Magnetic properties of perovskites
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7^{3+}}\text{Mn}_{0.3} - x^{4+}\text{Ti}_x\text{O}_3$: Monte Carlo simulation versus experiments

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Magnetic properties of perovskites $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}^{3+}_{0.7}\text{Mn}^{4+}_{0.3-x}\text{Ti}_x\text{O}_3$: Monte Carlo simulation versus experiments

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This work presents a Monte Carlo study of the phase transition in the perovskites $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}^{3+}_{0.7}\text{Mn}^{4+}_{0.3-x}\text{Ti}_x\text{O}_3$ ($x = 0.1, 0.2, \text{ and } 0.25$). We take into account nearest-neighbor (NN) interactions between magnetic ions $\text{Mn}^{3+} (S = 2)$ and $\text{Mn}^{4+} (S = 3/2)$ using a spin model describing a strong anisotropy on the $z$ axis. We have calculated the uniform and staggered magnetizations as well as the Edwards-Anderson order parameter as functions of temperature, with and without an applied magnetic field. Fitting the experimental Curie temperature at $x = 0$, we estimated values of various exchange interactions in the system. The dominant one is that between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ which is at the origin of the ferromagnetic ordering. Effects of the very small interaction $J_2$ between NN $\text{Mn}^{3+}$ is analyzed: we show that it can cause an antiferromagnetic phase above $T_c$ which disappears at smaller $J_2$ or at $\text{Mn}^{3+}$ concentrations smaller than 0.55. Our results show a good agreement with experiments on the magnetizations for substitution concentration $x = 0.1, 0.2$ and 0.3. We also studied the applied-field effect on the magnetization and our obtained results are compared with experiments performed at $x = 10\%$.

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I. INTRODUCTION

The study of phase transition in magnetic materials has been the subject of intensive studies both experimentally and theoretically in the last decades [1, 2]. In this paper, we confine ourselves to the family of perovskite compounds $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ which has rich magnetic behaviors and numerous practical applications. Experiments have been performed to determine magnetic properties of manganese oxides $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, with $\text{A}=\text{Sr}, \text{Ca}, \text{Ba},...$. These materials are currently attracting a considerable attention [3] because of the complex interplay among spins which induces a rich phase diagram as well as the colossal magnetoresistance (CMR) phenomenon [4–6]. The rapid development of the CMR field is due mainly to its many applications in particular in spintronics [7–9]. The diagram in the phase space defined by concentration $x$, temperature $T$, magnetic field $H$ and superexchange (SE) $J$ is not quite clear yet for different compounds. Jonker and Van Santen [10] have studied ferromagnetic compounds of manganese with perovskite structure. Their properties can be understood as the result of a strong ferromagnetic exchange interaction between nearest neighboring Mn ions via intercalated oxygen: $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$. The double exchange (DE) mechanism developed by Zener [11–13] explains the existence of ferromagnetism and the metallic behavior at low temperatures. There is now a consensus to recognize that the interesting properties observed in perovskites are fundamentally originated from the DE mechanism along the link $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$. This characteristic is at the origin of a new interesting observed phase transition in doped manganites [14, 15] from a magnetically-ordered phase to the disordered phase. Recent refinement of experimental techniques and the improvement of the sample quality have made possible to discuss critical phenomena of this
transition [16]. To see more details on the role of the DE, we quote a work by Urushibara et al. [17] which have investigated the transport and magnetic properties related to the insulator-metal transition of La$_{0.7}$Sr$_{0.3}$MnO$_3$ crystals. These experimental works allowed us to qualitatively understand properties of this magnetic system. Nevertheless, these phenomena have not been quantitatively modeled, though there has been a number of works dealing with this issue from a theoretical standpoint [18, 19].

In this paper we investigate by Monte Carlo (MC) simulation the magnetic properties in perovskite manganite La$_{0.7}$Sr$_{0.3}$MnO$_3$. Effects of Ti substitution on the magnetic properties are studied for La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Ti$_x$O$_3$ ($x = 0.1$, $0.2$ and $0.25$). Recent experimental works on Ti doping [20–23] show that doping with non-magnetic Ti allows one to change the relative concentration Mn$^{3+}$/Mn$^{4+}$ which in turn reduces the effective ferromagnetic interaction between them. As a consequence, one can increase the magnetic resistivity of the compound for application in spin transport.

