

Induced ferromagnetism in LaMnO_3 by Mn-site substitution: The major role of Mn mixed valency

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In order to know if the origin of ferromagnetism induced by the substitution of Co or Ni for Mn in LaMnO_3 could be due to their divalent oxidation states, a set of $\text{LaMn}_{1-x}M_x\text{O}_3$ samples has been prepared for $x \leq 0.2$ and $M = \text{Li}, \text{Zn}, \text{Ni}, \text{Co}, \text{Ga},$ and Rh . By combining resistivity, thermopower, magnetization, susceptibility measurements, and room-temperature structural refinements, we show that, similarly to Ni and Co, univalent (Li^+) and divalent (Zn^{2+}) $S=0$ cations induce both ferromagnetism and a more conductive behavior. In contrast, the $S=0$ trivalent cations (Rh^{3+} and Ga^{3+}) are found to preserve the orthorhombic O' structure, connected with the cooperative Jahn-Teller distortion of Mn^{3+} species in LaMnO_3 . Accordingly, Rh^{3+} - and Ga^{3+} substituted LaMnO_3 manganites are only weak ferromagnets, and the resistivity increases in comparison to LaMnO_3 . These results indicate that, for the investigated range of substitution (a maximum of 20%), both cobalt and nickel behave like divalent cations. The observation of ferromagnetism and the resistivity decrease, induced by univalent and divalent cations, Li^+ and Zn^{2+} , is due to the creation of Mn^{4+} species which favor $\text{Mn}^{3+}/\text{Mn}^{4+}$ double exchange.

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INTRODUCTION

A great deal of work has been carried out recently concerning the doping of Mn site in manganites. One of the most important results in this field concerns the possibility to induce ferromagnetism (FM) and metal-like behavior in an insulating CE-type antiferromagnetic manganites involving small A-site cations, $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\text{Ln} = \text{lanthanide}$ and $x \approx 1/2$), by doping these oxides with magnetic cations such as chromium,^{1,2} cobalt,¹ nickel,³ or ruthenium.⁴ These properties originate from the collapse of the simultaneous charge and orbital ordering of Mn^{4+} and Jahn-Teller JT Mn^{3+} species. The cooperative 90° ordering of the $3d_z^2$ orbitals of Mn^{3+} is thought to be responsible for the checkerboard arrangement of the Mn cations.⁵ By increasing the doping content, ferromagnetic clusters are created around the magnetic doping elements, in orbitally disordered regions, leading to phase separation.⁶ According to the double-exchange mechanism, charges become itinerant in the ferromagnetic zones. The size extension of the latter is then facilitated by a magnetic-field application, and the percolative pathways between conductive parts are responsible for the observed large resistivity decrease also called colossal magnetoresistance.

The substitution of magnetic cations for manganese in LaMnO_3 is different, leading to ferromagnetic but insulating materials as described mainly for nickel and cobalt doped LaMnO_3 .⁷⁻¹² Such a different situation is due to the fact that the LaMnO_3 pristine matrix contains only JT Mn^{3+} cations. Below $T_{\text{JT}} \sim 750$ K, a cooperative JT ordering of the e_g orbitals sets in, leading to an abrupt increase of the resistivity in the orbitally ordered phase. The temperatures of orbital and spin ordering are decoupled since LaMnO_3 becomes an A-type antiferromagnet only below $T_N \sim 140$ K. In the case of LaMnO_3 , FM can be induced by doping with Ni or Co on the Mn site, but there appears to be a lot of controversy between different authors about the mechanism which gov-

erns the ferromagnetic properties. In an earlier study, Goodenough *et al.*⁷ explained this behavior by ferromagnetic Mn^{3+} -O- M^{3+} interactions, according to the superexchange theory, considering that the involved species were $M = \text{Mn}^{3+}$ and Ni^{3+} or Co^{3+} . In their study of $\text{LnMn}_{0.5}M_{0.5}\text{O}_3$ ($M = \text{Ni}, \text{Co}$) manganites, Asai *et al.*⁸ proposed that nickel and cobalt are in the divalent state, and that Ni^{2+} (or Co^{2+}) and Mn^{4+} species align ferromagnetically, based on superexchanges Ni^{2+} (Co^{2+})-O- Mn^{4+} interactions. X-ray absorption near edge spectroscopy (XANES) measurements carried out in Ref. 9 strongly supported the divalent nature of cobalt in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ manganites, and explained the ferromagnetic state of this series by a double-exchange mechanism between Mn^{3+} and Mn^{4+} species. However, the latter statements were questioned by van Elp,¹³ whereas Troyanchuk *et al.*¹⁴ proposed Mn^{3+} -O- Mn^{3+} , Mn^{3+} -O- Mn^{4+} , and Mn^{4+} -O- Co^{2+} superexchange interactions to explain the properties of these compounds. Moreover the recent studies of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$, carried out in Ref. 10 emphasized the existence of two phases, depending on the method of synthesis, the first one involving low-spin Co^{3+} and the second one corresponding to the presence of Mn^{4+} and Mn^{3+} species. Furthermore, one cannot exclude that the establishment of the orbitally ordered structure below T_{JT} , associated with the structural distortion from orthorhombic O to O' in LaMnO_3 , can be hindered by the substitution of foreign cations, similarly to orbital disordering induced by several doping magnetic cations in the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ charge-orbital ordered pristine phase.¹⁻⁴

At this point of the investigations, in order to understand the origin of the induced ferromagnetism in LaMnO_3 , it is absolutely necessary to study the effect of substituting elements, other than cobalt and nickel, magnetic or not, and to control the oxygen stoichiometry of the so prepared material, bearing in mind that “ LaMnO_3 ” prepared in air or in oxygen contains generally an “oxygen excess,”^{15,16} depending on the synthesis conditions.

