Relationship between spin order and transport and magnetotransport properties in La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Al$_x$O$_y$ compounds

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We analyzed the magnetic, transport, and magnetotransport properties of La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Al$_x$O$_y$ as a function of aluminum concentration, temperature, and magnetic field and we found that when the aluminum concentration is increased, magnetization and T_c decrease while resistivity and magnetoresistance increase, respectively. Such results are in agreement with the literature dealing with differently doped La-Mn perovskites and from this it can be hypothesized that magnetic and transport properties are correlated. Based on the analysis of our data and the available literature, we have formulated a phenomenological description which accounts for the general relationships between magnetic and transport characteristics. In the case of fully ferromagnetically ordered materials the magnetoresistance effect was attributed to the spin alignment induced by the magnetic field which opposes the thermal motion. The comparison between the experimental resistivity and magnetization data, and those calculated on the basis of our model, proves to be reasonably consistent, even on quantitative levels. In mixed ferro- and antiferromagnetically ordered materials ($T_c < RT$), the model we propose does not account for the experimental data. In this case we suggest a different phenomenological approach based on a field-induced spin reorientation transition, which qualitatively justifies the observed data. [S0163-1829(96)05842-0]

INTRODUCTION

The discovery of giant magnetoresistance effects in metallic multilayers[1] and granular films[2] generated renewed interest in Re-*M*-Mn-O compounds, where Re is a rare earth and *M* an alkaline earth or Pb. Such magnetic perovskites were discovered and extensively investigated by Jonker and Van Santen[3,4] in 1950 and their peculiar magnetotransport characteristics were ascribed to the partial substitution of the divalent ion (*M*) for the trivalent one (Re):[5] this was claimed to induce the onset of a mixed valence state in Mn, i.e., 3+ and 4+,[4,5] which, in turn, induced a ferromagnetic ordering, responsible for the quasimetallic transport characteristics. Initial attempts to correlate the magnetic and transport properties were made by Zener;[6] he suggested a double exchange mechanism between oxygen coupled Mn^{3+} and Mn^{4+}, and attributed the conduction to the Mn^{3+}-Mn^{4+} electron diffusion, activated by the exchange energy. In 1994 McCormack *et al.*[7] reported ''colossal'' magnetoresistance effects in La-Ca-Mn-O and this stimulated plenty of interest in the scientific community. Numerous papers dealing with the phenomenology of the magnetic and electrical properties of these compounds have been published within the last two years. However, the experimental data of different groups, dealing with materials of similar nominal compositions, were not well consistent. This is mainly due to the fact that the magnetic and transport characteristics of these compounds are controlled by the Mn oxidation state, which is strongly dependent on the synthesis conditions and the material history. As an example, in Fig. 1, we summarized some data relevant to the maximum value of resistivity, measured in a magnetic field, H,=0 (ρ_0 max), of samples with nominal composition close to La$_{0.67}$Ca$_{0.33}$MnO$_y$,[7-14] as a function of the Curie temperature T_c; ρ_0 max values obtained in the present study

were also reported. What mainly emerges from the analysis of the available experimental data is that, in spite of the significant scattering of the numerical values, constant relationships exist between the transport and magnetic characteristics, i.e., magnetic order temperature T_c, saturation magnetization M_S, and resistivity ρ. They can be summarized as follows: (i) ρ_0 max increases as T_c decreases; (ii) ρ_0 max generally occurs at $T=T_c$; (iii) materials with the lowest ferromagnetic ordering temperature exhibit the largest magnetoresistance, $\Delta\rho/\rho$; (iv) a great deal of evidence[13,15] exists which suggests that the resistivity and the magnetization of the same compound are correlated, even if the relevant mechanism is not well understood. In the report of McCormack *et al.*[7] it was hypothesized that the colossal magnetoresistance effects observed in La-Ca-Mn-O films could be at-
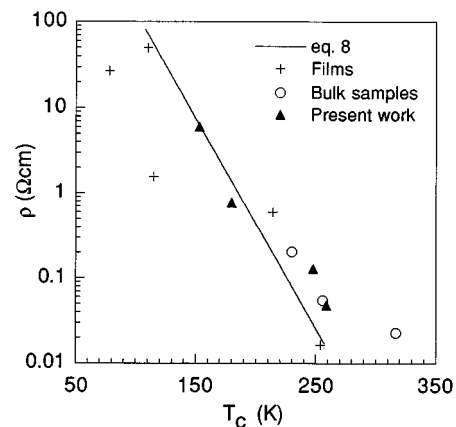

FIG. 1. Resistivity at $H=0$ (maximum values) vs T_c of Ca-substituted manganites, derived from independent experimental works (individual symbols), and calculated according to Eq. (8) (see text).