We use a discrete spin model to express the strong Ising-like anisotropy along the $z$ axis and we take into account various types of interactions between spins in the calculation of the magnetization. As seen in this paper, this model is justified by a good agreement with experimental measurements performed on this material.

The paper is organized as follows: in section II, we present our model and describe the MC method. Results are reported and discussed in section III, and our concluding remarks are given in section IV.

II. MODEL AND METHOD

A. Model

We consider the simple cubic lattice with the following Hamiltonian:

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \mu_0 H \sum_{\langle i \rangle} S_i^z \quad (1)$$

where $\mathbf{S}_i$ is the spin at the lattice site $i$, $\sum_{\langle i,j \rangle}$ is made over spin pairs coupled through the exchange interaction $J_{ij}$. In the following we shall take interactions between nearest-neighbors (NN) and between next nearest-neighbors (NNN) of magnetic Mn ions. $H$ is a magnetic field applied along the $z$ axis. Let us recall that there are two kinds of Mn ions in La$_{0.7}$Sr$_{0.3}$MnO$_3$: Mn$^{4+}$ with spin amplitude $S = 3/2$ and Mn$^{3+}$ with $S = 2$. They occupy the corner sites of the simple cubic lattice. It is experimentally found that interaction between neighboring Mn$^{3+}$ and Mn$^{4+}$ is strongly ferromagnetic while that between Mn$^{4+}$ as well as that between Mn$^{4+}$ are very weakly antiferromagnetic [20]. As we will see later, to fit with experiments we need a very small interaction between NNN Mn$^{4+}$ ions. Due to the strong disorder caused by La and Sr ions, the positions of Mn$^{4+}$ and Mn$^{4+}$ are at random. In addition, when one substitutes Mn ions by non-magnetic Ti the disorder becomes even stronger due to the magnetic dilution induced by Ti substitution. Experiments have been recently carried out on La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Ti$_x$O$_3$ by Kallel et al. [20–23] for several $x$. We will compare our results with the data of these works.

Before defining explicitly the interactions, let us discuss about the spin model we shall use. We suppose that the spins of Mn ions lie on the $z$ axis with a strong uniaxial anisotropy. We have first tried to calculate magnetic properties using the Heisenberg model with a strong anisotropy but we did not get an agreement with experimental data at low temperatures. On the other hand, using a discrete Ising-like spin model, we obtain a good agreement with experiments on magnetization at various substitution concentrations in the whole temperature range as shown in the next section.

We define now the interactions. The exchange parameters $J_{ij}$ are strongly correlated to the electric structure of the compound. In 1950, Goodenough [24, 25] and Kanamori [26] explained the magnetic interactions in manganites. More quantitative calculations of the magnitudes of the exchange have been attempted only recently for LaMnO$_3$ using first-principles electronic structure methods [27, 28]. Based on the crystal and electronic structures of this system, several coupling interaction can be taken into account in the present study:

$J_1$: interaction of a NN pair Mn$^{3+}$-Mn$^{4+}$,
$J_2$: interaction of a NN pair Mn$^{3+}$-Mn$^{3+}$,
$J_3$: interaction of a NN pair Mn$^{4+}$-Mn$^{4+}$.

In addition, we also introduce the following very small interactions between NNN ions:

$J_4$: interaction between Mn$^{3+}$ NNN,
$J_5$: interaction between NNN Mn$^{3+}$ and Mn$^{4+}$,
$J_6$: interaction between Mn$^{4+}$ NNN.