In the present work, we investigate the magnetic and transport properties of $\text{LaMn}_{1-x}\text{M}_x\text{O}_3$ doped with non magnetic cations ($M=\text{Li}, \text{Zn}, \text{Ga}, \text{Rh}$) and with magnetic ($M=\text{Co}, \text{Ni}$), for low substituting levels ($x \leq 0.20$). We fix the nominal oxygen stoichiometry to “ O_3 ” in order to avoid an oxygen excess, as for $\text{LaMnO}_{3+\delta}$, which would significantly modify the properties, independently of the Mn-site substitution. We show that the valency of the substituting element plays a prominent role in the appearance of ferromagnetism of $\text{LaMn}_{1-x}\text{M}_x\text{O}_3$. We indeed observe that non magnetic cations with a valency smaller than $3+$ ($\text{Li}^+, \text{Zn}^{2+}$), which create Mn^{4+} species in the Mn^{3+} matrix induce strong ferromagnetism, comparable to the one induced by magnetic cations such as nickel and cobalt. In contrast, with trivalent cations such as Ga^{3+} , Mn cations remain trivalent, and only weak ferromagnetism is induced. These results are interpreted in terms of $\text{Mn}^{3+}/\text{Mn}^{4+}$ double-exchange mechanism.

EXPERIMENTAL DETAILS

The samples were prepared at high temperature by solid state reaction (1250 °C during 24 h) in evacuated silica ampoula. The precursors (La_2O_3 , Mn_2O_3 , MnO_2 , and Ga_2O_3 or Rh_2O_3 or Co_3O_4 or NiO or ZnO or Li) were weighed in the stoichiometric ratio, with respect to the “ O_3 ” nominal stoichiometry, mixed and pressed in the form of bars that were then introduced in an alumina crucible in the silica ampoula. The Li-based samples were prepared in a glove box due to the Li used as a precursor.

The sample purity was checked by x-ray diffraction (by using a $\text{CuK}\alpha$ Philips diffractometer) at room temperature (RT). The electron-diffraction study and energy dispersive spectroscopy analyses were carried out with a JEOL 200CX electron microscope, equipped with a KEVEX analyzer. The cationic composition was determined by analyzing about 30 crystallites of each sample. All the samples involving the doping M elements Zn, Ga, Rh, Ni and Co, were found to be pure and homogeneous, from the viewpoint of their cationic distribution (the Li content cannot be measured by x-ray energy dispersive spectroscopy; only the La/Mn ratio was determined). The reconstruction of the reciprocal space was carried out for all the samples. It evidenced $Pnma$ -type orthorhombic cells, except for the Li-based samples ($R\bar{3}c$).

Magnetic measurements were performed using a VSM magnetometer with a magnetic field equal to 1.45 T applied after zero-field cooling. High-temperature susceptibility measurements ($T \leq 800$ K) were made on a Faraday balance with an applied magnetic field of 0.3 T. The transport measurements (resistivity and thermopower) were carried out in a Quantum Design Physical Properties Measurements system, with a homemade sample holder for thermopower based on a four-point steady-state method with separate measuring and power contacts.

RESULTS

A. Room-temperature structural characterizations

Except for Li-substituted compounds, all the x-ray diffraction patterns were refined in the $Pnma$ space group. In

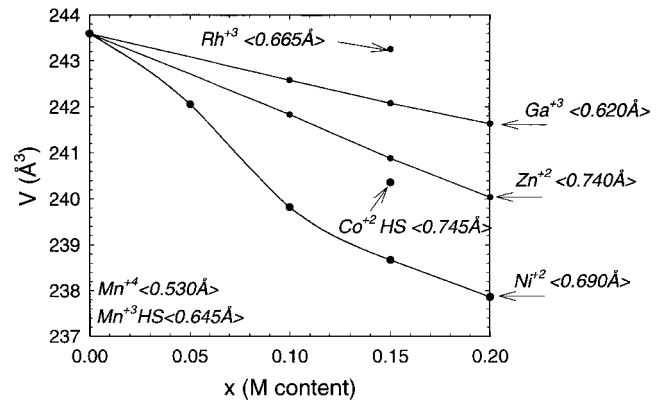


FIG. 1. Evolution of the cell volume determined from x-ray powder diffraction at RT as a function of the concentration of Rh, Ga, Zn, Co, or Ni. The cationic sizes (from Shannon tables) are also given.

Fig. 1, the x dependence of the cell volume is reported for Ga, Zn, and Ni; the volumes obtained for the 15% substituting level of Co and Rh are added. The cationic sizes of these doping elements are also given. The lattice parameters versus the substituting content ($0 \leq x \leq 0.20$) are exemplified in Fig. 2 for Ga and Ni.