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TABLE I. Lattice parameter and average Mn oxidation state in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$. The calculated oxygen and Mn^{4+} stoichiometries are shown in the last columns.

Aluminum content, x	"a" parameter (Å)	Average Mn oxidation state	Oxygen stoichiometry	Mn^{4+} stoichiometry
0	3.8566 (5)	3.25	2.96	0.25
0.01	3.8512 (10)	3.27	2.97	0.27
0.05	3.8520 (8)	3.26	2.96	0.25
0.1	3.8342 (13)	3.28	2.96	0.25

tributed to some inadvertent aluminum doping due to the $LaAlO_3$ substrate, heated at 900 °C during the film processing. We found such a hypothesis quite plausible for two reasons: first, the diamagnetic Al^{3+} is expected to abate the properties of the magnetic oxides, in line with the experimental data presented by the authors, and, secondly, the resulting enhancement of the magnetotransport characteristics fulfills the general trend previously mentioned. In order to get insights into such phenomena, we systematically investigated the $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ system, with $0 \leq x \leq 0.1$. Special attention was paid to the materials preparation and the annealing procedure, and to the control of the actual Mn oxidation state. We assumed, in fact, that if such parameters were kept constant in all samples, the ferromagnetic ordering temperature, as well as the resistivity and the magnetoresistance, were controlled only by the Al concentration. This allowed us to correlate the magnetic, transport, and magnetotransport characteristics in a series of compounds with constant Mn oxidation. On the basis of such findings we formulated a phenomenological model for explaining our experimental results, which is also consistent with a large part of the literature. It further provides a possible interpretation of the general materials features pointed out in (i)–(iv).

EXPERIMENTAL

$La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ compounds with $x=0$, 0.01, 0.05, and 0.1 were prepared by solid state reactions of La_2O_3, Al_2O_3, $CaCO_3$, and $MnCO_3xnH_2O$. Commercial La_2O_3 (99.99%) was heated overnight at 1000 °C, in order to dehydrate before weighing; the exact concentration of Mn in $MnCO_3xnH_2O$ was determined by a complexometric titration. Stoichiometric amounts of reagents were homogenized and milled under ethanol, in an agate container, hand-pressed in alumina crucibles and heated for a total of 100–150 h at 1200 °C, in air. Intermediate cooling and mechanical grinding steps were repeated in order to get an accurate homogenization and complete reaction. Pellets of 5 mm in diameter and 1 mm in height were produced by unidirectional pressing; they were sintered at 1200 °C and furnace cooled in air.

The specimen density was determined from the pellet weight and dimensions: it resulted to be $\approx 70\%$ of the theoretical value.

Lattice parameters were measured from a least-squares fitting to the relevant diffraction lines in x-ray powder diffraction experiments, carried out on a Siemens D-500 diffractometer, with a CuKa radiation, in steps of 0.05°, between 20° and 60°. All compounds exhibited cubic

structures, with an "a" parameter which slightly decreased with increasing Al concentration: at a maximum $x=0.1$, a 0.6% reduction in the "a" value was found with respect to the Al-free compound. The "a" values as a function of x are summarized in Table I. No traces of secondary phases were detectable, within the sensitivity limits of the experiment (a few percent).

The Mn average oxidation state was determined by iodometric titrations, with a dead-stop end point amperometric detection.[16] Details of the chemical process will be reported elsewhere.[17] Results are shown in Table I: the measurement reproducibility was better than 0.01. Also summarized in Table I are the data relevant to oxygen and, Mn^{4+} concentration per unit formula. Oxygen stoichiometry was calculated by assuming no cation vacancies and constant $2+$ and $3+$ valences for calcium and for lanthanum and aluminum ions, respectively. The Mn^{4+} content was calculated from the nominal cation stoichiometry and the average Mn oxidation state.