As said earlier, the DE interaction Mn$^{3+}$-O-Mn$^{4+}$ results in a strong ferromagnetic coupling ($J_1$) and the SE interactions Mn$^{3+}$-O-Mn$^{3+}$ ($J_2$) and Mn$^{4+}$-O-Mn$^{4+}$ ($J_3$) give rise to very weak antiferromagnetic exchange integrals [10, 29, 30]. We shall see below that though very small, these antiferromagnetic interactions cannot be neglected: they are at the origin of magnetic behaviors at very low $T$ and of the antiferromagnetic phase in a small temperature region above $T_c$, as discussed in the next section. As for $J_4$, $J_5$ and $J_6$ they are assumed to be even smaller than $J_2$ and $J_3$. They are to be used for fine tuning of the fit. We have tested them while fitting with Ti substitution shown below. Only $J_1$ may be necessary since the high Mn$^{4+}$ concentration (70%) allows for such a coupling to be visible. So from now on, we will neglect $J_5$ and $J_6$ for clarity.
B. Method

We have conducted standard MC simulation on samples of dimension \( N = L \times L \times L \), where \( L \) is the number of simple cubic cells in each of the three Cartesian directions. Periodic boundary conditions are used in all directions. Simulations have been carried out for different lattice sizes ranging from \( 12^3 \) to \( 20^3 \) lattice cells. Some runs with \( N = 24^3, 28^3 \) and \( 32^3 \) have also been performed to check finite-size effects as will be shown below.

The procedure of our simulation can be split into two steps. The first step consists in equilibrating the lattice at a given temperature. For the thermalization, two difficult regions are the low-temperature \( (T) \) one and the critical region. The low-\( T \) region have small ‘update’ probabilities [proportional to exp(\(-E/T\))] and therefore needs longer runs to ensure the equilibrium state before averaging: a simple check of energy behavior with time evolution and temperature evolution at low \( T \) suffices. Near the transition temperature \( T_c \), the critical slowing-down also necessitates long runs to ensure a good statistical average. Test runs with different run lengths were performed to estimate necessary run length before real simulations. The second step, when equilibrium is reached, we determine thermodynamic properties by taking thermal averages of various physical quantities [31, 32]. Starting from a random spin configuration as the initial condition for the MC simulation, we have calculated the internal energy per spin \( E \), the specific heat \( C_V \), the magnetic susceptibility \( \chi \), the magnetization of each sublattice and the total magnetization, as functions of temperature \( T \) and magnetic field \( H \). The MC run time for equilibrating is about \( 10^8 \) MC steps per spin. The averaging is taken, after equilibrating, over \( 10^3 \) MC steps.

Since the system has a strong disorder (random mixing of Mn ions), we will see that the size effects are not significant from \( 20^3 \) sizes. Most of the simulations have been therefore carried out at this size using 20 to 30 samples for largest \( x \). For smaller \( x \) and large sample sizes the configuration average needs smaller number of configurations (about 10 to 20). The results on \( T_c \) vary over an interval of 4K with various disorder samples. So errors are \( \pm 2 \) K around the mean value. These errors cover smaller errors \( \pm 1 \) K due to the peak determination of \( T_c \).

The total magnetization \( M_t \) is defined by

\[
M_t = \frac{1}{N} \sum_i S_i
\]  

(2)

where the sum is performed over spins of both Mn\(^{3+}\) and Mn\(^{4+}\) and \( \langle \ldots \rangle \) indicates the statistical time average. The magnetizations of Mn\(^{3+}\) and Mn\(^{4+}\) \( (M_1 \text{ and } M_2) \), their staggered magnetizations \( (M_{s1} \text{ and } M_{s2}) \) and the Edwards-Anderson order parameter \( Q_{EA} \) are defined by

\[
M_t = \frac{1}{N_t} \langle \sum_i S_i \rangle
\]

\[
M_{st} = \frac{1}{N_t} \langle \sum_i (-1)^i S_i \rangle
\]

\[
Q_{EA}(\ell) = \frac{1}{N_t} \langle \sum_i S_i \rangle^2
\]

where the sum is taken over Mn\(^{3+}\) \( (\ell = 1) \) or Mn\(^{4+}\) \( (\ell = 2) \) with \( N_t \) being the number of spins of each kind. Note that \( Q_{EA} \) is calculated by first taking the time average of each spin and secondly taking the spatial average over all spins. This parameter is used to calculate the freezing degree of the spins when a long-range ordering is absent or the nature of ordering is unknown such as in spin glasses or in disordered systems [33–36].