The lattice parameters refined for the pristine sample are in agreement with the results obtained in Ref. 15 for their LaMnO_3 ORT1 phase, confirming that this sample is oxygen stoichiometric. The substitution of Mn by Ga leads to a small decrease of the volume (Fig. 1) in agreement with the smaller size of Ga^{3+} compared to Mn^{3+} one. By increasing the Ga content, the distortion of the cell decreases only smoothly: a decreases, b increases and c remains nearly constant (Fig. 2). The lattice remains from O' type, that is $b/\sqrt{2} < c < a$, reflecting a cooperative Jahn-Teller effect. Conversely, for the Ni substitution, a large evolution of the cell parameters is observed; the distortion decreases very quickly and for $x > 0.15$ the structure becomes O -type (instead of O' type) that is the JT distortion has disappeared. This strongly suggests that nickel is divalent, inducing

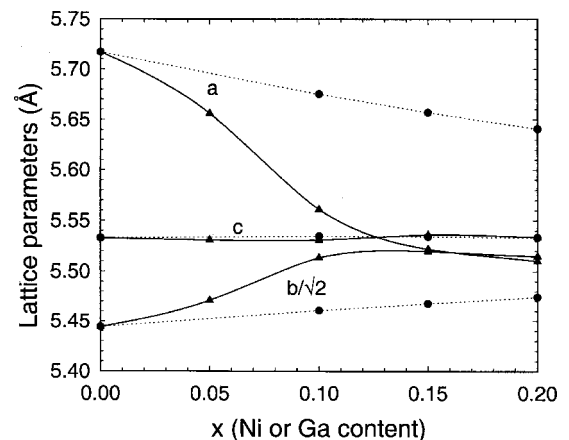


FIG. 2. Evolution of the RT cell parameters of $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ (circles and dashed line) and $\text{LaMn}_{1-x}\text{Ni}_x\text{O}_3$ (triangles and full lines) as a function of x .

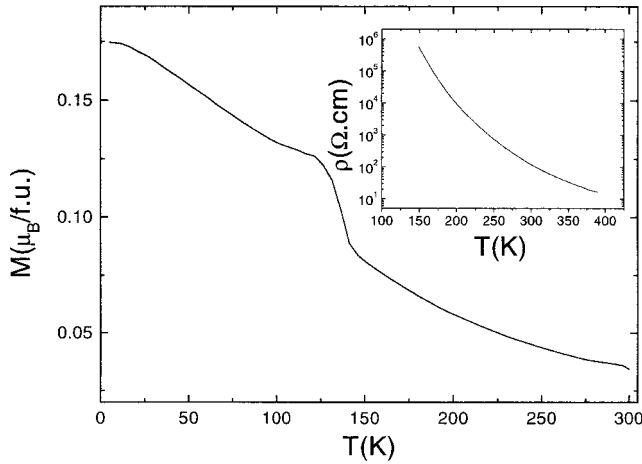


FIG. 3. $M(T)$ measured after zero-field cooling under 1.45 T and $\rho(T)$ curves (inset) of LaMnO_3 . Note that the $\rho(T)$ curves registered in 0 and 7-T curves are superimposed.

Mn^{4+} species according to the formula $\text{LaMn}_{1-2x}^{3+}\text{Mn}_x^{4+}\text{Ni}_x^{2+}\text{O}_3$. The ionic radius of Mn^{4+} , 0.53 Å, smaller than Mn^{3+} , 0.645 Å, would explain the large decrease of the cell volume also observed for zinc and cobalt cations. By substituting Ga for Mn, no valency effect has to be taken into account in agreement with the trivalent character of gallium leading to the formula $\text{LaMn}_{1-x}^{3+}\text{Ga}_x^{3+}\text{O}_3$. Such a difference, between the +2 or +3 valency effects, suggests a divalent state for cobalt and nickel in those oxides (Fig. 1).

For the Li substitution, the effect is more dramatic, a small amount of lithium inducing a large Mn^{4+} content as shown from the formula $\text{LaMn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{Li}_x^{1+}\text{O}_3$. In this case, a structural transition is observed from $Pnma$ to $R\bar{3}C$, when the Li content increases. For $R\bar{3}C$ “ $\text{Li}_{0.05}$,” a mixture of both space groups is evidenced at room temperature.

B. Magnetic and transport properties of LaMnO_3

To check the stoichiometry of LaMnO_3 , magnetic and transport properties have been investigated and compared to published results on $\text{LaMnO}_{3+\delta}$. Figure 3 presents the magnetic moment, measured for an applied field of 1.45 T after zero-field cooling. The magnetization is very small at low temperatures, reaching only $\sim 0.2 \mu_B$ at 5 K, consistently with the antiferromagnetic nature of the stoichiometric LaMnO_3 . The magnetic transition to the paramagnetic state is observed at $T_N \sim 140$ K. The high-temperature magnetic properties have been measured up to 800 K to determine the transition temperature T_{JT} above which the orbital ordering disappears. Figure 4 shows the evolution of $1/\chi$ versus T for an applied field of 3000 Oe. A clear magnetic transition is observed at $T_{JT} \approx 700$ K between two distinct paramagnetic regimes with the Curie constants equal to $C=4.04$ and 4.37, respectively, for the low and high-temperature phases, and the Weiss constant increases from $\theta=59$ K at low T to $\theta \sim 150$ K at high T . These values (T_N , the small magnetic moment at 5 K, and the Curie-Weiss law parameters) are in

