K for y = 0.5. When the Mn ions are dense, the probability for them to interact to each other is high. Assuming that the Mn ions exist in a mixed-valence state of Mn³⁺ and Mn⁴⁺, the recovery of the ferromagnetism is most probably due to the appearance of ferromagnetic Mn³⁺-O-Mn⁴⁺ DE interactions. In contrast, although the ferromagnetism is rapidly recovered, the resistivity continues increasing and exhibiting insulating behavior. This implies that the FM DE interactions are still strongly competed by AF SE interactions, and not strong enough to establish continuous pathways for the system to exhibit metallic behavior. A plausible explanation is that, in this doping range, the magnetic as well as electronic ordering is not uniform; the ferromagnetism signal comes from (metallic) ferromagnetic regions embedded in an insulating (non-ferromagnetic) matrix. For higher Mn concentrations, it was found in earlier experiments that, in this substitution range up to y = 1, Tc monotonously increases, and the metallic conductivity is gradually recovered when y being close to 1.

µeff increases strongly with increasing y from 0 to 0.1 and then slows down in the region 0.1 ≤ y ≤ 0.3. For the case of the lightly doped compounds, an over gain of µeff has told us that a number of Co ions must be converted to their higher-spin states. Nevertheless, that is not the case for the heavily doped compounds where the gain in µeff is moderate with respect to the substitution levels. Fortunately, the high values of µeff suggest that all of the Co ions are in high-spin states. For the case of y = 0.3, assuming that all Co and Mn ions are in high-spin states and the ratios Co³⁺/Co⁴⁺ and Mn³⁺/Mn⁴⁺ are kept at 7/3, we obtain µeff = 5.02μB, a value very close to that experimentally determined of 5.09μB. These facts lead to a suggestion that most of the Co ions are in high-spin states and no further spin-state conversion occurs when y goes above 0.3.

IV. CONCLUSION

The magnetic and transport properties of La₀.₇Sr₀.₃Co₁−yMn₉O₃ have been systematically studied and discussed in detail. The Mn substitution induces a conversion of Co ions to higher-spin states. The magnetic and transport properties of the system are tightly correlated. The obtained results provide a clear evidence for no double-exchange interaction between Mn and Co ions but strong antiferromagnetic superexchange ones. As a result, the competition of AF and FM interactions introduced by the substitution lead the system to become an insulating spin-glass at y = 0.1. For the samples with high Mn concentrations, y = 0.3 and 0.5, the magnetic as well as electronic phase is not uniform; (metallic) ferromagnetic clusters of Mn³⁺-O²⁻-Mn⁴⁺ bonds are formed on a (non-ferromagnetic) insulating background. We have also evidenced that a transition to glassy state could in principle destroy the ferromagnetic state metallicity of a double exchange ferromagnet.
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∗ Also at Physics Department, University of Cincinnati, Ohio; Electronic address: namdao@physics.uc.edu
† Also at The Ångström Laboratory, Uppsala University, Sweden.
1 C. Zener, Phys. Rev. 82, 403 (1951).
2 M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Jpn., 63, 1486 (1994).
3 D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Khiem, and N.X. Phuc, Phys. Rev. B 59, 4189 (1999).
4 R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M.A. Señarís-Rodríguez, P.G. Radaelli, D. Fiorani, and J.B. Goodenough, Phys. Rev. B 59, 1068 (1999).
5 Ll. Balcells, B. Martnez, F. Sandiumenge, and J. Fontcuberta, J. Magn. Magn. Mater. 211, 193 (2000).
6 J.B. Shi, F.C. Wu, and C.T. Lin, Appl. Phys. A 68, 577 (1999).
7 X.J. Fan, J.H. Zhang, X.G. Li, W.B. Wu, J.Y. Wan, T.J. Lee, and H.C. Ku, J. Phys.: Condens. Matter 11, 3141 (1999).