For \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) magnetic ions Mn\(^{3+}\) and Mn\(^{4+}\) have concentrations 0.70 and 0.30, respectively [20]. Hereafter, we study this “mother” compound and the case where Ti ions replace a fraction \( x \) of Mn\(^{4+}\). Note that in our procedure, we first generate the pure state (Mn\(^{3+}\) only) which is the fully antiferromagnetic state which has the site ‘parity’. Then we replace Mn\(^{3+}\) by Mn\(^{4+}\) at randomly chosen sites with a concentration of 0.3. In doing so we conserve the site ‘parity’ because we do not exceed the percolation limit for the simple cubic structure. This is the reason why we define the staggered magnetization which is useful for detecting an antiferromagnetic phase. Of course, this is artificially created state but physically the results will not change if we have large domains of Mn\(^{3+}\) in the compound. The substitution of Mn\(^{3+}\) by Ti is next performed also at randomly chosen Mn\(^{4+}\) ions.

III. RESULTS

A. Properties of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \)

Let us examine first the case without Ti doping in order to have an idea about the role of each interaction \( J_1, J_2, J_3 \) and \( J_4 \).

As said earlier, experiments found that \( J_1 \) dominates and gives rise to the ferromagnetic ordering up to very high temperatures \( T_c = 369 \) K [20]. For \( H = 0 \), we have fitted the MC transition temperature with experimental value \( T_c = 369 \) K using the mean-field approximation:

\[
T_c = \frac{2}{3k_B} Z S(S + 1) J_{eff}
\]

(6)

where \( Z = 6 \) is coordination number (all occupied neighbors) and \( S = \sqrt{3} \) the effective spin value calculated from \( S^2 = S(\text{Mn}^{4+})S(\text{Mn}^{3+}) = 2 \frac{7+3}{2} = 3 \). Putting \( T_c = 369 \) K, we obtain \( J_{eff} \approx 25.1 \) K. Note that in magnetic materials with Curie temperatures at room or higher temperatures the effective exchange interaction is of the order of several
dozens of Kelvin [37], just as what we found here. It is
not easy to determine each of the exchange interactions
defined earlier. Fortunately, we know that \( J_1 \) is much larger than the other interactions [20]. Writing in
the mean-field spirit \( J_{eff} \approx J_1 + |J_2| + |J_3| + J_4 \) and taking,
after comparing our calculated magnetizations with sev-
eral trying values of \( J_2, J_3 \) and \( J_4 \) we find the best fits of
magnetizations obtained with \( J_2 = J_3 = J_4 = -J_1/120 \),
as shown below. The best estimated values of the main
exchange interactions are \( J_1 \approx 24.5 \) K and \( J_2 = J_3 = -J_4 = -\frac{J_1}{20} \). We will take
\( J_3 = -J_4 = -0.20 \) K for all calculations and we will discuss below the effects of
\( J_2 \) since this parameter is found to be more relevant than
the other two.

We show in Fig. 1 the total magnetization \( M_t \) (green squares) and the sublattice magnetizations \( M_{t1,2} \) and sub-
lattice staggered magnetizations \( M_{s1,2} \). We calculated
the magnetization in the simulation using parameters
representing the magnetic moments of \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \).
We next fit our values found with simulations at the low-
est \( T \) with values found experimentally (see for example
experimental data in the references [20–23]). The unit
used for magnetizations in this paper (emu/g) is by this
fit. Several remarks on Fig. 1 are in order:

(i) \( M_t \) shows a transition at \( T_c \approx 369 \) K
(ii) The magnetizations of \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) vanish rather abruptly at that temperature. This suggests that
the transition may be weakly of first order.

(iii) Surprisingly, the staggered magnetizations become
non zero for \( T > T_c \) up to \( \approx 427 \) K. This indicates that
an antiferromagnetic ordering appears above the ferro-
magnetic phase.

(iv) The Edwards-Anderson order parameters show
“strong fluctuations” at and above \( T \approx 369 \) K. The fact
that \( Q_{EA} \) is not zero between 369 K and 427 K means
that there is a phase which is not paramagnetic. How-
ever \( Q_{EA} \) alone cannot determine the nature of the order-
ing. The non-zero staggered magnetization in this tem-
perature zone helps confirm an antiferromagnetic phase.