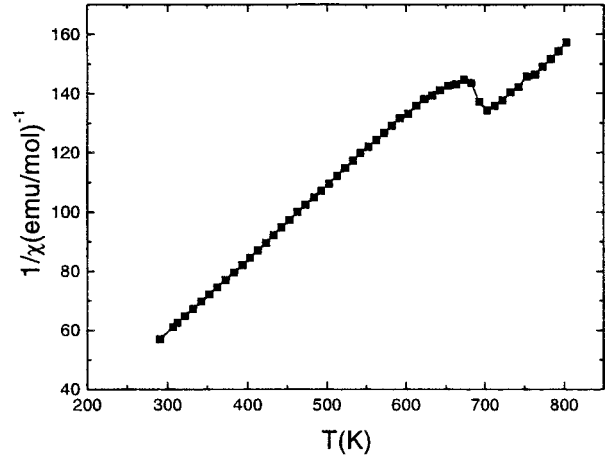


FIG. 4. Inverse of the high-temperature susceptibility vs temperature measured with an applied field of 0.3 T for LaMnO_3 .

good agreement with the results published on ceramics^{15,16} and single crystals,¹⁷ and confirm that LaMnO_3 has been prepared in stoichiometric conditions with no oxygen excess. An estimate of the hole doping level in the samples can be made using thermopower measurements. In Fig. 5, thermopower is plotted versus temperature. Measurements were recorded as a function of decreasing temperature, with no applied field. The value of S at 300 K is equal to $+460 \mu\text{V/K}$, close to the results obtained in stoichiometric LaMnO_3 ceramics.¹⁶ Following the Heikes formula, the fraction c of Mn sites occupied by carriers (Mn^{4+}) can be calculated: $S^{300\text{K}} = -(k/e)\ln[(1-c)/c]$, leading to $c \approx 0.005$, which confirms the controlled oxygen content of the samples. LaMnO_3 is insulating, with no magnetoresistance, as shown in the inset of Fig. 3, and the activation energy is equal to 210 meV, much larger than the typical values obtained in mixed-valent manganites.¹⁹

C. Properties of the substituted $\text{LaMn}_{1-x}\text{M}_x\text{O}_3$ Manganites

I. $M=\text{Ni, Co}$

Substituting the antiferromagnetic LaMnO_3 with Co and Ni on the manganese site results in a spectacular increase of

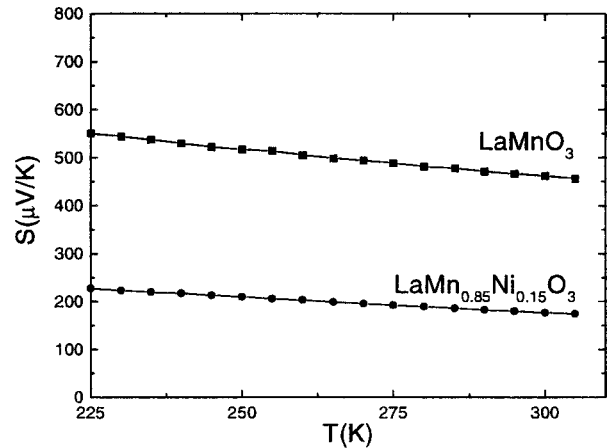


FIG. 5. Thermopower S versus T for LaMnO_3 (■) and $\text{LaMn}_{0.85}\text{Ni}_{0.15}\text{O}_3$ (●) under 0 T.

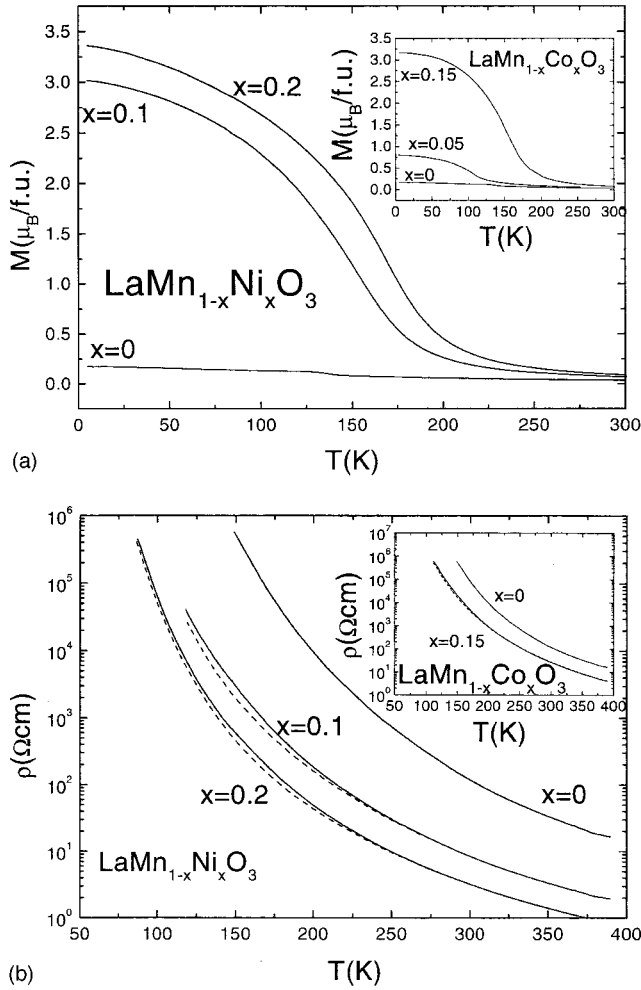


FIG. 6. (a) $M(T)$ under 1.45 T of $\text{LaMn}_{1-x}\text{Ni}_x\text{O}_3$ [inset: $M(T)$ of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$]. (b) $\rho(T)$ under 0 T (solid lines) and 7 T (dashed lines) of $\text{LaMn}_{1-x}\text{Ni}_x\text{O}_3$ (inset: $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$).

