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Electron paramagnetic resonance and magnetization in Co doped $La_{2/3}Ca_{1/3}MnO_3$

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Spin dynamics of the Mn-site substituted colossal magnetoresistance system were studied by means of electron paramagnetic resonance (EPR) and dc magnetic susceptibility in $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ $(0 \leqslant x \leqslant 0.1, \Delta x = 0.025)$. A dramatic increase in the high temperature limiting value for the EPR linewidth $(\Delta H_{pp}(\infty))$ was observed with doping. Structural analysis revealed that only negligible changes are produced in bond distances and angles at these low doping levels. On the other hand, dipolar contribution to $\Delta H_{pp}(\infty)$ was estimated in a few Gauss. To explain the effect of doping on $\Delta H_{pp}(\infty)$, we propose here a scenario including fast Mn-spin lattice relaxation through paramagnetic Co ions. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1358347]

Manganese oxides with general stoichiometry $A_{1-x}B_xMnO_3$ ($A = La^{3+}$, Pr^{3+}; $B = Ca^{2+}$, Sr^{2+}, etc.) show a remarkable correlation between magnetic order and electric transport with x.[1] Zener[2] explained the simultaneous occurrence of metallicity and ferromagnetism observed for intermediate doping levels ($0.2 \leqslant x \leqslant 0.5$) on the basis of a double exchange (DE) interaction, which qualitatively explains the colossal magnetoresistive response observed around the Curie temperature (T_C). Although several authors have shown how DE interaction can be affected by rare earth doping,[3] not much is known about the effect of the substitution in the Mn site, in spite of the fact that this gives rise to DE interaction.[4] In this work, we treat the problem of paramagnetic relaxation in Co doped $La_{2/3}Ca_{1/3}MnO_3$.

Polycrystalline samples of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ $(0 \leqslant x \leqslant 0{,}1, \Delta x = 0.025)$ were prepared through the conventional solid state method, with a final sintering treatment at 1300 °C for 100 h. Stoichiometry was checked by x-ray fluorescence. The results of these analyses show only slight deviations from the expected values (see Table I). Crystallographic parameters were derived by the Rietveld method and are plotted in Fig. 1. On the view of these results it can be concluded that the structural changes produced by the low doping levels of Co employed here are negligible. On the other hand, the continuous variation of the unit cell volume and lattice parameters with doping indicates an adequate accommodation of the randomly distributed Co ions in the lattice. Magnetic susceptibility $\chi(T)$ was measured above T_C up to 1000 K with a Faraday balance at 5 kOe. Electron paramagnetic resonance (EPR) spectra were taken at 9.5 GHz (X band) with a ESP 300 Bruker spectrometer.

The thermal evolution of $\Delta H_{pp}(T)$ for all doping levels is shown in Fig. 2. In spite of the fact that the lattice structure of $La_{2/3}Ca_{1/3}MnO_3$ remains practically unaffected by doping, there is an important increase of the $\Delta H_{pp}(T)$ with Co. Causa *et al.*[5] found that the temperature dependence of $\Delta H_{pp}(T > T_C)$ for $A_{1-x}B_xMnO_3$ ($A = La, Pr; B = Ca, Sr, Pb$) can be described by $\Delta H_{pp}(\infty)C/T\chi(T)$, where C is the Curie constant and $\Delta H_{pp}(\infty)$ is the high temperature limiting value of the linewidth. This limiting value is independent of temperature and is related to spin-only interactions. From this expression it follows that the changes produced by doping in $\Delta H_{pp}(T)$ are related to variations produced in the term $T\chi(T)$ by the dilution of DE interaction.

TABLE I. Nominal and experimental Co contents.