Magnetization and susceptibility measurements as a function of temperature and magnetic field were performed in a vibrating sample magnetometer: temperature intervals were between 78 and 300 K and between 78 and 700 K, respectively; the magnetic field was ≤ 19 kOe. Magnetization was determined on specimens containing precisely weighted powders, embedded in an epoxidic resin.

The transport and magnetotransport characteristics were determined by the van der Pauw method, over a 78–300 K temperature range, and in a maximum magnetic field=19 kOe. Disk-shaped specimens, 0.1 cm thick and 0.5 cm in diameter, were used. Four silver epoxidic resin dots were
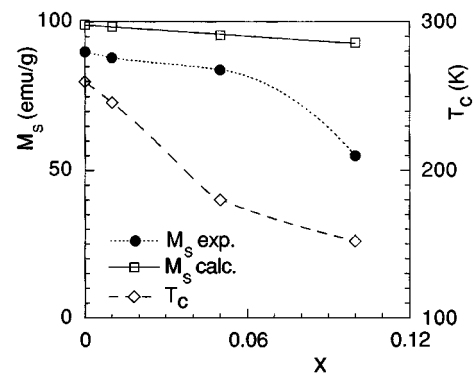
FIG. 2. Experimental and calculated saturation magnetization and T_c of $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ vs aluminum concentration x.
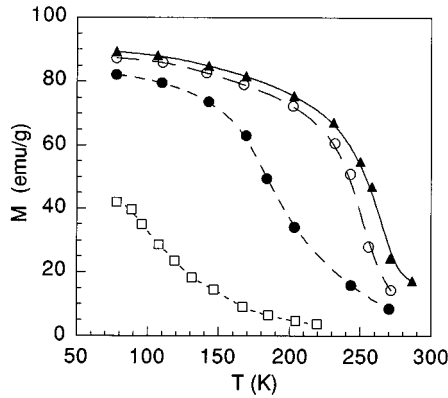
FIG. 3. Magnetization at 19 kOe vs temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ (▲: $x=0$; ○: $x=0.01$; ●: $x=0.05$; □: $x=0.1$).

placed on the disk in order to improve the contact conductivity.

RESULTS AND DISCUSSION

The saturation magnetization M_S and the Curie temperature T_c of $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ are reported in Fig. 2, as a function of x. They both regularly decrease with x, from $x=0$ to $x=0.05$; in the case of M_S, the experimental data are consistent with the values calculated by considering only the spin contribution in the Mn^{3+} and Mn^{4+} ions. With respect to such a series, the 10%Al-doped compound exhibits both a more reduced M_S as well as a higher T_c than the expected ones. Data relevant to the magnetization at constant $H=19$ kOe, M_{19}, and to the reciprocal susceptibility, $1/\chi$, are reported in Figs. 3 and 4, respectively, versus T, for different Al concentrations. Also in view of such characteristics, the peculiar behavior of the 10%Al-doped compound is evident, when compared to the undoped and to 1% and 5% Al-doped materials. In particular M_{19} is abnormally low; it exhibits a unique dependence on T, thus it is quite problematical to identify the ferromagnetic to paramagnetic transition temperature, and it does not annihilate at $T>T_c$. Such a M vs T behavior, which we observed also at $H<19$ kOe, has already
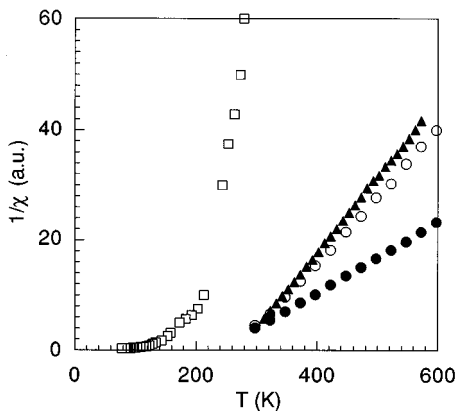

FIG. 4. $1/\chi$ vs temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ (▲: $x=0$; ○: $x=0.01$; ●: $x=0.05$; □: $x=0.1$).