(v) At very low \( T \), the antiferromagnetic interaction \( J_2 \)
between \( \text{Mn}^{3+} \) affects its magnetization behavior: weak
values (smaller than \(-0.20 \) K) keep the ferromagnetic or-
dering near \( T = 0 \) [Fig. 1(b)] but induces a reduction of
\( Q_{EA} \) in Fig. 1(c). This reduction is a signature of some
of the dynamical motion of \( \text{Mn}^{3+} \). We return to this point later
while showing results with other values of \( J_2 \). Note that
\( J_2 \) does not affect the magnetization and \( Q_{EA} \) of \( \text{Mn}^{4+} \).

To show that the phase transition at \( T_c = 369 \) K is of
first-order, we show in Fig. 2(a) the energy versus \( T \)
using the same parameters as those of Fig. 1, namely
\( J_1 = 24.5 \) K, \( J_2 = J_3 = -J_4 = -0.20 \) K. We observe a
discontinuity at 369 K. For comparison, we show in Fig.
2(b) the case where \( J_2 \) is smaller, \( J_2 = -0.08 \) K. We
observe that the transition temperature is very sensitive
to \( J_2 \): it moves to \( \approx 422 \) K.

We have made several simulations to search for the
parameter(s) responsible for the antiferromagnetic phase: we
find that the value of \( J_3 \) does not affect neither the
antiferromagnetic phase nor the value of \( T_c \) as long as it
is of the order of \( \approx -0.20 \) K. This is easily understood
because the concentration of \( \text{Mn}^{4+} \) is small (30\%) so that
the number of NN pairs of \( \text{Mn}^{4+} \) with interaction \( J_3 \) not
intercalated by \( \text{Mn}^{3+} \) is negligible.

![FIG. 1. (Color online) La_{0.7}Sr_{0.3}Mn_{4+}^{3+}Mn_{4+}^{3+}O_3 (no Ti dop-
ing): Results of Monte Carlo simulation for \( J_1 = 24.5 \) K,
\( J_2 = J_3 = -J_4 = -0.20 \) K: (a) the magnetization (blue cir-
cles) and staggered magnetization (orange void circles) of the
subsystem of \( \text{Mn}^{3+} \), (b) those of the subsystem of \( \text{Mn}^{4+} \), (c)
Edwards-Anderson order parameter \( Q_{EA} \) versus temperature
\( T \) for \( \text{Mn}^{4+} \) (red circles) and \( \text{Mn}^{4+} \) (cyan squares). The total
magnetization is also shown in the top figure by green squares.

We have checked that the antiferromagnetic phase dis-
appears if the antiferromagnetic interaction \( J_2 \) between
\( \text{Mn}^{3+} \) is small. Figure 3 shows no antiferromagnetic
phase for \( J_2 \approx -0.08 \) K. This is not surprising because
indicating a first-order character, (b) \( J \) where the phase transition occurs at \( T \) and \( J \). An example is the phase above the spin-glass phase. An example is the that in spin glasses that weak disorder can cause a ferromagnetic phase. At this stage, it is worth noting that if the concentration of Mn in a region narrower than that for 70%. We have verified shown in Fig. 4: the antiferromagnetic phase exists but of Mn concentrations are not symmetric such as 70%-30% there all antiferromagnetic ordering to occur. When the concentration: by symmetry -Mn and Mn ...-Mn and Mn-4+ and Mn-3+, has not been experimentally observed. An example with 60% Mn-3+ is shown in Fig. 4: the antiferromagnetic phase exists but in a region narrower than that for 70%. We have verified that if the concentration of Mn-3+ becomes smaller than 0.55, there is no more antiferromagnetic phase above the ferromagnetic phase. At this stage, it is worth noting that in spin glasses that weak disorder can cause a second phase above the spin-glass phase. An example is the ±J Ising spin glass: if the percentage of −J bonds is large with respect to that of +J then the antiferromagnetic phase exists above the spin-glass phase in a region called reentrance [33, 35]. We will take \( J_2 \) = −0.20 K for the results shown below with Ti substitutions at \( x \). As expected, the abrupt character of the transition increases and the antiferromagnetic phase becomes stronger in a larger temperature range. Note the strong variation of \( Q_{EA} \) at the transition from ferromagnetic to antiferromagnetic phase. Furthermore, at this strong value of \( J_2 \), there are at low \( T \) a number of antiferromagnetic NNN pairs which 'resist' the strong ferromagnetic Mn-3+-Mn-4+ coupling. This yield a reduction of the Mn-3+ magnetization at low \( T \) (< 100 K) as seen in Fig. 5(b). As already commented in remark (v) on Fig. 1, this instability is signaled by a reduction of \( Q_{EA} \) in this low-\( T \) region. By comparing the values at low \( T \) for three cases with increasing \( J_2 \): \( M = 69 \text{ emu/g} \) for \( J_2 = -0.08 \text{ K} \) [Fig. 3(b)], \( M = 60 \text{ emu/g} \) for \( J_2 = -0.20 \text{ K} \) [Fig. 1(b)] and \( M = 54 \text{ emu/g} \) for \( J_2 = -0.40 \text{ K} \) [Fig.
FIG. 4. (Color online) La$_{0.6}$Sr$_{0.4}$Mn$_{0.33}^+$Mn$_{0.33}^{4+}$O$_3$: Results at 60% of Mn$^{3+}$ (a) magnetization (blue circles) and staggered magnetization (orange void circles) of Mn$^{4+}$, (b) those of Mn$^{3+}$. We have used $J_2 = -0.20$ K ($J_1 = 24.5$ K, $J_3 = -J_4 = -0.20$ K). The total magnetization averaged over the whole system is also shown by green squares in the top figure. The antiferromagnetic phase is reduced with respect to that at 70% shown in Fig. 1.