% Co theoretical	0	2.5	5	7.5	10
% Co experimental	0	2.45	5.09	7.59	10.24

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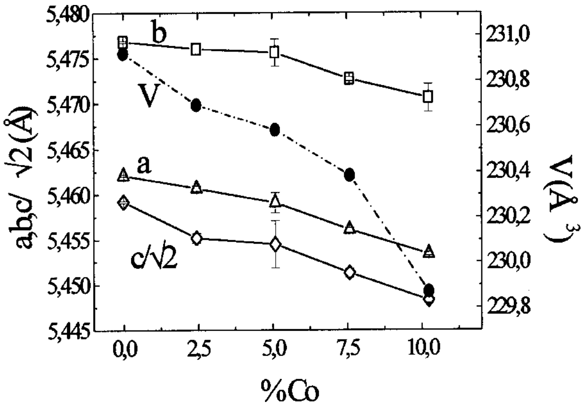

FIG. 1. Evolution of lattice parameters and volume of the perovskite unit cell with doping. This variation is compatible with the presence of Co^{3+}/Co^{4+} as Co^{2+} should produce a slight volume increase.

For samples with higher Co content, ΔH_{pp} is of the same order of magnitude as the resonance field H_r. In this case, the field dependence of the absorption line shape derivative is given by a complex function of ΔH_{pp}, H_r, and H; and both the linewidth and the intensity of the resonance must be corrected in order to obtain their exact values.[6,7] Once this correction was done, $\Delta H_{pp}(T)$ were fitted with the experimental susceptibility and extracted $\Delta H_{pp}(\infty)$ for each sample (Fig. 3). Co doping produces an increase in the value of $\Delta H_{pp}(\infty)$ from ~2500 G for $x=0$ to ~14 750 for $x=0.1$. In the exchange narrowing theory, $\Delta H_{pp}(\infty) \propto (w_p^2/w_{ex})$, where w_p is the frequency associated to anisotropic interactions (dipolar, crystal field terms, Dzialoshinski–Moriya antisymmetric exchange coupling, etc...) and w_{ex} the frequency of isotropic interactions. $\Delta H_{pp}(\infty)$ can also be calculated from the spectral moments technique[7] for a Lorentzian line shape in this exchange narrowing limit as $(\pi/2)^{1/2}(M_2^{3/2}/M_4^{1/2})$.

The dipolar contribution to M_2 can be modeled as[7]

$$M_2=5.1\gamma^4(h/2\pi)^2[S(S+1)]d^{-6}, \tag{1}$$

where γ is the gyromagnetic factor ($\gamma=ge/2mc$). Considering an effective spin as the weighted average of Mn^{3+}/Mn^{4+} spins ~1.83; $d=4$ Å (the Mn–Mn distance), and using the experimentally determined values of exchange constant from the high temperature fits of $\chi(T)$, the dipolar contribution to $\Delta H_{pp}(\infty)$ was calculated to be only of ~6 G, very similar to that determined by Huber (~3 Oe) in Ref. 8.

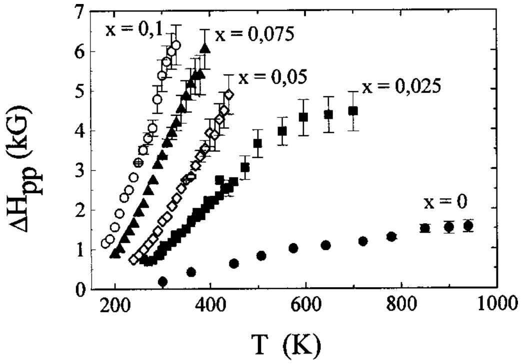

FIG. 2. Temperature dependence of the EPR linewidth for all samples. A continuous increase of the linewidth with doping is observed.

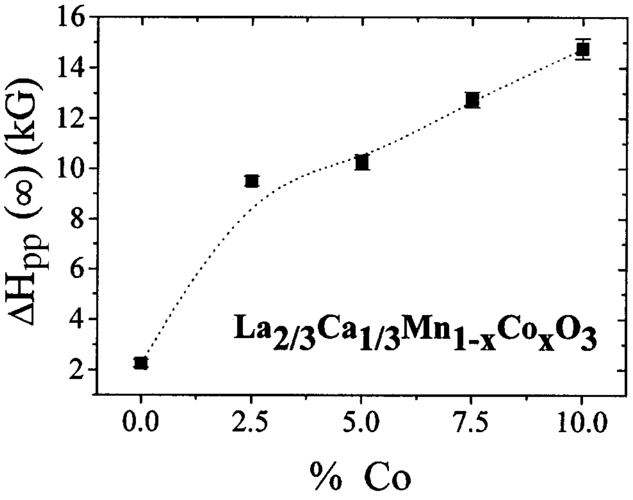

FIG. 3. High temperature limiting value of the linewidth ($\Delta H(\infty)$) vs the doping level.