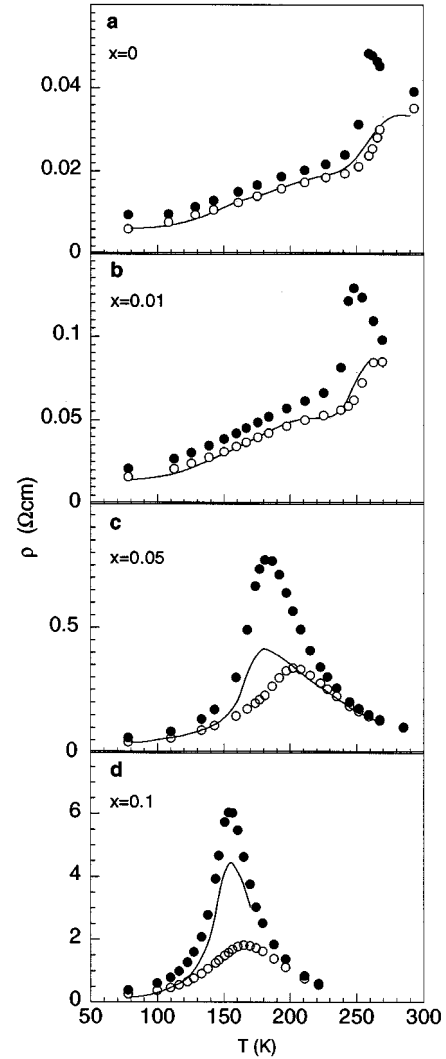FIG. 5. Experimental $\rho_{0,T}$ (filled symbols) and $\rho_{19,T}$ (empty symbols) vs temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ (different x). The continuous lines represent $\rho_{19,T}$ calculated according to Eq. (6).

been mentioned by other authors.[7] As far as the $1/\chi$ dependence on temperature is concerned, it linearly decreases by decreasing T in 0–5% Al-doped materials, while in the 10%Al-doped compound it exhibits significant slope variations, which seem to suggest the presence of different phases with varying T_c. In Figs. 5 and 6 the resistivity vs temperature at $H=0$ ($\rho_{0,T}$) and at $H=19$ kOe ($\rho_{19,T}$) and $\Delta\rho/\rho$ [i.e., $(\rho_{0,T}-\rho_{19,T})/\rho_{19,T}$] are reported, respectively. In samples with $x=0$, 0.01, 0.05 $\rho_{0,T}$ max occurs at $T=T_c$. $\rho_{0,T}$ min and $\rho_{0,T}$ max, as well as $\Delta\rho/\rho$, increase with decreasing T_c. $\rho_{19,T}$ max occurs at a temperature higher than that corresponding to $\rho_{0,T}$ max, thus suggesting that the magnetic field improves the ferromagnetic interaction.

In order to understand this we think that two main points must be investigated: (i) the carrier scattering dependence on the magnetic spin order (MSO) as a function of temperature and magnetic field; and (ii) the ρ dependence on the intrinsic magnetic characteristics (ρ_0 strongly increases with decreasing T_c).

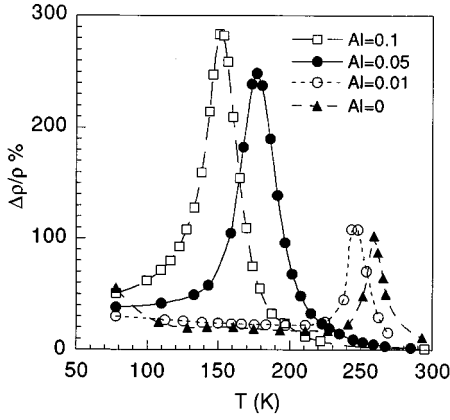As far as point (i) is concerned, we assume, as a working

FIG. 6. $\Delta\rho/\rho$ percent vs temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$ ($\blacktriangle$: $x=0$; $\bigcirc$: $x=0.01$; $\bullet$: $x=0.05$; $\square$: $x=0.1$).