magnetization. Figure 6(a) presents the magnetization measured under 1.45 T for the $\text{LaMn}_{1-x}\text{Ni}_x\text{O}_3$ compounds with $x \leq 0.2$, and the inset presents the results for $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$. The magnetic moment increases from $0.175\mu_B$ ($x=0$) to $\approx 3.4\mu_B$ for $x=0.2$ in the case of Ni at 5 K, while the Curie temperature is increased up to 150 K. Similar results are obtained for Co. Simultaneously the resistivity in $\text{LaMn}_{1-x}M_x\text{O}_3$ ($M=\text{Co},\text{Ni}$) progressively decreases as x increases. Figure 6(b) shows the $\rho(T)$ curves in the case of Ni (the Co effect is presented in the inset): the ρ values at 300 K are reduced by more than one order of magnitude when 20% of Ni is introduced in LaMnO_3 , and the activation energy is strongly decreased to 125 meV, to be compared to the value of 210 meV for the parent compound LaMnO_3 . This smaller value is typical of mixed-valent manganites as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.¹⁹ Nevertheless, even if ferromagnetism is induced in Co- and Ni-substituted samples, no insulator-to-metal transition is observed in any of these samples and the magnetoresistance remains very small [Fig. 6(b)], contrary to the case of A-site aliovalent substitution. The thermopower is also drastically affected by the doping. In Fig. 5, the thermopower of $\text{LaMn}_{0.85}\text{Ni}_{0.15}\text{O}_3$ is presented.

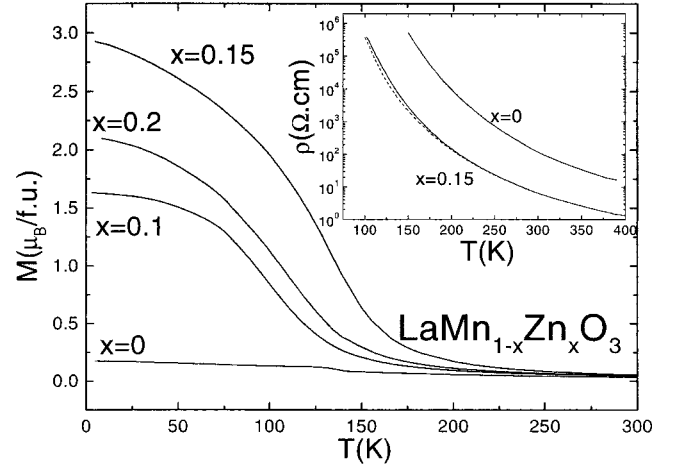


FIG. 7. $M(T)$ under 1.45 T and $\rho(T)$ (inset) under 0 T (solid lines) and 7 T (dashed lines) of $\text{LaMn}_{1-x}\text{Zn}_x\text{O}_3$.

Compared to LaMnO_3 , a sharp drop of S at 300 K is observed, with S decreasing from +460 to +175 $\mu\text{V}/\text{K}$. This value of S at 300 K makes the Ni-substituted sample similar to self-doped $\text{LaMnO}_{3+\delta}$ with $\delta \approx 0.055$,¹⁶ suggesting the presence of Mn^{4+} cations in $\text{LaMn}_{0.85}\text{Ni}_{0.15}\text{O}_3$.

2. $M=\text{Zn}^{2+}, \text{Li}^+$

To understand the origin of ferromagnetism and better conductivity in the case of Ni- and Co-substituted samples, the influence of a possible valency effect, as proposed in Refs. 8 and 9, was investigated. First, the influence of univalent and divalent magnetic dopants in $\text{LaMn}_{1-x}M_x\text{O}_3$ was studied.

Figure 7 presents the results obtained for Zn^{2+} , a non-magnetic cation, for which only a valency effect can thus be expected. As for Co and Ni, Zn induces ferromagnetism with a saturation moment close to $3\mu_B$ for $x=0.15$, and a Curie temperature close to 150 K as shown in Fig. 7. The resistivity is decreased by the introduction of Zn: as in the case of Ni, ρ at 300 K is also decreased by a factor of 10 when 15% of Zn is introduced, and the activation energy is equal to 130–140 meV smaller than the one of LaMnO_3 . As for Co and Ni, no insulator-to metal transition is observed, and magnetoresistance remains very small [maximum $(\rho(H) - \rho(0))/\rho(0) \sim 35\%$].

In the case of zinc, Mn^{4+} species are introduced in the matrix, and the influence of a mixed valency $\text{Mn}^{3+}/\text{Mn}^{4+}$ has drastic effects on the magnetic and transport properties of $\text{LaMn}_{1-2x}^{3+}M_x^{4+}\text{Zn}_x^{2+}\text{O}_3$, similar to the ones observed with Ni and Co. Contrary to Co and Ni cations, Zn^{2+} is a nonmagnetic cation, with filled $3d^{10}$ orbitals, and no ferromagnetic interactions are possible between manganese and zinc species. Thus, the valency effect seems to be crucial. Because of the introduction of Mn^{4+} into the Mn^{3+} matrix, double-exchange interactions can appear and induce ferromagnetism. This valency effect can be further evidenced by doping with monovalent Li^+ , for which a more rapid increase of the Mn^{4+} content is expected compared to divalent cations.

