

Magnetic behavior of the $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ perovskites

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The magnetic ordering of the compounds $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ where $0.2 < y < 0.5$ and $0 < x < 0.1$ has been studied within the molecular field theory. We introduce a model based on the competition between ferromagnetic coupling between the Mn ions and strong antiferromagnetic coupling induced by the presence of Fe ions. The magnetization as a function of temperature and the critical temperature have been calculated for several values of the parameter x . We show that even for very small x , the magnetic order of the system is reduced. Our results are in good agreement with experimental findings on these systems. © 2000 American Institute of Physics.

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The discovery of colossal magnetoresistance (CMR) in the mixed valence compounds of the type $\text{A}_{1-y}\text{A}'_y(\text{A}, \text{A}' = \text{La}, \text{Ca}, \text{Ba})\text{MnO}_3$ has raised the interest in the perovskite based oxides. The interest has focused on the phase diagram and the magnetic and transport properties. Materials of this type with a rich phase diagram which have been studied intensively experimentally¹⁻³ are the $\text{La}_{1-y}\text{Ca}_y\text{MnO}_3$ compounds.

At low Ca doping ($y < 0.2$) these materials are ferromagnetic insulators, for high Ca doping ($y > 0.5$) the materials become antiferromagnetic insulators. In the intermediate doping ($0.2 < y < 0.5$) they become ferromagnetic and CMR is measured near the ferromagnetic critical temperature T_c . The ferromagnetic ordering and the appearance of CMR at the intermediate doping range have been initially attributed to the double exchange (DE) mechanism.⁴ According to this mechanism the electrons hop between the manganese ions using oxygen as an intermediate, therefore tunneling takes place between two configurations in which the Mn ions of different charge (Mn^{+3} and Mn^{+4}) interchange their valence. However recent experimental and theoretical studies⁵ have shown that the carriers in ferromagnetic manganites are holes on the oxygen sites rather than on manganites. Edwards and his co-workers⁶ have shown that the scattering rate given by the DE model is too small to explain the appearance of CMR and theoretical calculations in Ref. 5 have shown that the resistivity of the LaCaMnO compounds can be interpreted in terms of bipolaron formation above T_c .

More recently several experimental studies appeared, concerning the doping of Mn ions with another transition metal, e.g., Fe or Co.⁷⁻¹¹ In this case modification in the magnetic and transport properties has been observed. The substitution with Fe has the advantage that it does not cause lattice distortion since the Fe ion has ionic radius of the same size as the Mn ions, as it has been demonstrated by powder x-ray diffraction experiments. Early experimental studies have shown that Fe ions are a direct replacement of Mn^{+3} ions.¹² In the $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds the effect of the iron is to induce superexchange interaction between the

Mn and Fe ions via the oxygen ions, which is of antiferromagnetic nature.

The main point we wish to investigate here is the effect of the competition between the Mn–Mn and Mn–Fe interactions which are of opposite signs, on the magnetic properties of the $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ perovskites. We start with a simple model considering a simple cubic lattice in which the magnetic ions (Mn and Fe) are placed randomly (Fig. 1). The Mn–Mn coupling leads to ferromagnetic order with coupling constant J_F while the coupling between Mn–Fe ions and Fe–Fe ions leads to strong antiferromagnetic order with coupling constant J_A . The Hamiltonian is

$$H_{\text{exch}} = \sum \kappa_{ij} J_{ij} \sigma_i \sigma_j S_{iz} S_{jz}, \quad (1)$$

where the sum is over nearest neighbors. The z components S_{iz} of the spins can take two values, $1/2$ and $-1/2$, and the σ_i are parameters that allow ion dependent couplings. We take $\sigma_i = 1$ if the site is occupied by an Fe atom and $\sigma_i = 0.56$ if the occupancy is Mn. J_{ij} is the exchange coupling constant.

The parameter κ_{ij} allows for two types of interaction. We set $\kappa_{ij} = -1$ if the coupling constant $J_{ij} = J_F$ and $\kappa_{ij} = 1$ if $J_{ij} = J_A$. We study the effect of the parameter x (Fe concentration) on the magnetic properties of the $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds, considering that y is al-

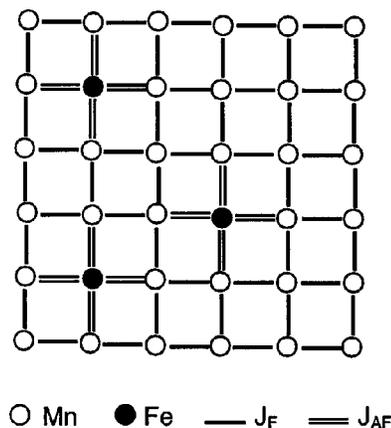


FIG. 1. Schematic representation of the magnetic lattice studied.

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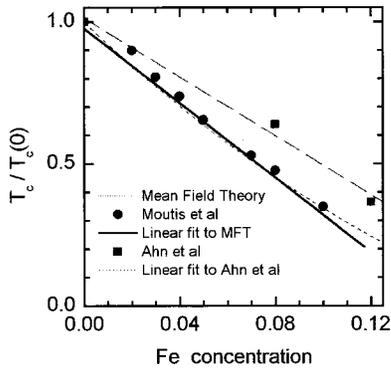


FIG. 2. The function $f_\lambda(x) = T_c(x)/T_c(0)$ for $\lambda=2$ (dashed line), together with the linear fitting (full line) and the experimental data (full circles and squares).

ways in the range that creates ferromagnetic ordering between the Mn atoms.