hypothesis, that $\rho_{H,T}$ can be expressed as

$$\rho_{0,T}=\rho_{0,0}[1+f(T)] \qquad (1)$$

under a null magnetic field, or as

$$\rho_{H,T}=\rho_{0,0}[1+f(T)f'(H,T)] \qquad (2)$$

under H field, where $\rho_{0,0}$ represents the resistivity in the unperturbed state ($T=0$ K and $H=0$), $f(T)$ is the function describing the ρ dependence on temperature, and $f'(H,T)$ is the temperature-dependent function describing the magnetic spin order (MSO) variation induced by the magnetic field. In order to select the most appropriate $f'(H,T)$ it is necessary to establish if MSO, responsible for the magnetic scattering, depends on the average angle between moments of adjacent atoms and/or on the macroscopic order connected with the magnetic domain and with the domain boundaries. To clarify this we measured ρ and M as a function of H at constant temperature and reported the relevant values in Fig. 7. They show that ρ slightly decreases until the magnetization reaches its technical saturation (suppression of domain walls) and then decreases at a higher rate; correspondingly slight increments of M occur, which can be attributed to the action of the applied field against the thermal motion of the magnetic moments (high field susceptibility). Such a phenomenology suggests that ρ is mainly dependent on the spin or-
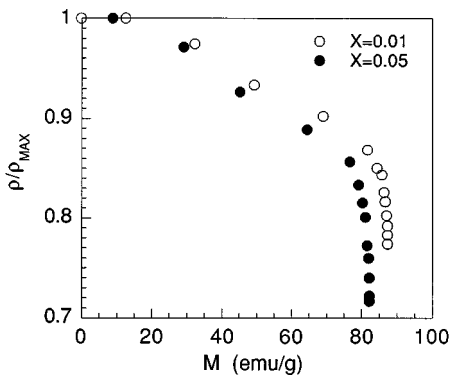

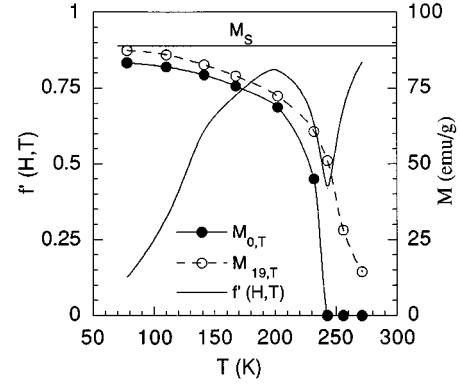FIG. 7. Normalized resistivity vs magnetization at 78 K in $La_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_y$, for two different x.

FIG. 8. Magnetization at $H_{int}\rightarrow0$ and $H=19$ kOe and the relevant $f'(H,T)$ [Eq. (4)] vs temperature in $La_{0.67}Ca_{0.33}Mn_{0.99}Al_{0.01}O_{2.97}$. The M_S line represents the saturation magnetization extrapolated at 0 K.

der variation due to the application of the magnetic field after technical saturation is reached. Thus, the simplest macroscopic function related to MSO variation can be expressed as $(M_{H,T}/M_S)-(M_{0,T}/M_S)$, where $M_{H,T}$ indicates the magnetization at H field, $M_{0,T}$ represents the technical saturation at internal field, $H_{int}\rightarrow0$, and M_S the intrinsic saturation magnetization. Furthermore, because ρ is proportional to the magnetic disorder, we expressed it as

$$\rho_{0,0}f(T)=k(T)(1-M_{0,T}/M_S) \qquad (3)$$

and

$$\rho_{0,0}f(T)f'(H,T)=k(T)(1-M_{H,T}/M_S) \qquad (3')$$

where $(1-M_{H,T}/M_S)$ is the function we choose to represent the spin disorder, as a function of temperature and magnetic field, and $k(T)$ is the proportionality constant. By substituting Eq. (3) within Eq. (3') we have

$$f'(H,T)=(1-M_{H,T}/M_S)/(1-M_{0,T}/M_S). \qquad (4)$$

As an example in Fig. 8 the experimental values of $M_{0,T}$ and $M_{19,T}$, and the resulting $f'(19,T)$, calculated according to Eq. (4), relevant to the 1% Al-doped compound are shown. By substituting $f'(H,T)$ in Eq. (2) we have

$$\rho_{H,T}=\rho_{0,0}[1+f(T)(1-M_{H,T}/M_S)/(1-M_{0,T}/M_S)], \qquad (5)$$

and by combining Eq. (5) with Eq. (1), we obtain

$$\rho_{H,T}=\rho_{0,0}+[(\rho_{0,T}-\rho_{0,0})(1-M_{H,T}/M_S)/(1-M_{0,T}/M_S)], \qquad (6)$$

The values of $\rho_{H,T}$ calculated according to Eq. (6) at $H=19$ kOe are reported in Fig. 5 and compared to the relevant experimental results. At low Al concentration ($x=0$ and 0.01) the two sets of data are consistent, even on a quantitative basis; no adjusting factor has to be introduced: this suggests that the function $(1-\langle\cos\theta\rangle)=(1-M_{H,T}/M_S)$ is a convenient approximation for describing the dependence of resistivity on MSO in such compounds.