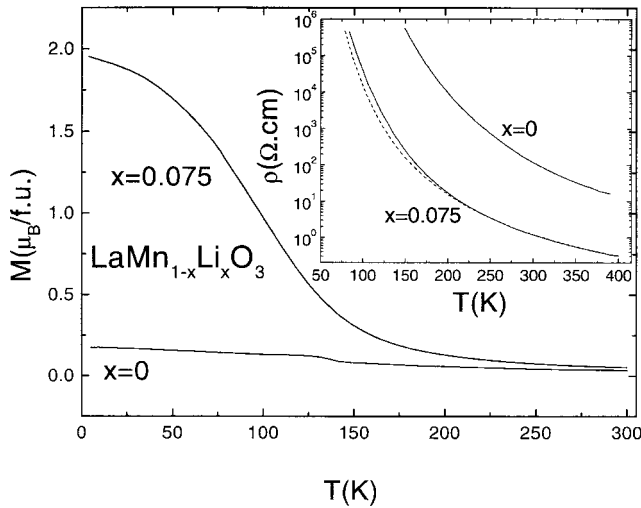


FIG. 8. $M(T)$ under 1.45 T and $\rho(T)$ (inset) under 0 T (solid lines) and 7 T (dashed lines) of $\text{LaMn}_{1-x}\text{Li}_x\text{O}_3$.

Figure 8 shows the $M(T)$ curve for the Li substitution. Ferromagnetism is induced in $\text{LaMn}_{1-x}\text{Li}_x\text{O}_3$, and even a small content of 7.5% is sufficient to induce a ferromagnetic moment of $\approx 2\mu_B$. This can be compared to the case of the nonmagnetic divalent cation Zn^{2+} , for which a doping level larger than $x=0.1$ (i.e., almost double than for Li) is needed to reach $2\mu_B$ (see Fig. 7). Resistivity (inset of Fig. 8) decreases with Li content: ρ at 300 K is reduced by a factor 100 with 7.5% of Li, and the activation energy is equal to 130 meV. The ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$ is thus a key parameter for the establishment of ferromagnetism. The influence of a trivalent cation should therefore strongly differ from the results obtained for Zn and Li.

3. $M = \text{Ga}^{3+}, \text{Rh}^{3+}$

Different trivalent cations have been introduced in the LaMnO_3 matrix and the results will be presented for the nonmagnetic Ga^{3+} (with the same electronic structure as $\text{Zn}^{2+} 3d^{10}$) and $\text{Rh}^{3+} (4d^6)$. Figure 9 presents the magne-

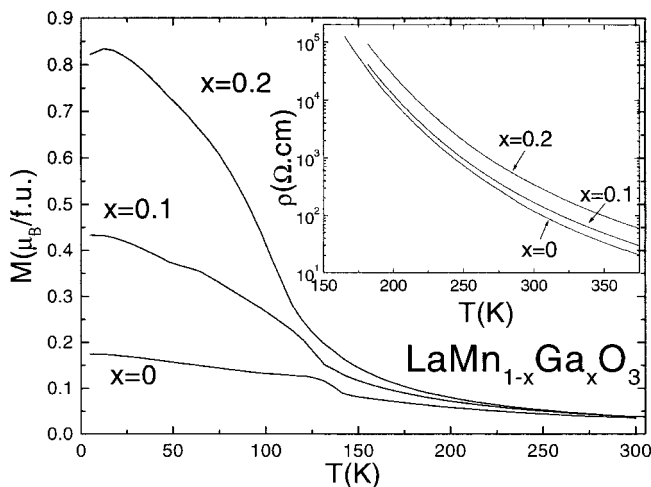


FIG. 9. $M(T)$ under 1.45 T and $\rho(T)$ curves (inset) under 0 and 7 T of $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ (curves under 0 and 7 T are superimposed).

tization curves of $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ with $x \leq 0.20$. A maximum moment of $0.8\mu_B$ is obtained for $x=0.20$, much smaller than the values obtained in the cases of Co, Ni, Zn, or Li. The series of $\text{LaMn}_{1-x}\text{M}_x\text{O}_3$ samples, with $M = \text{Ga}^{3+}$ or Rh^{3+} , remain insulating as for divalent cations, but the resistivity is increased rather than decreased by the introduction of the foreign element (Fig. 9), and the activation energy is increased compared to the undoped compound.