5(b)], we conclude that even the ferromagnetic ordering dominates the compound at low $T$, the stronger $J_2$ yields a smaller magnetization of Mn$^{3+}$. However, this reduction of magnetization at low $T$ is weakened at higher $T$: the curvature of $M$ shows a decreasing tendency with increasing $T$ for $T > 100$ K.

Let us in Fig. 6 how we determine $T_c$ in order to establish a phase diagram in the parameter space $(T_c, P)$ where $P$ is the concentration of Mn$^{3+}$. As said in the previous section, we have carried out most simulations with the lattice size 20$^3$ because from this size up, finite-size effects are not strong. There are two error estimations: the first one consists of making many runs in the critical region using temperature steps as small as 2 K. The peak of the susceptibility is identified with error $\pm 1$ K. The second error estimation consists of making runs with differently generated disordered samples: we observed that $T_c$ changes in an interval of 4 K. So the error over disorder is $\pm 2$ K around the median value. Fortunately, this error includes the error due to discrete temperature steps. We show in Fig. 6 an example of finite-size effects for $J_1 = 24.5$ K, $J_3 = -J_4 = -0.20$ K and $J_2 = -0.08$ K. This case is an easy one due to the absence of the antiferromagnetic case. The sizes used are $L = 12, 16, 20, 24, 28$ and 32. In spite of small $J_2$, the susceptibility has strong fluctuations around each peak. The peak positions can be recognized without difficulty. For curve presentation we used the most typical runs, namely the ones which correspond to the mean values of $T_c$ at each size. The error bars around each point are $\pm 1$. The extrapolated point at the infinite size is $426 \pm 1$ K. The peak temperatures...
are displayed in Fig. 6(b). Note that we should not use the peak heights for finite-size scaling to calculate critical exponents because the discretized temperatures do not allow one to localize the peak height with high precision. To do that we should use continuous-temperature methods such as histogram MC techniques which give the exact peak (position and height) at $T_c$ (see for example [38]).

FIG. 6. (Color online) La$_{0.7}$Sr$_{0.3}$Mn$_{3+}$Mn$_{4+}$O$_3$: Example of finite-size effects for $J_1 = 24.5$ K, $J_3 = -J_4 = -0.20$ K and $J_2 = -0.08$ K. (a) Susceptibility $X$ calculated from fluctuations of the total magnetization for sizes $N = L^3$ with $L=12$ (cyan void triangles), 16 (green filled triangles), 20 (red void squares), 24 (blue filled squares), 28 (blue void circles) and 32 (gray filled circles), many points have been removed for the sake of clarity. (b) Curie temperature versus $1/L$, note that the point for $1/L = 0$ (infinite lattice size) is extrapolated using the smooth function of csplines.