As far as the resistivity dependence on temperature is concerned, the relevant $f(T)$ function, according to Eq. (3), can be expressed as
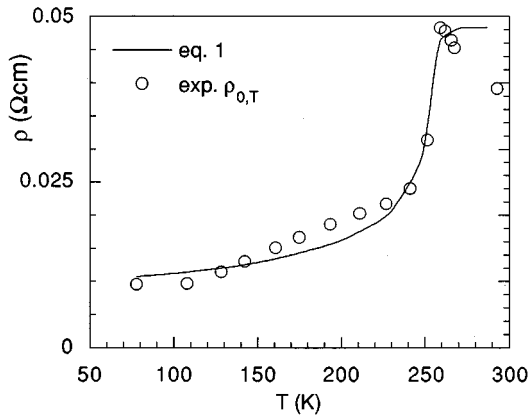
FIG. 9. Resistivity at $H=0$ vs temperature in $La_{0.67}Ca_{0.33}MnO_{2.96}$, derived from experiments and calculated according to Eq. (1).

$$f(T) = [k(T)/\rho_{0,0}](1 - M_{0,T}/M_S). \qquad (7)$$

By assuming as the first approximation that $k(T)$ is independent of T, it is possible to calculate $\rho_{0,T}$ by substituting $f(T)$ in Eq. (1). The resulting values are reported in Fig. 9 and they are in reasonable agreement with the experimental curves. The discrepancy between the experimental and calculated plots can reasonably be attributed to the fact that factors, such as lattice dimensions and atom vibrations, which influence resistivity, are not temperature independent, as had been assumed.

The model we have presented so far, and which is summarized in Eq. (6), however, does not properly fit the experimental data for $\rho_{H,T}$ in 5% Al-doped material [Fig. 5(c)], and it is quite inadequate in the case of 10% Al-doped manganite [Fig. 5(d)]. This is reasonable considering that compounds with low ferromagnetic ordering temperature ($T_c < 220$ K) exhibit very large magnetoresistance effects and ρ_0/ρ_H ratios, thus requiring an order function $f'(H,T)$ approaching zero. On the contrary, in compounds with low T_c, the magnetization, $M_{H,T}$, at $H \neq 0$ and at $T \approx T_c$ is lower than the saturation at 0 K. As a consequence $(1 - M_{H,T}/M_S) > 0$, and because $(1 - M_{0,T}/M_S) \lesssim 1$, $f'(H,T)$ never approaches 0. For such systems different mechanisms must then be hypothesized for explaining the exponential dependence of ρ on T_c and its collapse under the action of the magnetic field.

On the other hand, we have already pointed out that the magnetic characteristics of manganites do not change at a constant rate as a function of dopant concentration (Figs. 2, 3, and 4), when the Al level is increased. A reasonable hypothesis for explaining such phenomena is that the Al doping weakens the ferromagnetic double exchange coupling postulated by Zener,[6] although it still dominates at $x=0.01$. With increasing Al concentration, i.e., $x=0.05$ and 0.1, an antiferromagnetic spin order arises and coexists with the ferromagnetic one. A similar mechanism may also account for the experimental data relevant to Ca-doped La-Mn perovskites, which exhibit a significant reduction of M when Ca concentration is reduced from 33 to 0%.[3,4] In such compounds the coexistence of ferro- and antiferromagnetic interactions has indeed been proved on the basis of neutron diffraction experiments, carried out as a function of temperature and Ca

concentration.[18] In order to explain, the measured ρ dependence on the intrinsic magnetic properties we propose the following phenomenologial description. According to Zener[6] the carriers responsible for the conduction are those involved in the ferromagnetic double exchange coupling, and their number per unit volume must be proportional to the number of ferromagnetically ordered atoms. On the other hand, the antiferromagnetically ordered atoms hinder the electron migration, so that their number can be assumed to be proportional to ρ. According to Ref. 6, the probability of the Mn^{3+}-Mn^{4+} electron diffusion is proportional to the double exchange energy ϵ, which, in turn, is proportional to T_c, so that ρ can be expressed as