DISCUSSION

The results obtained for the different substituted cations are summarized in Fig. 10, where the evolution of magnetization measured at 5 K and 1.45 T is plotted as a function of x for all the cations studied [Fig. 10(a)], as well as the evolution of activation energy [Fig. 10(b)]. A clear separation is observed between the univalent and divalent Li^+ and Zn^{2+} cations which are efficient to induce ferromagnetism and the trivalent ones— Rh^{3+} and Ga^{3+} —for which the magnetization always remains very small. The influence of divalent and monovalent cations is twofold: the dopant can suppress the anisotropic magnetic interactions of the A-type structure, and induce three-dimensional ferromagnetic interactions in

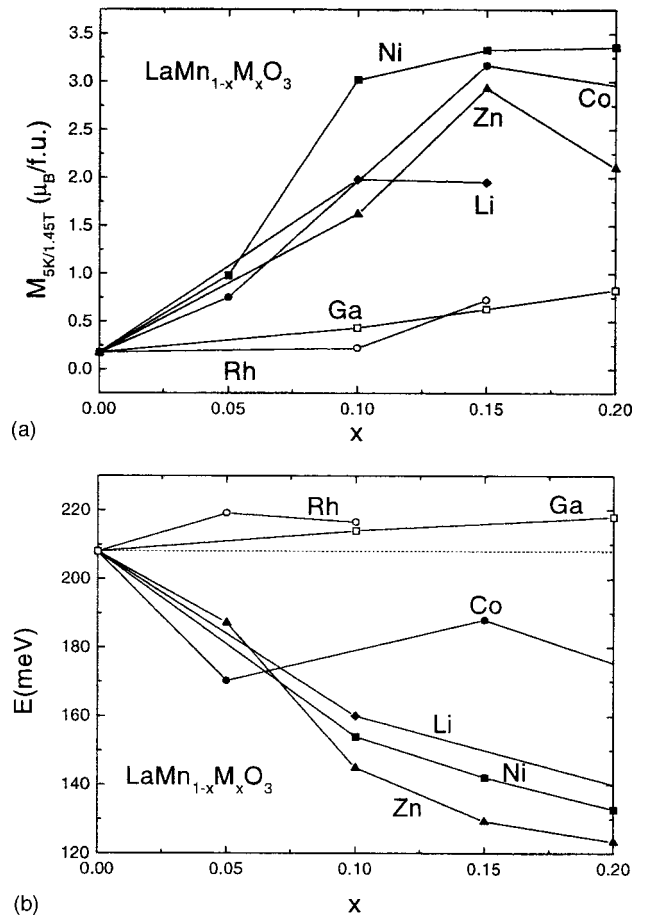


FIG. 10. (a) M measured at 5 K under 1.45 T vs x for the different dopants. (b) Activation energy as a function of x . For $M = \text{Li}^+$, the x value has been arbitrarily multiplied by 2 for the sake of comparison with the divalent cations.

the compounds by introducing mixed-valent manganese $\text{Mn}^{3+}/\text{Mn}^{4+}$; on the other hand, they induce disorder on the manganese site, and prevent the establishment of conducting paths along the Mn-O-Mn bonds. Conversely, the introduction of trivalent cations does not induce a strong ferromagnetism and the electronic transport is obviously hindered by these foreign cations on the manganese site. From this comparison, Co and Ni behave more like Zn^{2+} than Ga^{3+} or Rh^{3+} . Co and Ni could thus be in a divalent state as proposed in Refs. 8 and 9. However, a difference with amagnetic cations, Li^+ , Zn^{2+} , and Ga^{3+} is that Co and Ni cations are magnetic, so that possible superexchange interactions can also exist between manganese ions and Co or Ni, and induce or reinforce the ferromagnetism. In this respect, one should also consider the ability of Ni and Co species to hinder the orbitally ordered (OO) structure in charge-ordered AFM manganites, and to induce ferromagnetism.¹⁻⁴ This effect is not similarly reached with amagnetic cations.²⁰ Furthermore, when Ni or Co cations are substituted into ferromagnetic manganites, the ferromagnetic state is weakened and the resistivity is increased.²¹ This shows that Ni and Co play peculiar roles in collapsing OO structures and to induce FM.

The establishment of an A-type antiferromagnetic state in LaMnO_3 is intimately linked to the existence of OO which establishes at $T_{\text{JT}} \approx 700$ K.¹⁷ The creation (or not) of ferromagnetism and its link with OO has been studied in the case of Zn^{2+} and Rh^{3+} substitutions. In Fig. 4, the high-temperature evolution of the inverse susceptibility is shown for LaMnO_3 , and in Fig. 11 for the 10% Zn sample and for the 15% Rh-sample. The transition corresponding to orbital ordering observed at $T_{\text{JT}} \approx 700$ K in LaMnO_3 has clearly disappeared in the Zn-substituted compound: no accident or change in slope is observed in the $1/\chi(T)$ curve. Conversely, the accident on the susceptibility curve of the Rh-doped sample shows that OO still exists in Rh-doped compounds: a transition between two paramagnetic regimes as in the case of LaMnO_3 is observed at $T_{\text{JT}} \approx 625$ K for $x=0.15$, corresponding to an orbital ordering transition. Similar results were reported in Ref. 18 for Ga^{3+} -doped samples for which a transition was observed for $x \leq 0.35$. The orbital ordering is thus not strongly affected by the introduction of a trivalent amagnetic cation in LaMnO_3 : there is a gradual disappearance of OO as x increases (i.e., as the Mn^{3+} lattice becomes more and more disturbed, the cooperative Jahn-Teller effect is progressively suppressed), whereas the transition is completely destroyed when substituting divalent cations are used. A similar conclusion can be drawn from the X-ray investigation of the Ni-substituted samples (Fig. 2): the room-temperature crystallographic structure of $\text{LaMn}_{1-x}\text{Ni}_x\text{O}_3$ is changing from O' type (with OO) for $x=0$ to O type as the Ni content increases. These parameters evolve more smoothly (with the three parameters becoming closer) for the Ga series, but remain O' type until $x \leq 0.2$ (Fig. 2). The structural and magnetic changes corresponding to the collapse of the OO structure induced by Zn^{2+} and Li^+ , substituted for Mn in LaMnO_3 , demonstrate that the magnetic nature of the foreign cation is not necessary to induce FM. The effect is driven by the induced mixed valency of Mn. It is thus tempting to associate the similarities between Zn^{2+}