On the other hand, contribution from Dzialoshinski–Moriya coupling to the Mn–O–Mn superexchange interaction, allowed in the *Pbnm* perovskite structure due to the tilting of MnO_6 octahedra, should be constant attending the crystal structure invariance (Fig. 1). Also the contribution from the crystal field to the second and fourth moments of the resonance is expected to be constant as we have not observed any structural transition with doping.[9]

In order to explain the observed increase of $\Delta H_{pp}(\infty)$, we treated the problem like that of a system with two spin species exchange coupled to each other. In Fig. 4, the possible host↔Co, host↔lattice, and Co↔lattice interaction pathways are shown (host being the Mn^{3+}/Mn^{4+} matrix). In this diagram ν_0 represents the normal relaxation rate of the undoped compound, and ν_{HI}, ν_{IH}, and ν_{IL}, the host↔Co, Co↔host, and Co→lattice relaxation rates, respectively.

Co ions (Co^{3+}/Co^{4+}) present degenerate orbital ground states, so these ions are expected to be strongly coupled to the lattice, and hence to have short relaxation times.

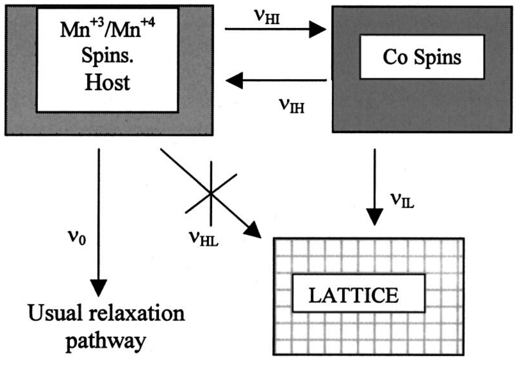

FIG. 4. Relaxation pathways scheme for the magnetization of doped system. The usual relaxation of the undoped compound is governed by spin–spin interactions, since spin–lattice relaxation is suppressed. Mn spins can relax across the Co spins to the lattice, increasing the linewidth characteristic of $La_{2/3}Ca_{1/3}MnO_3$.

Co increases ν_{IL} and broadens the resonance line, this broadening depending on the ratio ν_{HI}/ν_{IH}. We expect $\nu_{HI} < \nu_{IH}$ by pure consideration of relative spin concentrations, and the process of relaxation and broadening depends on Co concentration. Gulley and Jaccarino[10] obtained a solution for the linewidth in the limit $T \rightarrow \infty$ to describe the effect of spin-lattice damping of an impurity on the EPR linewidth of the exchange coupled system

$$\Delta H(\infty) = \Delta H_0(\infty) + \frac{x}{\gamma}\nu_{IL}, \tag{2}$$

where $\Delta H(\infty)$ and $\Delta H_0(\infty)$ represent the linewidth in the limit when $T \rightarrow \infty$ for the doped and undoped compound, respectively. From Eq. (2) and the data shown in Fig. 2, we have derived values for ν_{IL} on the order of $3-8 \times 10^{11}\,\mathrm{s}^{-1}$. In the limit $\nu_{IL}/\nu_{IH} \ll 1$, the impurity relaxes very little magnetic energy to the lattice and the system is bottlenecked. In this situation, the characteristic value of $\Delta H(\infty)$ for the undoped crystal is obtained. On the other hand, following Eq. (2), relaxation to the lattice increases with x, producing the observed broadening of the resonance. Cobalt, like other ions with unquenched orbital angular momentum, plays an intermediate role in the transfer of energy from the relatively undamped host to the lattice, providing a thermal path of high conductivity.

In summary, we observed an important increase of the $\Delta H(\infty)$ of $La_{2/3}Ca_{1/3}MnO_3$ with Co doping, and the spin-lattice relaxation time was calculated.

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