The full diagram is shown in Fig. 7. This phase diagram is easily understood: near 50% each of Mn$^{3+}$ is surrounded by Mn$^{4+}$ ions so that antiferromagnetic interactions between Mn$^{4+}$ or between Mn$^{4+}$ are almost absent, there is thus no antiferromagnetic phase. Now, for larger concentrations near 100%, the ferromagnetic phase disappears leaving the place for an antiferromagnetic phase because the number of Mn$^{4+}$ ions is so small, not sufficient to induce a ferromagnetic order: the system is then composed of Mn$^{3+}$ with weak antiferromagnetic interaction $J_2$ between them. This induces an antiferromagnetic phase at very low temperatures. Let us give the value of the temperature at the ferromagnetic transition for several values of Mn$^{3+}$ concentration $P$: $T_c \simeq 445 \pm 5$ K for 50% and 55% (large errors are due to large disorder at these concentrations). From 60% the system undergoes the ferromagnetic transition at $T_c \simeq 430 \pm 3$ K for 60%, 369$\pm$1 K for 70%, $T_c \simeq 315 \pm 1$ K for 80% and $T_c \simeq 240 \pm 1$ K for 90%. However, for concentrations from 60% to 90%, the antiferromagnetic ordering sets in above $T_c$ up to $T_N \simeq 444$ K (for 60%), 427 K (for 70%) and 380 K (for 80%). For $P > 90%$, only the antiferromagnetic phase exists.

We emphasize here that the phase diagram in Fig. 7 is shown for $J_1 = 24.5$ K, $J_2 = J_3 = -J_4 = -0.20$ K. If $J_2$ is smaller, say $J_2 = -0.08$ K, the antiferromagnetic phase above the ferromagnetic phase disappears as seen in Fig. 3 for $P = 70%$. We have checked the absence of the antiferromagnetic phase at other Mn$^{3+}$ concentrations (not shown), except naturally the one in the zone $P \in [0.91, 1]$.

![FIG. 7. (Color online) La$_{0.7}$Sr$_{0.3}$Mn$_{3+}$Mn$_{4+}$O$_3$: Phase diagram in the space ($P$, $T$) where $P$ is the Mn$^{3+}$ concentration. Black circles denote the ferromagnetic transition temperatures, red void circles indicate the transition from the antiferromagnetic to paramagnetic phase. F, AF and Para denote the ferromagnetic, antiferromagnetic and paramagnetic phases, respectively. One has used $J_1 = 24.5$ K, $J_2 = J_3 = -J_4 = -0.20$ K. Lines are guides to the eye. See text for comments.](image)

At this stage, we would like to recall that the existence of a partially-disordered antiferromagnetic phase above the ferromagnetic phase is frequently seen in many frustrated systems [39]. For example, in exactly solved frustrated Ising models such as the honeycomb lattice [40] Kagomé lattice [41] among others [42], it has been shown that the transition from the ferromagnetic phase to an antiferromagnetic phase takes place via a very narrow intermediate paramagnetic phase called “reentrant phase”. When this reentrance is not possible, the direct transition between the ferromagnetic and the antiferromagnetic phases should be of first-order because one of these two phases is not a symmetry subgroup of the other as in second-order phase transitions. A direct ferrromagnetic-antiferromagnetic first-order transition has been seen in Ref. 43. The model simulated here has a strong disorder due to the random mixing of Mn$^{3+}$ and Mn$^{4+}$ so that we cannot deal with it analytically, but competing interactions included in the model (ferromagnetic $J_1$, antiferromagnetic $J_2$ and $J_3$) can cause the ferromagnetic-
antiferromagnetic transition. The abrupt change of the total magnetization and the staggered magnetization observed at the transition shown in Figs. 1 and 5 suggest a direct transition with a first-order character.

B. Properties of La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$O$_3$ and La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Ti$_x$O$_3$

In this doped material, Ti atoms replace a fraction $x$ of Mn$^{4+}$ with $x$ varying from 0 to 0.3. Since Ti is non magnetic, the substitution introduces a dilution. Let us take into account interactions $J_1$, $J_2$ and $J_3$ between Mn ions as defined above. In addition, we have added a very small ferromagnetic interaction between Mn$^{3+}$-NNN.