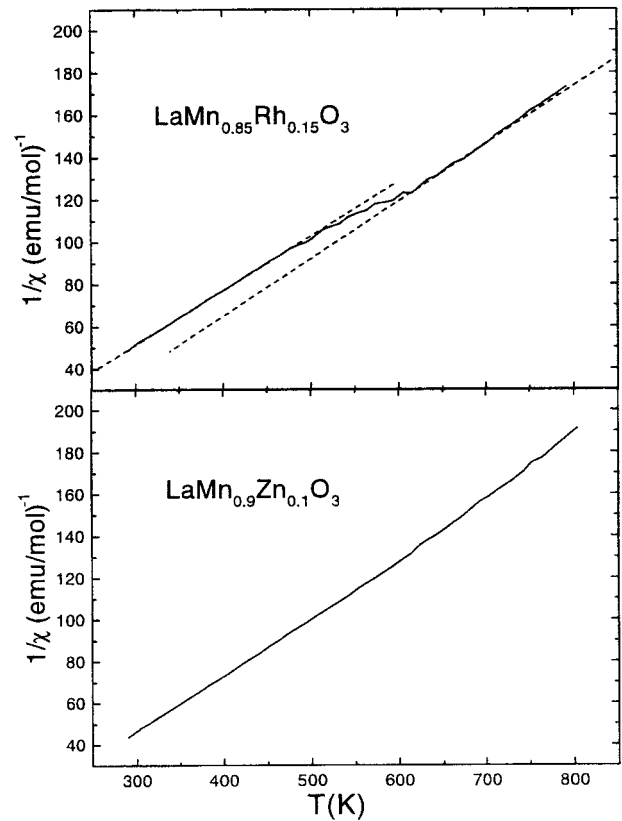


FIG. 11. Inverse of the high-temperature susceptibility of $\text{LaMn}_{0.85}\text{Rh}_{0.15}\text{O}_3$ (a) and $\text{LaMn}_{0.9}\text{Zn}_{0.1}\text{O}_3$ (b).

and Ni/Co cations with their common divalent oxidation state.

Nevertheless, if we consider trivalent Ni and Co, the effect of their substitution cannot be ascribed to the Mn mixed valency. Thus, in this scenario, Ni^{3+} and Co^{3+} would have to be much more efficient than Rh^{3+} and Ga^{3+} , and as efficient as univalent or divalent amagnetic cations to destabilize the OO structure of LaMnO_3 . The magnetization similarities obtained for Ni(Co) and Zn^{2+} and Li^+ would imply that the exchange energy of the Mn^{3+} -O- Ni^{3+} (Co^{3+}) ferromagnetic superexchange is similar to that of the Mn^{3+} -O- Mn^{4+} ferromagnetic double exchange.

CONCLUSION

This study of the substitution at the manganese site of the stoichiometric LaMnO_3 by various cations shows that the valency of the amagnetic foreign element plays a prominent role in destroying the orbital ordering and inducing ferromagnetism. As ferromagnetism is observed for amagnetic cations (M^+ or M^{2+}), the origin of ferromagnetism cannot be explained by the possible ferromagnetic superexchange between Mn^{3+} and M^+ (or M^{2+}) species. The introduction of Mn^{4+} , which can induce double exchange, is necessary to efficiently break orbital ordering and associated A-type antiferromagnetism leading to strong ferromagnetism. For the Ni- and Co-substituted systems the divalent nature of these substituting elements could also be responsible for the induced ferromagnetism. Moreover, a rapid similar disappear-

ance of the magnetic signature of the LaMnO₃ JT transition is observed as the content of substituted cation (Zn²⁺, Ni^{2+/3+}, Co^{2+/3+}) increases. This is in contrast with the weak effect on T_{JT} of trivalent amagnetic cation such as Ga³⁺,¹⁸ which demonstrates the ability of the JT cooperative effect of LaMnO₃ to accommodate a large amount of foreign trivalent amagnetic cations. All these results suggest that Ni and Co are mainly divalent when substituted for Mn in LaMnO₃.

Substitutions with trivalent Ni³⁺ (Co³⁺) could also explain the ferromagnetic existence by ferromagnetic superexchange with Mn³⁺, which could destroy, more efficiently than Rh³⁺ and Ga³⁺, the OO state of LaMnO₃. As they would not create Mn⁴⁺ species, this would imply that these

cations could be ferromagnetically coupled to Mn by superexchange. Since trivalent cobalt is generally thought to be on the low-spin state t_{2g}^6 when substituted in LaMnO₃ ($S=0$), Co³⁺ alone cannot induce such a strong FM. Also, since trivalent nickel is difficult to stabilize in perovskite prepared in air, it is also hardly believable that all the nickel cations are trivalent. Nevertheless, since both Ni and Co can exhibit a “II-III” mixed valency, it is difficult to discriminate the pure divalent state from this mixed-valency.

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