$$\rho = \rho_0 [(NA/NF)(T_c \max/T_c)], \qquad (8)$$

where NA and NF are the number of Mn atoms antiferromagnetically and ferromagnetically coupled, respectively, and T_c max is T_c of the material fully ferromagnetically ordered. In order to verify the validity of this assumption we calculated ρ, accordingly to Eq. (8), by using the experimental values of NA, NF, and T_c reported in Refs. 3, 4, and 18. In particular we assumed NF as the ratio between the experimental and the calculated values, respectively, of M_S, at a given Mn^{4+} concentration (Fig. 6 in Ref. 4), and NA as (1-NF). NA and NF values were then related to T_c of the material with the same Mn^{4+} concentration (Fig. 5 in Ref. 4). The results, represented in Fig. 1 as a continuous line, are in reasonable agreement with the experimental values: in particular, they prove that variations of ρ as a function of T_c as large as many orders of magnitude are justified. An exponential dependence of $\rho_{0,T}$ max on T_c is also deducted from the data of Gupta et al.,[19] relevant to laser ablated epitaxial films of $La_xMnO_{3-\delta}$ ($0.67 < x < 1$), and from those of Ju et al.,[20] relevant to bulk $La_{0.67}Ba_{0.33}MnO_z$ ($2.85 < z < 3$). Both groups also stress that the T_c decreasing is always accompanied by significant reduction of M in the manganites. These data seem to support the hypothesis that the resistivity of the material is related to the intrinsic magnetic order, i.e., the relative amount of ferro- and antiferromagnetic aligned spins. This description also accounts for the experimental data relevant to the dependence of $\Delta\rho/\rho$ on T at $T \approx T_c$ (many orders of magnitude): at $T \approx T_c$, in fact, the exchange interactions become less effective due to the thermal energy; thus the action of an applied magnetic field can induce a reorientation transition of the antiferromagnetically aligned spins to a ferromagnetic state. On the other hand, a reorientation phenomenon, even if modest, significantly modifies the NA/NF ratio, and, proportionally, ρ, according to Eq. (8). The possibility of a field-activated reorientation transition was already suggested by von Helmolt et al.[9] and it is consistent with the experimental data of Guo-Qiang et al.,[12] for the $La_{0.5}Ca_{0.5}MnO_3$ compound.

Finally, we want to mention the results of Ju et al.[20] and to point out how they can be interpreted within the framework of our description. These authors, in fact, present some experimental evidence of significant ρ variation induced by the application of a magnetic field before reaching technical saturation; this could seem to be in disagreement with our data. The Ju experiments indeed were done on a fully ferromagnetically ordered system at a very low temperature ($T \approx 4$ K), where almost null magnetic scattering inside domains is

expected; under such conditions the scattering induced by the spin misalignment at the domain wall boundary becomes predominant and can produce macroscopic effects. These peculiar conditions no longer exist at higher temperature and/or in partially antiferromagnetically ordered systems, where the scattering inside domains is predominant and masks the magnetic effects at the domain boundaries.

CONCLUSIONS

The analysis of the experimental data presented in this work as well as that of numerous independent groups indicate that the intrinsic characteristics of La-Mn perovskites (T_c, M, ρ) show recurrent relationships, i.e., the resistivity and $\Delta\rho/\rho$ increase as T_c and magnetization decrease. Such a behavior has been observed in different compounds, independently of the method used for controlling the materials characteristics, i.e., Ca doping,[12] oxygen stoichiometry at fixed Ca doping,[20] La vacances,[19] pressure,[21] Al doping (present study). In particular, the spin order seems to be the main magnetic parameter affecting the transport and magnetotransport properties. We propose different phenomenological approaches to explain the relationship between magnetic and transport characteristics, which respectively apply in the case of fully ferromagnetically ordered materials ($T_c \approx RT$), or for mixed ordered compounds ($T_c < RT$). In the first case the correlation between ρ and macroscopic magnetic properties is expressed in Eq. (6), which quantitatively accounts for the ρ dependence on the spin order as a function of temperature and magnetic field. In the second case our interpretation is based on the assumption that the ratio between antiferro- and ferromagnetic coupled atoms determines the transport characteristics of the materials. We expressed such a relationship in Eq. (8), which well fits the experimental data (Fig. 1). In this case we also suggest that the large magnetoresistive effect, observed at T approaching T_c, can be explained by assuming that the applied field induces a spin reorientation, which strongly modifies the number of free carriers and their intrinsic mobility.

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