While there is no experimental proof so far on the existence of the antiferromagnetic phase above $T_c$, we choose to study the effect of Ti substitution at $J_2 = -0.20$ K hereafter (larger $J_2$ induces an AF phase as seen above). The agreement with experiments justifies this choice.

Using $J_1 \approx 24.5$ K, $J_2 = J_3 = J_4 \approx -0.20$ K we have simulated this system with several values of $x$: 0.1, 0.2 and 0.25. The reason why we did not take $x = 0.3$ is because at this dilution, there is no more Mn$^{4+}$ in the system so that there is no Mn$^{3+}$-Mn$^{4+}$ interaction, namely no ferromagnetic phase. Experiments have been carried out at this concentration but we believe that there remains a small number of Mn$^{4+}$ in the material as it has been noticed by Jonker and Van Santen [10]. Not surprisingly, our results for $x = 0.25$ agree very well with experimental observations for $x = 0.3$. The full results of the magnetization with applied magnetic field $\mu_0 H = 0.05$ Tesla are shown in Fig. 8 to compare with experiments at the same field [20]. Let us comment these results: (i) the overall agreement with experiments is excellent, given the fact that no other parameter adjustments were necessary (we used only exchange parameters while fitting with $T_c$ as described above), (ii) the slight down-turn curvature at very low $T$ is sensitive to $J_2$: smaller $J_2$ will suppress this but then the agreement is less perfect at higher temperatures.

We have also calculated at five temperatures the total magnetization as a function of the applied magnetic field $\mu_0 H$. These results are shown in Fig. 9 together with experimental data taken from Ref. 23. A good agreement is observed except at very low fields where precision of parameters and experimental details of lattice structure and disorder play certainly an important role.

At this point, we would like to emphasize that doping La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$O$_3$ with other ions such as Ni can alter magnetic structures in a drastic way such as domains with different lattice deformations and creation of ferromagnetic clusters which change the low-$T$ behaviors [44]. We believe that strong Ti-substitution also induces these aspects but probably in a less drastic manner. The good agreement obtained above without introducing such factors may be a proof of the absence of complicated structure deformations.

Before closing this section, let us mention that our present model can also be used to study the case where a number of La is substituted by magnetic Ce$^{3+}$ ions of spin $S = 1/2$: Ce occupy the centered sites of the bcc lattice. Additional interactions between Ce$^{3+}$ ions and Mn$^{3+}$ and Mn$^{4+}$ have to be introduced. Experiments have been performed on La$_{0.56}$Ce$_{0.14}$Sr$_{0.3}$MnO$_3$ [45, 46]. Work is under way to explain by MC simulations magnetic behaviors observed in this system.

IV. CONCLUSION

Perovskite compounds La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Ti$_x$O$_3$ have very rich magnetic behaviors when substituting Mn ions with other non magnetic atoms. In this paper we have
studied this compound without and with Ti substitution by the use of MC simulations. Fitting only the experimental value of the critical temperature $T_c = 369$ K in the case of non substitution, we have estimated various exchange interactions of which the ferromagnetic one between Mn$^{3+}$ and Mn$^{4+}$ is dominant ($\approx 24.5$ K). The other interaction which is though small but plays an important role is $J_2$ between Mn$^{3+}$ ($\approx -0.20$ K); it is at the origin of an antiferromagnetic phase observed in a small temperature region above $T_c$. This phase diminishes progressively with decreasing $J_2$ and disappears when $J_2$ becomes smaller (see Fig. 3 for $J_2 \approx -0.08$ K, for example). Experiments did not see this phase. There are two possible explanations. The first one is that experiments have overlooked it because experimental techniques used so far were not suitable to detect an antiferromagnetic ordering. The second explanation is that if the value of $J_2$ in experimental samples is smaller than -0.20 K then the antiferromagnetic phase does not exist as shown above.

We have also investigated the effect of Ti substitution on the magnetization as a function of $T$ at several substitution concentrations. Our results on the magnetization agree remarkably with experiments over the whole range of temperature, showing that the estimated parameters are precise enough to reproduce experimental data at several substitution concentrations (Fig. 8). For the field effect, our results agree with experiments except at very low fields where there may be many other finer aspects such as a possible existence of magnetic domains, impurity clusters, etc. in real crystals which should be taken into account.

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