The magnetic ions (of Mn and Fe) are randomly distributed on the sites of a simple cubic lattice. The probability for a site to be occupied by a Mn^{+4} or Fe^{+3} ion is $1-x$ and x respectively. The probability for Mn–Mn, Mn–Fe, and Fe–Fe ions to be next to each other is $(1-x)^2$, $2x(1-x)$, and x^2 , respectively. The formation of clusters of n Fe ions has a probability of the order of x^n . This case has been neglected. Provided that we are interested in the area $x < 0.1$, this probability is of the order of 10^{-n} and we can therefore restrict our considerations to the cases where all Fe ions have Mn ions as nearest neighbors.

We consider Ising interactions between the spins. By applying standard mean field theory for ferromagnetism,¹³ we find that the critical temperature is

$$T_c = (1-2x)Ng^2\mu_B^2\gamma/k_B. \quad (2)$$

The molecular field coefficient is $\gamma = 2z\langle J \rangle / (Ng^2\mu_B^2)$. In our model $z=6$, for nearest neighbor interactions, and $\langle J \rangle = J_F(x^2 - 2x + 1) + J_A(-2x^2 + 2x)$ is the mean value of the exchange constant. T_c then becomes

$$T_c = (1-2x) \left(x^2 - 2x + 1 + \frac{J_A}{J_F}(-2x^2 + 2x) \right) \frac{12J_F}{k_B}. \quad (3)$$

The critical temperature of the undoped system is $T_c(x=0) = 12J_F/k_B$. We set $\lambda = -J_A/J_F$ and find that $T_c(x)/T_c(x=0) = -2(2\lambda+1)x^3 + (6\lambda+5)x^2 - 2(\lambda+2)x + 1$. In Fig. 2 we plot the function $f_\lambda(x) = T_c(x)/T_c(x=0)$ for $\lambda=2.0$ for several values of the Fe concentration x (dashed line) in the range $0 < x < 0.1$. We have chosen the value $\lambda=2$ because it is close to the ratio of the antiferromagnetic versus the ferromagnetic interaction strength. In the same figure we have plotted the linear fitting (full line) of this function. We observe that the linear fitting is very good, although the function $f_\lambda(x)$ is a third power law. This is expected because we are interested in the low Fe concentration values, so nonlinear terms are negligibly small. In the same figure we plot the experimental values for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ (full circles).¹⁴ As it can be seen there is a very good agreement between the theoretical and experimental values.

Also in the same figure we have plotted the experimental values for the system $\text{La}_{0.63}\text{Ca}_{0.37}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ (squares) from Ref. 8. We observe that for this compound also the

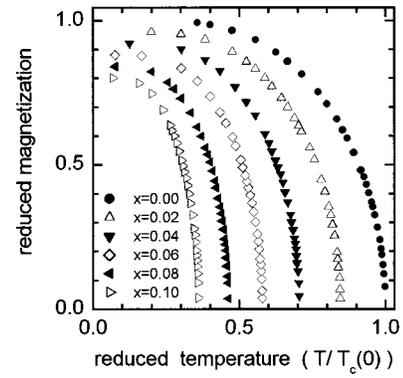


FIG. 3. The magnetization per site (in units of $g\mu_B$) vs temperature, for $\lambda=2$ and several values of the Fe concentration x .

critical temperature shows the same linear behavior with the variation of x , in this case a field of 0.01 T has been applied in the sample; this explains the higher values of T_c . So we conclude that the linear behavior of T_c is due only to the presence of Fe and not to the variation of La or Ca.

The net magnetization of the system is

$$M = (1-2x)Ng\mu_B B_{1/2}(h), \quad (4)$$

where $h = g\mu_B H / (k_B T)$ and $H = H_0 + \gamma M$. H is the total magnetic field (molecular and external) on each spin. To find the spontaneous magnetization as a function of temperature, we set the external field equal to zero and solve numerically Eq. (4) using an iteration procedure. The results are shown in Fig. 3 for $\lambda=2$ and several values of Fe doping x between 0 and 0.1. From this figure we observe a reduction in the magnetization with increasing Fe doping in agreement with the experimental results of Refs. 7, 8, and 10. This reduction in the magnetization can be easily understood considering that the substitution of Fe creates competition between the ferromagnetic and antiferromagnetic interaction in the system.

In conclusion, we have developed a phenomenological model based on the molecular field theory in order to study the magnetization behavior of the $\text{La}_{1-y}\text{Ca}_y\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ perovskites with $0.2 < y < 0.5$, which exhibit ferromagnetic metallic behavior. We observe that even a small amount of Fe doping has a great influence in the magnetic behavior of these compounds. Due to the antiferromagnetic coupling caused by the Fe atoms the magnetization and the Curie temperature show a decrease even in the case where only 5% of Mn atoms have been substituted by Fe atoms. This is in agreement with experimental findings.

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